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1 **Triple oxygen isotope compositions of globally distributed soil carbonates record**
2 **widespread evaporation of soil waters**

3 *Manuscript for submission to Geochimica et Cosmochimica Acta*

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27
28 **Abstract**

29 The stable isotopic composition of pedogenic carbonates is central to many studies of
30 past climate and topography, providing a basis for our understanding of Earth's terrestrial history.
31 A core assumption of many applications of oxygen isotope values ($\delta^{18}\text{O}$) of pedogenic carbonate
32 is that they reflect the $\delta^{18}\text{O}$ value of precipitation (rain/snow). This assumption is violated if soil
33 carbonates form in evaporated soil waters. In this work, we develop a means to identify
34 evaporation in ancient soils using the triple oxygen isotope composition (^{16}O - ^{17}O - ^{18}O) of
35 pedogenic carbonates. Both theoretical predictions of isotope kinetics during evaporation and

36 studies of triple oxygen isotopes in other geological materials show that the deviation in the
37 relationship between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ from a reference line, evaluated using the parameter $\Delta^{17}\text{O}$, is
38 sensitive to evaporation. As a first step in developing the use of $\Delta^{17}\text{O}$ in ancient pedogenic
39 carbonates, we report $\Delta^{17}\text{O}$ values from 47 near-modern pedogenic carbonate samples from
40 globally distributed environments that vary in aridity (hyper-arid to humid). The $\Delta^{17}\text{O}$ values of
41 pedogenic carbonate range from -154 to -60 per meg (as CaCO_3 , measured via O_2 , VSMOW-
42 SLAP), corresponding to calculated soil water values of -66 to +27 per meg (VSMOW-SLAP)
43 (using a carbonate-water triple oxygen isotope fractionation exponent of 0.5250 and clumped
44 isotope-derived carbonate growth temperatures). The $\Delta^{17}\text{O}$ values indicate that evaporative
45 modification of soil water from which pedogenic carbonate forms is common, especially in arid
46 environments. Arid environments host pedogenic carbonates formed from soil waters ranging
47 from highly to minimally evaporated, while humid environments host pedogenic carbonates
48 formed from waters that are only minimally evaporated. The variability in $\Delta^{17}\text{O}$ within
49 environments classified by the same aridity may relate to the fact that pedogenic carbonates
50 record soil conditions only during times of carbonate mineralization, which may deviate from
51 annual conditions. Thus, $\Delta^{17}\text{O}$ may be useful in understanding the specific circumstances of
52 pedogenic carbonate formation but may not provide incontrovertible evidence of the magnitude
53 of environmental aridity. Evaporative modification of $\delta^{18}\text{O}$ values of pedogenic carbonates can
54 be detected with $\Delta^{17}\text{O}$, thereby improving estimates of $\delta^{18}\text{O}$ of unevaporated waters. Our data
55 show that evaporation must be (re)considered for all paleoclimate inferences based on the $\delta^{18}\text{O}$
56 of pedogenic carbonate. The addition of $\Delta^{17}\text{O}$ will re-energize paleoclimate studies that use (or
57 have avoided using) $\delta^{18}\text{O}$ of pedogenic carbonate.

58

59

60 **Key Words**

61 *soils; triple oxygen isotopes; clumped isotopes; terrestrial paleoclimatology; evaporation*

62 **1. Introduction**

63 The relative abundance of ^{18}O and ^{16}O in pedogenic carbonates ($\delta^{18}\text{O}_{\text{carb}}$) has been a
64 foundational tool used in major discoveries of Earth history events, such as uplift of the Andes
65 and Himalaya mountains, fluctuations in air and soil temperatures, and changes in water balance
66 amidst grassland expansion in North America and Africa (Cerling, 1992; Cole and Monger,
67 1994; Fox and Koch, 2003; Garzzone et al., 2008; Levin et al., 2011; Eagle et al., 2013; Snell et
68 al., 2013; Rech et al., 2019). While variations in $\delta^{18}\text{O}_{\text{carb}}$ have allowed workers to discover major
69 environmental changes, the precise driving processes are difficult to constrain without additional
70 information because $\delta^{18}\text{O}_{\text{carb}}$ is sensitive to multiple environmental factors. The two primary
71 factors that control $\delta^{18}\text{O}_{\text{carb}}$ are carbonate growth temperature and the $\delta^{18}\text{O}$ value of soil water,
72 which varies with evaporation and/or with changes in the $\delta^{18}\text{O}$ value of meteoric waters that
73 recharge the soil (e.g., due to precipitation seasonality, moisture source, or infiltration paths).
74 With the development of carbonate clumped isotope thermometry, we can now constrain
75 carbonate growth temperatures and calculate the $\delta^{18}\text{O}$ value of parent soil water (Quade et al.,
76 2007a; Eiler, 2007; Huntington and Petersen, 2023). This leaves workers who wish to interpret
77 $\delta^{18}\text{O}$ of soil water reconstructed from $\delta^{18}\text{O}_{\text{carb}}$ with a quandary: when has $\delta^{18}\text{O}$ been modified by
78 evaporation, and when can it be trusted as a record of primary meteoric waters? And a corollary:
79 does evaporative enrichment in ^{18}O indicate arid conditions?

80 In many applications, $\delta^{18}\text{O}_{\text{carb}}$ is used primarily to infer $\delta^{18}\text{O}$ values of meteoric waters
81 and to investigate hydrologic processes including the seasonal balance of precipitation (Smith et

82 al., 1993; Oerter et al., 2016; Kukla et al., 2022), local temperature of rainfall (Nordt et al., 2003;
83 Fricke and Wing, 2004), water-energy balance (Kukla et al., 2019; van Dijk et al., 2020),
84 regional circulation patterns including monsoon intensity, continentality, and moisture recycling
85 (Liu et al., 1996; Monger et al., 1998; Fricke et al., 2010; Winnick et al., 2013, 2014; Methner et
86 al., 2016; Licht et al., 2017; Caves Rugenstein and Chamberlain, 2018), and paleoelevations
87 (Garzzone et al., 2008; Hoke et al., 2009, 2014; Fan et al., 2011; Chamberlain et al., 2012; Mulch
88 et al., 2015; Song et al., 2018). These applications assume that $\delta^{18}\text{O}_{\text{carb}}$ has been minimally
89 affected by evaporation, especially at depths > 40 cm below the surface, but this is a known
90 simplification that is at odds with an abundance of isotopic data showing evaporatively enriched
91 pore waters in deep and shallow vadose zones (Barnes and Allison, 1983; Allison et al., 1983;
92 Quade et al., 1989; Wang et al., 1996; Liu et al., 1996; Hsieh et al., 1998; Monger et al., 1998;
93 DePaolo et al., 2004; Brooks et al., 2010; Evaristo et al., 2015; Oerter and Amundson, 2016). In
94 another class of applications, workers interpret increases in $\delta^{18}\text{O}_{\text{carb}}$ as primarily or possibly
95 reflecting evaporation, which is often linked to changes in environmental aridity (Amundson and
96 Lund, 1987; Amundson et al., 1989, 1994; Kleinert and Strecker, 2001; Levin et al., 2004, 2011;
97 Fox and Koch, 2004; DeCelles et al., 2007; Zhou and Chafetz, 2010; Chamberlain et al., 2014; Ji
98 et al., 2017; Kelson et al., 2018; Rech et al., 2019; Broz et al., 2021). These varied uses of
99 $\delta^{18}\text{O}_{\text{carb}}$ demonstrate the need for a tool that can disentangle evaporation in soil pore waters from
100 the various drivers of change in $\delta^{18}\text{O}$ of meteoric water. We also need to understand if the
101 magnitude of evaporation in soil waters reconstructed from carbonates can be used to assess
102 aridity in the geologic record.

103 Ecohydrologists have used oxygen and hydrogen isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$) to show that
104 shallow (<30 cm) soil water worldwide is often evaporated, and that in arid and semi-arid

105 climates the depth of evaporated soil waters may be deeper (Sprenger et al., 2016). Evaporated
106 soil water is isotopically distinct from local meteoric waters such as rain, river, and ground water
107 (Brooks et al., 2010; Evaristo et al., 2015; Bowen et al., 2018). Though the potential for
108 evaporative effects on $\delta^{18}\text{O}$ of soil carbonate was recognized early in the field (Quade et al.,
109 1989; Cerling and Quade, 1993), it remains unclear the extent to which carbonate-parent soil
110 water has an evaporative signature, and how its isotopic composition ultimately relates to that of
111 meteoric waters (Kelson et al., 2020). This uncertainty persists in part because of spatial and
112 temporal heterogeneity in the isotopic composition of soil water that results from percolation of
113 isotopically variant input water, evaporation, mixing with antecedent pore water, redistribution
114 by vegetation (Gazis and Feng, 2004; Sprenger et al., 2016; Benettin et al., 2018), and the
115 possibility of multiple pools of water within soil pores (Brooks et al., 2010; Sprenger and Allen,
116 2020). Furthermore, the most common carbonate minerals (calcite, aragonite) do not contain
117 structural hydrogen, and so carbonate minerals cannot be directly compared to $\delta^{18}\text{O}$ - $\delta^2\text{H}$
118 meteoric water lines. Thus, even with $\delta^{18}\text{O}_{\text{water}}$ and $\delta^{18}\text{O}_{\text{carb}}$ measurements in modern soils, it is
119 difficult to infer the source and the evaporative trajectory of the soil-carbonate parent waters
120 (Breecker et al., 2009; Takeuchi et al., 2009; Oerter and Amundson, 2016; Havranek et al., 2020;
121 Beverly et al., 2021).

122 Recent work has shown that the relative abundances of the three isotopes of oxygen (^{16}O ,
123 ^{17}O , ^{18}O) in water are sensitive to evaporation (Barkan and Luz, 2007; Luz and Barkan, 2010;
124 Surma et al., 2015) and that this signal is preserved and can be measured in carbonates (Passey et
125 al., 2014; Barkan et al., 2015; Fosu et al., 2020; Wostbrock et al., 2020b). Evaporation is a
126 kinetic process that causes the slope between $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ to deviate from a reference slope
127 (here $\lambda_{\text{ref}} = 0.528$) that approximates the relationship observed in meteoric waters, evaluated with

128 the term $\Delta^{17}\text{O}$ (Figure 1) (Barkan and Luz, 2007) (notation defined in 2.1). $\Delta^{17}\text{O}$ has been
129 shown to be sensitive to evaporation in meteoric waters (Landais et al., 2010; Luz and Barkan,
130 2010; Li et al., 2015; Evans et al., 2018; Surma et al., 2018, 2021; Aron et al., 2021a, b, 2023;
131 Giménez et al., 2021; Voigt et al., 2021; Xia, 2023) and leaf waters (Landais et al., 2006; Li et
132 al., 2017). Authigenic minerals inherit their parent water's evaporative signature, including in
133 $\Delta^{17}\text{O}$ values, as measured in silicates (Ibarra et al., 2021), lake carbonates (Passey and Ji, 2019;
134 Katz et al., 2023), gypsum hydration waters (Herwartz et al., 2017; Gázquez et al., 2018), soil
135 phytoliths (Alexandre et al., 2018; Voigt et al., 2023), and tooth enamel (Pack et al., 2013;
136 Passey et al., 2014; Lehmann et al., 2022). Because of its sensitivity to evaporation, $\Delta^{17}\text{O}$ has
137 been proposed to be a proxy for environmental aridity in soil phytoliths, mammal tooth enamel,
138 and pedogenic carbonates (Alexandre et al., 2018; Beverly et al., 2021; Lehmann et al., 2022).
139 Pedogenic carbonates are a logical target for this emerging technique given that they form in the
140 shallow vadose zone waters that are vulnerable to evaporation, as initially discussed in Passey et
141 al. (2014). In a regionally focused study, Beverly et al. (2021) showed that the $\Delta^{17}\text{O}$ of Holocene
142 pedogenic carbonates related to aridity in Tanzania, suggesting that $\Delta^{17}\text{O}$ relates to the
143 magnitude of local evaporation. Although these initial findings are promising, they need to be
144 validated across diverse ecosystems before $\Delta^{17}\text{O}$ of pedogenic carbonates can be used in
145 paleoclimate applications to detect evaporation and/or to reconstruct aridity.

146 The first purpose of this study is to evaluate the prevalence of evaporation in soil waters
147 from which pedogenic carbonates form. This objective will test the often-made assumption that
148 $\delta^{18}\text{O}_{\text{carb}}$ primarily reflects $\delta^{18}\text{O}$ of minimally evaporated meteoric waters (see citations above).
149 The second purpose of this study is to determine if $\Delta^{17}\text{O}$ in pedogenic carbonates can be used to
150 indicate paleo-aridity. To meet these objectives, we measure $\Delta^{17}\text{O}$ of pedogenic carbonates from

151 varying climate regimes. We also estimate carbonate growth temperatures, using carbonate
152 clumped isotope thermometry (Δ_{47}) where possible, which we use to calculate $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of
153 parent soil water ($\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$). We assess evaporation by comparing the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$
154 of reconstructed soil water to that of global meteoric waters. We predict the effects of
155 evaporation on pedogenic carbonate $\Delta^{17}\text{O}$ values with a simple mathematical model (Barnes and
156 Allison; 1983). Finally, we use geographically related samples as a basis to suggest how $\Delta^{17}\text{O}$
157 can be most useful for paleoclimate workers to evaluate the importance of evaporation in $\delta^{18}\text{O}$
158 values and improve estimates of pristine $\delta^{18}\text{O}$ of recharge waters.

159

160

161 **2. Site Descriptions and Methods**

162 *2.1 Triple oxygen isotope notation*

163 Mass-dependent fractionation for triple oxygen isotope systems is described with a power
164 law relationship that relates the fractionation factor (α) between two phases (A and B) with an
165 exponent (θ):

$$^{17}\alpha_{(A-B)} = \left(^{18}\alpha_{(A-B)}\right)^\theta \quad (1)$$

166 The exponent θ denotes fractionation that occurs from a single process whose value is
167 derived from experiments or theory. Equilibrium exchange between water vapor and liquid water
168 is described by $\theta_{\text{eq}} = 0.529$ (Young et al., 2002; Barkan and Luz, 2005). Evaporation is a kinetic
169 process that involves the diffusion of water vapor through air and is described with $\theta_{\text{diff}} = 0.5185$
170 (Barkan and Luz, 2007). The difference between θ_{eq} and θ_{diff} is the basis for using triple oxygen
171 isotopes to detect evaporation (Figure 1A). The notation λ is often used in place of θ in Equation
172 1 to describe empirically observed triple oxygen isotope relationships that might combine

173 multiple processes (i.e., evaporation in natural soils that combines equilibrium and diffusive
174 fractionation, or λ_{soil}). For practicality of visualizing and working with triple oxygen isotope data,
175 the power law relationship in Equation 1 can be linearized using δ' notation (Miller, 2002):

$$\delta' = \ln(R_{SA}/R_{ST}) \quad (2)$$

176 And then the $\Delta^{17}\text{O}$ parameter can be defined as the deviation from an empirically derived reference
177 line of meteoric waters (λ_{ref}):

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda_{\text{ref}} * \delta^{18}\text{O} \quad (3)$$

178 We use the reference slope (λ_{ref}) of 0.528, a value that was established to describe global
179 meteoric waters (Luz and Barkan, 2010; Aron et al., 2021a) and has been adopted in the
180 reporting $\Delta^{17}\text{O}$ of geological materials that track the hydrosphere (Evans et al., 2018; e.g., Sharp
181 et al., 2018; Passey and Ji, 2019; Sengupta et al., 2020; Ibarra et al., 2021; Sharp and Wostbrock,
182 2021; Huth et al., 2022; Kelson et al., 2022; Lehmann et al., 2022). The parameters θ and λ are
183 used to describe slopes of linear regressions where $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are the predicted and response
184 variables, respectively (Figure 1A), and generally have a physical basis (i.e., evaporation). We
185 also use apparent trends in $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ space for ease of plotting and conceptualization (Figure
186 1B; Figure 2C).

187

188 *2.2 Theoretical prediction of triple oxygen isotopes in soil water resulting from evaporation*

189 We modified an existing, relatively simple, mathematical model for the distribution of
190 H_2^{18}O and HDO in soil water (Barnes and Allison, 1983) to predict the distribution of H_2^{17}O in
191 soil water resulting from evaporation in a soil profile in quasi-steady state conditions. The goal
192 was to provide a basic framework for understanding the influence of evaporation on $\Delta^{17}\text{O}$ values
193 of soil water, in terms of direction and magnitude, relationship with $\delta^{18}\text{O}$, and depth distributions

194 (Supplementary Text Section 1). We modeled evaporation as diffusive transport of water vapor
195 from the soil water surface (e.g., Criss, 1999). The soil profile was modeled with two zones: a
196 shallow ‘dry’ zone (vapor transport only, relative humidity varies from 100% to the value of the
197 overlying atmosphere) that is above a ‘wet’ zone (dominated by liquid transport, with relative
198 humidity of 100%). The boundary between these zones was termed the evaporation front (z_{ef}).
199 Kinetic isotope fractionation due to evaporation occurs at the evaporation front, and liquid water
200 influenced by evaporation diffuses downward into the ‘wet’ zone. There is upward advection of
201 unevaporated water from the water table in the ‘wet’ zone. The model equations can be found in
202 Barnes and Allison (1983), Fischer-Femal and Bowen (2021), and in Supplementary Text
203 Section 1. We built on the existing model of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ by calculating $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$ via the
204 triple oxygen isotope exponents for equilibrium and diffusive processes ($\theta_{eq} = 0.529$, $\theta_{diff} =$
205 0.5185) (Figure 2) (Barkan and Luz, 2007). To explore the scale and magnitude of isotopic
206 changes caused by evaporation, we varied the physical and isotopic parameters in the model
207 (Supplementary Text Section 1, Figures S1-S4).

208

209 *2.3 Site and sample selection, age control, and climate data*

210 To maximize our potential to observe a large range in evaporative states and in $\Delta^{17}\text{O}$
211 values, we targeted soil carbonates from sites that vary in climate regime, including variation in
212 aridity (hyper-arid to subhumid), elevations, and seasonal temperatures (Table 1) (Figure 3).
213 Vegetation cover varies across the sites, but most are shrub- or grassland (or a mix), and some
214 have very sparse vegetation. Very few of the sites have trees (only the sites in Texas and
215 Myanmar could be considered forested) (Supplementary Text Section 2). Most of the soil
216 carbonate samples were originally collected for other studies (e.g., typically focusing on $\delta^{18}\text{O}$ or

217 Δ_{47}); some were newly collected (Table 1; Supplementary Text Section 2). The pedogenic
218 carbonate morphologies include rinds, diffuse carbonate, and nodules (see Figures S5–S11 for
219 site pictures). While we have sought to sample stable geomorphic surfaces, for some soil sites
220 the depth of sampling may not be equivalent to the depth of carbonate formation because land
221 surfaces can undergo erosion and accumulation, resulting in generations of pedogenic
222 overprinting (e.g., Deutz et al., 2002). We sampled and analyzed pedogenic carbonate at multiple
223 depths in a soil profile where possible to test if evaporative effects are more pronounced near the
224 surface.

225 One assumption in this work (and previous studies focusing on $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, and Δ_{47}) is
226 that modern climate data can be used to contextualize the conditions of pedogenic carbonate
227 formation in surface (i.e., not buried or relict) soils (e.g., Quade et al., 2007b, 2013; Breecker et
228 al., 2009; Peters et al., 2013; Burgener et al., 2016; Gallagher and Sheldon, 2016; Oerter and
229 Amundson, 2016; Ringham et al., 2016; Gallagher et al., 2019; Huth et al., 2019; Beverly et al.,
230 2021). To minimize inaccuracies introduced because of this assumption, we targeted pedogenic
231 carbonates that are near-modern (i.e., Holocene, though some are late Pleistocene). Some
232 pedogenic carbonate samples have age controls based on dating of the geomorphic surface
233 and/or the carbonate itself; where age constraints did not exist we sampled carbonates that were
234 likely to be young based on incipient soil and carbonate development (Gile et al., 1966) and
235 geomorphic context (Supplementary Text Section 2). To classify the moisture availability at each
236 site, we extracted Aridity Index (AI), the ratio between mean annual precipitation and potential
237 evapotranspiration, from World Clim 2 and Version 3 of the Global Aridity Index and Potential
238 Evapotranspiration Database (30 arc-second grid resolution) (Fick and Hijmans, 2017; Zomer et
239 al., 2022). This is an updated version of the Global AI database compared to what was used in

240 Beverly et al. (2021), so the absolute values differ (but patterns remain) compared to what was
241 reported in that publication. To test if depletion in $\Delta^{17}\text{O}_{\text{rsw}}$ is accompanied by enrichment in
242 $\delta^{18}\text{O}_{\text{rsw}}$ relative to $\delta^{18}\text{O}$ of recharge waters, we needed an estimate of $\delta^{18}\text{O}$ of recharge waters.
243 We turned to estimates of amount-weighted mean annual $\delta^{18}\text{O}$ of precipitation ($\delta^{18}\text{O}_{\text{ann}}$) at each
244 site, while acknowledging that this method overlooks potential seasonal bias in recharge and
245 complexities in soil water hydrology (Gazis and Feng, 2004; Sprenger et al., 2016). We also
246 considered the mean $\delta^{18}\text{O}$ value of monthly precipitation during the estimated season of
247 carbonate formation, in accordance with evidence that pedogenic carbonate $\delta^{18}\text{O}$ is seasonally
248 biased (Hough et al., 2014; Kelson et al., 2020) (Supplementary Text Section 3). We extracted
249 estimates of $\delta^{18}\text{O}$ values of precipitation (monthly and $\delta^{18}\text{O}_{\text{ann}}$) from the Oxygen Isotopes of
250 Precipitation Calculator (OIPC) (Bowen and Revenaugh, 2003) (estimates of $\Delta^{17}\text{O}$ precipitation
251 are not currently available). For the samples from Ethiopia (Table 1), the range of precipitation
252 $\delta^{18}\text{O}$ and $\delta^{18}\text{O}_{\text{ann}}$ are derived from the long-term, amount-weighted mean of rainfall at Addis
253 Ababa (-1.3 ± 2.3 ‰) from the Global Network of Isotopes in Precipitation (GNIP) (Rozanski et
254 al. 1993; IAEA 2013) instead of the OIPC value because of known inaccuracies in the OIPC in
255 that region (Levin et al., 2009; Kebede et al., 2021) (OIPC-derived $\delta^{18}\text{O}_{\text{ann}}$ is $+3.4$ ‰). We also
256 employed GNIP data (1982-1984) for the NAC soil site at the Ñacuñán Biosphere Reserve
257 because of their collocation, although we note that at this location the difference between the
258 OIPC and GNIP values of $\delta^{18}\text{O}_{\text{ann}}$ is minor (0.3 ‰). At each site, we estimated $\Delta^{17}\text{O}_{\text{mw}}$ using the
259 mean of $\Delta^{17}\text{O}$ values of global, unevaporated meteoric waters (Aron et al., 2021a) within the
260 range of precipitation $\delta^{18}\text{O}$ values.

261

262 *2.4 Analytical Methods*

263

264 *2.4.1 Triple Oxygen Isotope Analytical and Normalization Methods*

265 We consider $\Delta^{17}\text{O}$ values measured in pedogenic carbonate that are new to this study (21
266 samples), values from Beverly et al. (2021) (14 samples), values from Passey et al. (2014) (7
267 samples), and values from Ji (2016) (5 samples). We describe the methods for measuring $\Delta^{17}\text{O}$
268 values of the samples new to this study and then discuss normalization steps taken to make
269 previously published data comparable to the newly generated data.

270 The $\Delta^{17}\text{O}$ measurements of carbonate new to this study were made at the University of
271 Michigan (UM) following the acid digestion-reduction-fluorination method described in detail in
272 Passey et al. (2014) and Passey and Levin (2021). In brief, we converted the carbonate samples
273 (CaCO_3) to O_2 gas for analysis on a mass spectrometer to avoid a mass interference between ^{13}C
274 and ^{17}O in CO_2 . We digested the carbonates in a common phosphoric acid bath held at 90°C to
275 yield CO_2 gas. The resulting CO_2 was purified then reduced with hydrogen gas, aided by an iron
276 catalyst to produce H_2O . The resulting H_2O was fluorinated in a cobalt fluoride (III) reactor held
277 at 360°C to produce O_2 (Barkan and Luz, 2005). We measured masses 32–36 of O_2 on a Nu
278 Perspective isotope ratio mass spectrometer. We observed a memory effect within the cobalt
279 fluoride (III) reactor that is minimized by analyzing samples in isotopic order (Huth et al., 2022).
280 We typically measure the $\delta^{18}\text{O}$ value of a sample as CO_2 with a mass spectrometer before
281 measuring $\Delta^{17}\text{O}$. Sample analyses with $\delta^{18}\text{O}$ values that were $>5\text{‰}$ different from the previous
282 sample were removed from the dataset.

283 We defined analytical sessions based on when we refreshed the CoF_3 material in the
284 fluorination reactor or performed other maintenance (e.g., changing the filament of the mass
285 spectrometer, power outages). In each analytical session, we measured both water and carbonate

286 standards. Water standards, VSMOW2 and SLAP2, provided the normalization basis for the
287 VSMOW2-SLAP2 reference frame (Schoenemann et al., 2013) (henceforth abbreviated as
288 VSMOW-SLAP). Water standards were analyzed using the same fluorination and vacuum line
289 as the carbonate-derived waters. Multiple analyses (2 to 4 replicates) of VSMOW2 and SLAP2
290 were performed at the start, middle and end of each analytical session (see supplementary tables
291 for run order and standard values). International carbonate standards (NBS-18, NBS-19, IAEA
292 603, IAEA C1) and an internal carbonate standard (102-GC-AZ01) were analyzed along with
293 unknowns. We corrected the O₂-derived delta values of sample gas to carbonate mineral delta
294 values via the Wostbrock et al. (2020b) values of international standards, using empirically
295 derived fractionation factors which include all fractionations imparted in our analytical method
296 (acid digestion, reduction, and fluorination) (Passey et al., 2014; Huth et al., 2022). The
297 fractionation factors were calculated using the carbonate mineral value of IAEA-603 derived by
298 Wostbrock et al (2020b) via carbonate fluorination ($\delta^{17}\text{O} = 14.831 \pm 0.007 \text{‰ VSMOW-SLAP}$,
299 $\delta^{18}\text{O} = 28.470 \text{‰ VSMOW-SLAP}$, $\Delta^{17}\text{O} = -100 \pm 7 \text{ per meg VSMOW-SLAP}$) and the long term
300 average of IAEA-603 measured in our laboratory ($\delta^{18}\text{O} = 36.233 \pm 1.224 \text{‰ VSMOW-SLAP}$,
301 $\Delta^{17}\text{O} = -146 \pm 15 \text{ per meg VSMOW-SLAP}$) (described in Huth et al., 2022). The UM
302 fractionation factors are $^{17}\alpha_{\text{mineral-90}^\circ\text{C acid, O}_2} = 0.9957458$ and $^{18}\alpha_{\text{mineral-90}^\circ\text{C acid, O}_2} =$
303 0.9918723 ($\theta_{\text{mineral-90}^\circ\text{C acid, O}_2} = 0.5224$) (Huth et al., 2022). Finally, we corrected the $\Delta^{17}\text{O}$
304 mineral values for drift on a session-by-session basis using the average mineral $\Delta^{17}\text{O}$ values of
305 IAEA-603 and IAEA-C1 (-100 per meg, by definition; IAEA 603 and IAEA C1 are isotopically
306 identical, Huth et al., [2022]). This session-specific drift correction is usually less than ± 12 per
307 meg. $\delta^{17}\text{O}$ values are re-calculated based on the corrected $\Delta^{17}\text{O}$ values.

308 The long-term standard deviation (S.D.) of $\Delta^{17}\text{O}$ of 102-GC-AZ01 (13 per meg, $n = 95$
309 replicates) is considered our minimum external error and is used to calculate standard error in
310 place of 1 S.D. of sample replicates when the S.D. of sample replicates is smaller. We observe
311 typical external reproducibility (1 S.D.) of 2 to 20 per meg for replicate analyses of a sample.
312 Measurements are replicated 1-4 times for individual samples.

313 To compare our $\Delta^{17}\text{O}$ data to previously published soil carbonate $\Delta^{17}\text{O}$ data from
314 Beverly et al. (2021), Ji (2016), and Passey et al. (2014), we adjusted the previously reported
315 values so that they are consistent with the normalization schemes used in this study. The soil
316 carbonate $\Delta^{17}\text{O}$ data of Beverly et al. (2021) were generated in the same laboratory following the
317 same preparation and analytical methods as the data new to this study. However, the Beverly et
318 al. (2021) data were originally presented as O_2 values. We calculated the mineral values for those
319 samples using the UM-specific empirically derived fractionation factors as described above.
320 Additionally, we screened 6 of the 39 original analyses for the $\delta^{18}\text{O}$ memory effect (this memory
321 effect had not yet been described in the UM laboratory at the time of that study). These
322 renormalization efforts do not affect the major findings of that study.

323 We also re-report $\Delta^{17}\text{O}$ values of soil carbonates that were produced at Johns Hopkins
324 University (JHU), using a similar reduction - fluorination analytical procedure as employed at
325 the UM (data from Ji, 2016 and Passey et al., 2014). These $\Delta^{17}\text{O}$ data were originally reported as
326 O_2 gas values. We normalized the JHU data to carbonate mineral values (Wostbrock et al.,
327 2020b; Sharp and Wostbrock, 2021) using empirically derived fractionation factors specific to
328 JHU. The mineral-(90°C acid- O_2) fractionation factors were calculated using the mineral value of
329 NBS-19 from Wostbrock et al. (2020b) ($\delta^{17}\text{O} = 14.923 \pm 0.010 \text{ ‰ VSMOW-SLAP}$, $\delta^{18}\text{O} =$
330 $28.650 \text{ ‰ VSMOW-SLAP}$, $\Delta^{17}\text{O} = -102 \pm 10 \text{ per meg VSMOW-SLAP}$) and the long term

331 average NBS-19 value from JHU (excluding two problematic sessions, $n = 43$, $\delta^{18}\text{O} = 36.998 \pm$
332 0.6930‰ VSMOW-SLAP, $\Delta^{17}\text{O} = -139 \pm 10$ per meg VSMOW-SLAP). The JHU fractionation
333 factors are $^{17}\alpha_{\text{mineral-90}^\circ\text{C acid, O}_2} = 0.9957782$ and $^{18}\alpha_{\text{mineral-90}^\circ\text{C acid, O}_2} = 0.9919498$
334 ($\theta_{\text{mineral-90}^\circ\text{C acid, O}_2} = 0.5234$). Finally, we applied a session-specific drift correction to the
335 $\Delta^{17}\text{O}$ mineral values using the mineral value of NBS-19 defined by Wostbrock et al. (2020b) (-
336 102 per meg, VSMOW-SLAP). For sessions including JHU analytical numbers 1104-1208
337 (sample IDs GON07-4.6-02; GON07-4.7-1; CA08-005-1; ET05-AWSH-48-1), NBS-19 was not
338 analyzed, so we relied on a tank CO_2 standard to perform a final drift correction. The "mineral"
339 value of tank CO_2 is defined via analysis in other sessions against NBS-19 ($\Delta^{17}\text{O}$ value = -0.077
340 ‰).

341

342 2.4.2 Clumped Isotope Analytical and Normalization Methods (Δ_{47} , $\delta^{13}\text{C}$, $\delta^{18}\text{O}$)

343 We present clumped isotope (Δ_{47}) data for 40 of the 47 soil carbonate samples considered
344 in this study. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are generated simultaneously as a part of the Δ_{47} measurement.
345 Some data were previously published, and some are new to this work (Table 1, Table 3). For the
346 samples with clumped isotope data that have been reported in previous publications, we use the
347 Δ_{47} and $T\Delta_{47}$ values as originally reported. All Δ_{47} data are reported relative to 25 °C acid
348 digestion (Table 3). There are minor differences in the acid fractionation factor used (i.e.,
349 Beverly et al., (2021) used 0.082 from Defliese et al., (2015); most others used 0.088 of Petersen
350 et al., (2019)), and minor differences in the reference frames (i.e., some data pre-date the ICDES
351 and the CDES) (Table 3). The Δ_{47} data that are new to this study were generated at UM in two
352 different laboratories (Table 3).

353 Clumped isotope data for six of the samples from this study were generated at the Stable
354 and Clumped Isotope for Paleoclimate and Paleoceanography (SCIPP) Laboratory at UM in
355 July-December of 2020 (Table 3) (including the two samples of Licht et al., (2022)). Carbonate
356 samples (4–7 mg) were digested in phosphoric acid held at 70 °C in individual vials and purified
357 using a NuCarb automated sample preparation device (Jones et al., 2022; O’Hora et al., 2022).
358 Resulting CO₂ gas was analyzed on a Nu Perspective mass spectrometer. Raw Δ_{47} values were
359 calculated with the ¹⁷O correction parameters of Brand et al. (2010) (Schauer et al., 2016; Daëron
360 et al., 2016). These Δ_{47} values were standardized using an equal proportion of standards ETH 1-
361 4, by assigning the community-defined InterCarb (ICDES90) values (Bernasconi et al., 2021)
362 which inherently include an acid fractionation factor of 0.088 ‰ to account for the difference in
363 Δ_{47} between CO₂ reacted at 25 °C and 90 °C (Petersen et al., 2019). Temperatures were
364 calculated using the calibration of Anderson et al. (2021), which is reported in the ICDES90
365 reference frame. The error reported for sample Δ_{47} values is calculated as standard error of 2-4
366 measured replicates. The standard deviation used is the larger value of either the standard
367 deviation of Carrara Marble in the session (0.013 ‰, n = 23) or the standard deviation of sample
368 replicate values. Finally, we report the sample values in the ICDES25 reference frame (adjust the
369 values by an acid fractionation factor of 0.088 from Petersen et al. [2019]) to present the data in
370 Table 3 alongside previously published data that had been reported relative to digestion at 25 °C.

371 Clumped isotope data for four of the samples from this study were generated at the
372 Isotopologue Paleosciences Laboratory (IPL) at UM (Table 3). Carbonate samples (6–8 mg of
373 carbonate equivalent) were digested in a common phosphoric acid bath held at 90°C. The
374 resulting CO₂ was cryogenically separated from water and then carried with helium through a
375 Poropak Q trap held at -20 °C in a bespoke extraction line that is directly connected to a Nu

376 Perspective. Raw Δ_{47} values were calculated with the ^{17}O correction parameters of Brand et al.
 377 (2010) (Schauer et al., 2016; Daëron et al., 2016) and were normalized with a hybrid gas and
 378 carbonate standards approach similar to the InterCarb (ICDES) framework (Bernasconi et al.,
 379 2021). Equilibrated and heated gases (30°C and 1000 °C) (known values from Petersen et al.,
 380 2019) were combined with carbonate standards ETH1-3 (accepted values from Bernasconi et al.,
 381 2021) to correct the sample Δ_{47} values for compositional nonlinearity and project them into the
 382 ICDES-90 reference frame, using the single equation formulation of Daeron et al. (2016).
 383 Temperatures were calculated using the calibration of Anderson et al., (2021). Finally, we
 384 correct the samples to relative to acid digestion at 25 °C (i.e., place them into the ICDES25
 385 reference frame) using an acid fractionation factor of 0.088 from Petersen et al. [2019]). This
 386 allows us to present the data alongside previously published data that had been reported relative
 387 to digestion at 25 °C (Table 3).

388

389 2.4.3 Reconstructing soil waters ($\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$) from carbonates ($\delta^{18}\text{O}_{\text{carb}}$, $\Delta^{17}\text{O}_{\text{carb}}$, Δ_{47})

390 We calculate the reconstructed soil water values ($\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$) so that we can
 391 compare the carbonate-generated isotope data directly to isotopic compositions of meteoric
 392 water. We calculated $\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$ using empirically derived carbonate-water
 393 fractionation factors for $\delta^{18}\text{O}_{\text{sw}}$ (Kim and O'Neil, 1997) and $\lambda_{\text{cc-w}}$:

$$1000\ln^{18}\alpha_{\text{cc-w}} = 18030/T - 32.42 \quad (4)$$

$$^{17}\alpha = (^{18}\alpha)^{\lambda_{\text{cc-w}}} \quad (5)$$

394 Using the expression for $^{18}\alpha_{\text{cc-w}}$ of Wostbrock et al. (2020a) rather than Kim and O'Neil (1997)
 395 results in $\delta^{18}\text{O}_{\text{rsw}}$ values that differ by 1 ‰ and $\Delta^{17}\text{O}_{\text{rsw}}$ values that differ by ~2–5 per meg
 396 (Figure S12) (a magnitude of difference that is not relevant to our interpretations). We use

397 $\lambda_{cc-w} = 0.5250 \pm 0.0021$ that was established empirically in our laboratory through analysis of
398 synthetic and natural calcites and their parent waters (Huth et al., 2022; Kelson et al., 2022)
399 (Figure S17). Although most studies find a similar λ_{cc-w} value (range from 0.5231 to 0.5254),
400 the discrepancies in the fourth decimal place will change the reconstructed $\Delta^{17}\text{O}$ water values on
401 the order of 10 per meg (Bergel et al., 2020; Voarintsoa et al., 2020; Wostbrock et al., 2020; see
402 Figure 5 of Huth et al. [2022]). The discrepancies in λ_{cc-w} are poorly understood; we rely on our
403 in-house λ_{cc-w} value because the empirically derived λ_{cc-w} values may incorporate fractionation
404 inherent to each analytical procedure. The $\Delta^{17}\text{O}_{\text{rsw}}$ values could be revised in the future as
405 λ_{cc-w} values become better constrained.

406 We used the $\delta^{18}\text{O}_{\text{carb}}$ values obtained by mass spectrometry via analysis as CO_2 (usually
407 simultaneous with Δ_{47} analyses) (Table 3) to calculate $\delta^{18}\text{O}_{\text{rsw}}$ because these values are more
408 accurate and precise than the $\delta^{18}\text{O}$ values obtained via O_2 -based analysis. The $\delta^{18}\text{O}_{\text{carb}}$ values
409 measured via O_2 as part of the $\Delta^{17}\text{O}_{\text{carb}}$ measurement vs. via CO_2 as part of the Δ_{47} measurement
410 typically agree within 1 ‰, though there are discrepancies greater than 2 ‰ for eight of the
411 samples (19ND04 and PDJ 4055 115a that are new to this paper, 18-SS-236A-C, 18-SS-69A, 18-
412 SS-79A, GON07 samples, CA08-005-1, and BUR-MH-30Buff in previously reported samples).
413 Some of this discrepancy could be natural heterogeneity in soil carbonates; some could be due to
414 fractionation during the reduction-fluorination preparation steps (Passey et al., 2014). Where
415 possible, a clumped isotope temperature was used to constrain the growth temperature to
416 calculate α^{18} . For the Fish Lake Valley sites that do not have Δ_{47} data, we use spring and summer
417 average soil temperatures measured at 100 cm to approximate carbonate formation temperatures
418 (Oerter and Amundson, 2016). For the sites from Iran and New Mexico that do not have Δ_{47}
419 temperatures, we used a mean warm quarter air temperature from local meteorological stations

420 (Table 3) (Quade et al., 2013; Kelson et al., 2020; Fischer-Femal and Bowen, 2021). The cp3 site
421 did not have sufficient material for Δ_{47} analysis, so we use the Δ_{47} temperature from the other
422 Tibetan site, cp4 (Table 3). For the samples with Δ_{47} data, the uncertainty in mineral growth
423 temperature is based on the external error in Δ_{47} and is typically less than 5 °C. For the samples
424 without Δ_{47} data, the uncertainty in growth temperature is estimated using the difference between
425 mean annual air temperature and mean warm quarter temperature. We estimated error in $\delta^{18}\text{O}_{\text{rsw}}$
426 and $\Delta^{17}\text{O}_{\text{rsw}}$ by propagating error in growth temperature and external error in isotopic
427 measurements with Monte Carlo resampling. The calculated $\delta^{18}\text{O}_{\text{rsw}}$ values are sensitive to
428 growth temperature: a 5 °C temperature difference results in a ~1 ‰ difference in $\delta^{18}\text{O}_{\text{rsw}}$, which
429 is large compared to the typical uncertainty of 0.1 ‰ in a $\delta^{18}\text{O}$ measurement but is the same
430 order of magnitude as uncertainty associated with calibration of $^{18}\alpha$ -temperature relationship. In
431 comparison, $\Delta^{17}\text{O}_{\text{rsw}}$ is less sensitive to growth temperature: a 5 °C temperature difference
432 results in a ~3 per meg difference in $\Delta^{17}\text{O}_{\text{rsw}}$, which is smaller than typical external error of 5 to
433 13 per meg in a $\Delta^{17}\text{O}$ measurement.

434

435 **3. Results**

436

437 *3.1 Predictions for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ in a profile of soil water considering evaporation*

438 The ^{17}O -modified Barnes and Allison (1983) model predicts that evaporation causes soil
439 water to have higher $\delta^{18}\text{O}$ values and lower $\Delta^{17}\text{O}$ values relative to input water (Figure 2). The
440 maximum isotopic offset occurs at the evaporation front, the depth of which varies with relative
441 humidity and evaporation rate (z_{ef} , typical depths of 0.1 to 0.3 m) (Figure 2; Figure S1). Above
442 the z_{ef} , the isotopic composition of pore space water vapor is dominantly controlled by exchange

443 with the atmospheric water vapor, and below the z_{ef} , it is dominated by downward diffusion of
444 evaporatively-affected water. For the suite of model predictions with varying physical
445 parameters, we predicted maximum isotopic offsets that ranged from +3 to +40 ‰ in $\delta^{18}\text{O}$ and -
446 40 to -260 per meg in $\Delta^{17}\text{O}$ (Figure S2). The maximum isotopic offset due to evaporation is
447 particularly sensitive to the humidity of the overlying atmosphere (Figure 2D). We calculate
448 linear regressions between $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ as predictor and response variables, respectively. The
449 resulting slopes (i.e., λ_{soil} values) range from 0.514 to 0.525 with a median of 0.517. There is
450 curvature in the relationship between $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, but we describe a linear trend because it
451 can be compared to trends observed in natural systems where the low precision in $\Delta^{17}\text{O}$
452 (typically ± 10 per meg) masks curvature. The model-derived λ_{soil} values correspond to trends in
453 $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ that range from -2 to -14 per meg/‰ with a median of -10.7 per meg/‰. The
454 corresponding slopes in $\delta^{18}\text{O}$ - $\delta^2\text{H}$ space have a median value of 2.5.

455

456 *3.2 Stable isotope ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$, and Δ_{47}) results from natural pedogenic carbonates*

457 Tables 2 and 3 present stable isotope data from 47 individual pedogenic carbonates from
458 30 localities including 6 profiles, each with $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ data. Of the 47 pedogenic
459 carbonates, 40 have accompanying Δ_{47} data. The range of $\delta^{13}\text{C}$ values is -13.9 to 2.1 ‰ (VPDB)
460 and the range of $\delta^{18}\text{O}_{\text{carb}}$ values is -17.0 to 4.3 ‰ (VPDB) (Tables 2 and 3). There is weak
461 covariation in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Figure S13). The range of Δ_{47} values is 0.582 to 0.761 ‰
462 (ICDES25), corresponding to temperatures of 1 to 42 °C (Table 3).

463 The range of $\Delta^{17}\text{O}_{\text{carb}}$ values is -154 to -60 per meg, corresponding to calculated $\Delta^{17}\text{O}_{\text{rsw}}$
464 values of -66 to +27 per meg ($\lambda_{cc-w} = 0.5250$). Many, but not all, of the soil carbonates plot
465 outside of the $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ population defined by global, un-evaporated meteoric waters (tap

466 water, springs, rivers or streams, precipitation, and groundwater, compiled in Aron et al. (2021))
467 (Figure 4). The $\Delta^{17}\text{O}_{\text{rsw}}$ values determined from the pedogenic carbonates form a population
468 that is distinct from that of the global meteoric waters; the means of the populations of $\Delta^{17}\text{O}$ of
469 reconstructed soil waters and of meteoric waters are statistically different according to a z-test
470 (p-value < 2.2e-16).

471 The data from the pedogenic carbonates show a wedge-like relationship between $\Delta^{17}\text{O}$
472 and AI that does not change if $\Delta^{17}\text{O}_{\text{carb}}$ or $\Delta^{17}\text{O}_{\text{rsw}}$ values are considered (Figure 5) or if the
473 difference between $\Delta^{17}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{mw}}$ is considered (Figure S14). We found a step-like pattern
474 where low $\Delta^{17}\text{O}$ values are more common in more arid environments. The threshold occurs near
475 an AI value of 0.4: environments with AI values < 0.4 (hyper-arid to semi-arid environments)
476 have $\Delta^{17}\text{O}_{\text{carb}}$ values that range from -154 to -67 per meg values ($\Delta^{17}\text{O}_{\text{rsw}}$ of -67 to + 26 per meg)
477 and environments with AI values > 0.4 (semi-arid to humid environments) have $\Delta^{17}\text{O}_{\text{carb}}$ carb
478 values that range from -86 to -60 per meg ($\Delta^{17}\text{O}_{\text{rsw}}$ of -4 to + 27 per meg) (excluding one sample
479 collected from a depth of 7 cm, cp3, Table 2) (Figure 5). The mean $\Delta^{17}\text{O}$ value of pedogenic
480 carbonates within each aridity class decreases with increasing aridity (Figure 5). The mean
481 $\Delta^{17}\text{O}_{\text{carb}}$ values are -118 per meg (hyper-arid, n = 3), -92 per meg (arid, n = 13), -80 per meg
482 (semi-arid, n = 21), -77 per meg (dry sub-humid, n = 5), and -74 per meg (sub-humid, n = 1), and
483 -77 per meg (humid, n = 1) (Figure 5).

484 In soil carbonate samples from single profiles, we observed four profiles with $\delta^{18}\text{O}$ values
485 higher near the soil surface than at depth (20MOJrighthand, cp3 Tibet, GON07, CAN01). In
486 three of these four profiles, we measured low $\Delta^{17}\text{O}_{\text{rsw}}$ values near the surface (Figure 6), and in
487 one of the profiles, we measured near-constant $\Delta^{17}\text{O}_{\text{rsw}}$ values with depth. We documented two

488 profiles with near-constant $\delta^{18}\text{O}$ values with depth (NAC and Diablo); in those profiles we
489 observed a decrease in $\Delta^{17}\text{O}_{\text{rsw}}$ near the surface (NAC) and constant $\Delta^{17}\text{O}_{\text{rsw}}$ (Diablo) (Figure 6).

490 We observed no covariation in $\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$ amongst the samples altogether
491 (Figure 4), which is as expected given that the soils are forming from pore water with disparate
492 initial $\delta^{18}\text{O}$ values and varying degrees of evaporation. We did observe covariation between
493 'normalized' $\delta^{18}\text{O}$ (calculated as $\delta^{18}\text{O}_{\text{rsw}}$ minus $\delta^{18}\text{O}_{\text{ann}}$) and $\Delta^{17}\text{O}_{\text{rsw}}$ (Figure 4C). Covariation due
494 to evaporation (or lack thereof) in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ in related samples is described on a case basis
495 as examples for paleoclimate applications (Section 4.5, Figure 7). We observed a wedge-like
496 pattern between $\delta^{13}\text{C}$ and $\Delta^{17}\text{O}_{\text{carb}}$ (Figure S13). This pattern might indicate increased soil water
497 evaporation in mixed $\text{C}_3\text{-C}_4$ and in C_4 -dominant ecosystems (grass and shrublands) compared to
498 C_3 -dominant ecosystems, or that respiration rates are especially low in some soils that
499 experienced a lot of evaporation. It could also be related to an oversampling of C_4 ecosystems
500 due to the large number of samples from the Serengeti (Beverly et al., 2021).

501

502 **4. Discussion**

503

504 *4.1 Theoretical predictions for triple oxygen isotope patterns in soil waters*

505 The predicted direction and magnitude of isotopic offset due to evaporation is instructive
506 for natural soil carbonates, even though they are unlikely to have formed in the quasi-steady state
507 conditions invoked for the Barnes and Allison (1983) model (i.e., upward diffusion of water
508 from the water table, and no vapor transport below an evaporation front). The model predicts that
509 evaporation of soil water should lead to the following patterns: (1) an increase in $\delta^{18}\text{O}$ and
510 decrease in $\Delta^{17}\text{O}$ relative to input water, with increasing fractionation within the top 0.1 to 0.3

511 m, (2) increased isotopic offset with decreasing relative humidity of the atmosphere, and (3)
512 maximum evaporative offsets large enough to influence paleoclimate applications, if they are
513 indeed recorded in pedogenic carbonates (Figure 2). Future work could compare these
514 predictions by modifying other models of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in soil water, such as drying from a
515 saturated soil (Zimmerman et al., 1967; Chamberlain et al., 2014) and time-varying models
516 (Mathieu and Bariac, 1996; Zhou et al., 2021).

517 The apparent λ_{soil} values from the soil water evaporation model (median value of 0.517)
518 are within the range of reported slopes resulting from progressive evaporation of a water body
519 (i.e., λ_{lake}) (Barkan and Luz, 2007; Luz and Barkan, 2010; Surma et al., 2015, 2018; Gázquez et
520 al., 2018; Passey and Ji, 2019; Voigt et al., 2021; Katz et al., 2023) (Figure S3). The median of
521 the slopes of a linear model in $\delta^{18}\text{O}$ - $\delta^2\text{H}$ space (2.5) is consistent with theoretical values for
522 evaporation trajectories reported elsewhere based on the Craig-Gordon (1965) model (Barnes
523 and Allison, 1988; Benettin et al., 2018; Bowen et al., 2018; Shi et al., 2021). However, in
524 natural soil waters, the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ trajectories have slopes of 5-6 ‰ as a result of mixing between
525 antecedent pore water and isotopically variant incoming precipitation (Gibson et al., 2008; Oerter
526 and Bowen, 2017; Sprenger et al., 2017; Benettin et al., 2018). By extension, we expect that the
527 $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ relationships (λ_{soil}) in natural soil waters and carbonates would be steeper than the
528 theoretically predicted values due to mixing. Our model-based predictions for λ_{soil} remain to be
529 validated through studies of triple oxygen isotope compositions in natural soil pore waters.

530

531 *4.2 Empirical evidence for prevalent evaporation in pedogenic carbonate parent waters*

532 Our data suggest that non-negligible evaporation of parent soil waters is common across
533 a variety of climate regimes (Figure 4). Evaporation is the most parsimonious explanation for the

534 observation that the $\Delta^{17}\text{O}_{\text{rsw}}$ values from pedogenic carbonates tend to be lower (by up to ~60
535 per meg) than the $\Delta^{17}\text{O}$ values of unevaporated global meteoric waters ($\Delta^{17}\text{O}_{\text{mw}}$), which are
536 typically 20-40 per meg (Aron et al., 2021a) (Figure 4). Evaporation in soil pore waters has been
537 shown previously (Evaristo et al., 2015; Sprenger and Allen, 2020); our data add that these
538 evaporated soil waters are commonly the host waters from which pedogenic carbonates form.
539 While we favor evaporation as the dominant process responsible for lowering $\Delta^{17}\text{O}$ in soil
540 carbonates, we discuss the potential role of two other processes: isotopic disequilibrium and
541 mixing.

542 We cannot strictly rule out the possibility that soil carbonate precipitated under periods of
543 isotopic disequilibrium due to CO_2 degassing. Theoretical predictions suggest that CO_2 degassing
544 would result in offsets in the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values of the dissolved inorganic carbon (DIC)
545 species of up to +8 ‰ and +70 per meg, respectively, that could be inherited by the mineral (Guo
546 and Zhou, 2019). The factors that drive calcite precipitation in soils (temperature, water content,
547 and/or CO_2) generally change slowly (days to weeks) at the soil depths we sampled (e.g., Huth et
548 al., 2019), much slower than DIC equilibration timescales (hours) (Uchikawa and Zeebe, 2012;
549 Guo and Zhou, 2019), and the mineral remains buffered in the pore water (unlike stalagmites, for
550 example). Furthermore, there is no evidence for widespread or large kinetic isotope effects: soil
551 carbonate $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} values generally conform with expectations (Cerling et al., 1989;
552 Cerling and Quade, 1993; Quade et al., 2013) except in cryogenic environments (Burgener et al.,
553 2018). We observe almost no $\Delta^{17}\text{O}_{\text{rsw}}$ values that are higher than the range of $\Delta^{17}\text{O}_{\text{rsw}}$ values. We
554 suggest that kinetic isotope effects due to degassing are either small or nonexistent in the soils in
555 this dataset. Equilibrium formation of soil carbonates could be tested more robustly with Δ_{47} - Δ_{48}
556 clumped isotope thermometry (Fiebig et al., 2019; Guo, 2020).

557 Due to the nonlinearity in $\Delta^{17}\text{O}$ notation, mixing between waters with different $\delta^{18}\text{O}$
558 values but the same $\Delta^{17}\text{O}$ values results in a lower $\Delta^{17}\text{O}$ value (e.g., Aron et al., 2021a). The
559 signal due to nonlinearity is small compared to the observed offset between $\Delta^{17}\text{O}_{\text{rsw}}$ and typical
560 $\Delta^{17}\text{O}_{\text{mw}}$ in our soil carbonate data. For example, as an estimate of the maximum lowering in
561 $\Delta^{17}\text{O}$ due to nonlinear mixing, we consider a mix of equal proportions of waters that differ in
562 $\delta^{18}\text{O}$ by 20 ‰ with identical $\Delta^{17}\text{O}$ values (i.e., two successive rainfall events with $\delta^{18}\text{O}$ values
563 that spans the typical seasonal range at midlatitudes). This scenario results in a mixed water with
564 a $\Delta^{17}\text{O}$ value that is about 10 per meg lower than the starting value. Achieving a lowering in
565 $\Delta^{17}\text{O}$ that would completely explain the offset between $\Delta^{17}\text{O}_{\text{rsw}}$ and typical $\Delta^{17}\text{O}_{\text{mw}}$ (i.e., a
566 lowering of ~60 per meg) through nonlinearity alone would require a 50% mix of two rain events
567 that differ in $\delta^{18}\text{O}$ by >40 ‰. That scenario is unlikely to occur in natural settings. Thus,
568 nonlinearity in mixing alone could contribute a minor amount (~10 per meg) but does not fully
569 explain the observed low $\Delta^{17}\text{O}_{\text{rsw}}$ values.

570 However, successive mixing between isotopically light rainfall and evaporatively
571 enriched soil water is important to consider (e.g., Sprenger et al., 2016). The resulting mixed
572 rain-soil water will have an isotopic composition that reflects some of the antecedent
573 evaporation. A 50/50 mix between highly evaporated soil pore water ($\delta^{18}\text{O} = +20$, $\Delta^{17}\text{O} = -200$
574 per meg) and isotopically light incoming precipitation ($\delta^{18}\text{O} = -20$, $\Delta^{17}\text{O} = +32$) would result in
575 soil water with an intermediate composition ($\delta^{18}\text{O} = 0$ and $\Delta^{17}\text{O} = -110$). In a mix of the same
576 endmembers but with a smaller fraction of antecedent, highly evaporated soil water (i.e., 10%),
577 the resulting water will more closely resemble recharge (resulting in 'mixed' water with $\delta^{18}\text{O} = -$
578 16‰, $\Delta^{17}\text{O} = -9$ per meg). Thus, mixing with antecedent evaporated soil water is very likely to
579 contribute to the observed low $\Delta^{17}\text{O}_{\text{rsw}}$ values.

580 If evaporation is driving the lowering of $\Delta^{17}\text{O}_{\text{rsw}}$ relative to typical global meteoric
581 waters, it should be accompanied by an increase in $\delta^{18}\text{O}_{\text{rsw}}$ values compared to the $\delta^{18}\text{O}$ of
582 recharge waters (Figure 1, Figure 2). In practice, this is difficult to definitively show because we
583 do not know the $\delta^{18}\text{O}$ values of recharge water; we used $\delta^{18}\text{O}_{\text{ann}}$ as a first approximation (Figure
584 4C) (Figure S15 shows the correlation using $\delta^{18}\text{O}$ of precipitation during the approximated
585 season of soil carbonate formation). $\delta^{18}\text{O}_{\text{rsw}}$ is often greater than $\delta^{18}\text{O}_{\text{ann}}$, a finding that is
586 consistent with evaporative modification of soil water and has been previously documented
587 (Quade et al., 2007a; Kelson et al., 2020; Beverly et al., 2021) (Figure 4B). Our pedogenic
588 carbonate data show that low $\Delta^{17}\text{O}_{\text{rsw}}$ values generally co-occur with $\delta^{18}\text{O}_{\text{rsw}}$ values that exceed
589 $\delta^{18}\text{O}_{\text{ann}}$ (Figure 4C), providing strong evidence in favor of evaporation driving fractionation of
590 oxygen isotopes in soil water. Based on our data and typical evaporation slopes in triple oxygen
591 isotopes, we estimate that enrichments in $\delta^{18}\text{O}$ on the order of 1–5 ‰ are common
592 (corresponding to depletions in $\Delta^{17}\text{O}$ of approximately 10 to 50 per meg). The apparently
593 commonplace signal of evaporation has significant implications for paleoclimate reconstructions
594 that center around interpretations of $\delta^{18}\text{O}_{\text{carb}}$.

595 One source of uncertainty is that we are inferring evaporation by comparing $\Delta^{17}\text{O}_{\text{rsw}}$ to
596 $\Delta^{17}\text{O}$ of meteoric waters (Figure 4). There is uncertainty in the calculated $\Delta^{17}\text{O}_{\text{rsw}}$ values that is
597 introduced by uncertainty in the $\lambda_{\text{cc-w}}$ value used to calculate water values from carbonates
598 (Bergel et al., 2020; Voarintsoa et al., 2020; Wostbrock et al., 2020a; Huth et al., 2022; Kelson et
599 al., 2022) (Section 2.4.3). Lower $\lambda_{\text{cc-w}}$ values result in higher $\Delta^{17}\text{O}_{\text{rsw}}$ values, which would
600 imply less evaporation overall in our dataset. One estimate of the error in $\lambda_{\text{cc-w}}$ is ± 0.00021 ,
601 which is ± 1 S.D. of measured $\lambda_{\text{cc-w}}$ values from 8 paired carbonate-water samples in our
602 laboratory (Huth et al., 2022; Kelson et al., 2022); this uncertainty translates to a maximum

603 difference in $\Delta^{17}\text{O}_{\text{rsw}}$ of 13 per meg in the pedogenic carbonate samples. When $\Delta^{17}\text{O}_{\text{rsw}}$ values
604 are calculated using the maximum $\lambda_{\text{cc-w}}$ value, the $\Delta^{17}\text{O}_{\text{rsw}}$ values remain distinct from global
605 meteoric waters, and the negative trend between $\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$ remains (Figure S15).
606 Improved constraints on $\lambda_{\text{cc-w}}$ in the future would allow us to revise the $\Delta^{17}\text{O}_{\text{rsw}}$ values and to
607 precisely estimate the magnitude of evaporation in each of the reconstructed soil water values;
608 but it is unlikely to alter our main interpretation that many $\Delta^{17}\text{O}_{\text{rsw}}$ values are evaporatively
609 modified.

610

611 *4.3 Depth profiles of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in natural soils*

612 We examine $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values at multiple depths in natural soils to evaluate if $\Delta^{17}\text{O}$
613 adheres to the expected depth-dependent patterns for evaporation. The soil profiles also allow us
614 to re-evaluate the assumption made in many paleoclimate applications that pedogenic carbonate
615 from depths > 40 cm records unevaporated soil water (Barnes and Allison, 1983; Allison et al.,
616 1983; Quade et al., 1989; Pendall et al., 1994; Liu et al., 1995, 1996; Oerter and Amundson,
617 2016; Kelson et al., 2020; Fischer-Femal and Bowen, 2021).

618 First, we examine if $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ -depth relationships in natural soils generally agree with
619 theoretical predictions that evaporation should result in higher $\delta^{18}\text{O}$ and lower $\Delta^{17}\text{O}$ values in
620 shallower soil waters (0 to 40 cm) compared to deeper soil waters (Section 3.1, Figure 2) (for
621 $\delta^{18}\text{O}$ and $\delta^2\text{H}$: Barnes and Allison, 1983; Mathieu and Bariac, 1996; Hsieh et al., 1998; Zhou et
622 al., 2021). In four of the profiles, we observe higher $\delta^{18}\text{O}_{\text{rsw}}$ values coupled with lower $\Delta^{17}\text{O}_{\text{rsw}}$
623 values at shallower depths (Figure 6; 20MOJrighthand, cp3, GON07, CAN01) (Figure S4
624 compares the Barnes and Allison 1983 model and the cp3 profile). Additionally, in each of these
625 four profiles, the shallow-sample $\delta^{18}\text{O}_{\text{rsw}}$ is high compared to the possible range of $\delta^{18}\text{O}$ of

626 precipitation and $\Delta^{17}\text{O}_{\text{rsw}}$ is low compared to typical $\Delta^{17}\text{O}_{\text{mw}}$ values. Evaporation likely drives
627 fractionation in these soil pore waters and is recorded in the pedogenic carbonates.

628 The inverse of this prediction is that if evaporation is unimportant, and no other processes
629 affect the oxygen isotope values of soil water (i.e., seasonal deep recharge), there should be no
630 variation in $\delta^{18}\text{O}$ or $\Delta^{17}\text{O}$ with depth, and both values should reflect possible pristine $\delta^{18}\text{O} / \Delta^{17}\text{O}$
631 water values. In Diablo, a soil from the Coast Ranges of California, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values are
632 constant within the depths examined (50 and 80 cm). The $\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$ values are within
633 ranges expected for meteoric waters (Figure 6). This soil profile conforms with theoretical
634 predictions that evaporation should not affect the oxygen isotope values of soil water at depths
635 greater than 30 to 40 cm (shallower carbonate did not exist at this location) (Figure 6). This
636 sample has a relatively cold clumped isotope temperature that suggests carbonate formation
637 during the winter wet season. Additional study of the seasonal dynamics of pedogenic carbonate
638 formation and soil water recharge at this site would be needed to explain why pedogenic
639 carbonates form in un- or minorly- evaporated water (e.g., Gallagher and Sheldon, 2016; Huth et
640 al., 2019; Kelson et al., 2020).

641 We observed one soil profile that does not conform to predictions for either the absence
642 or presence of evaporation. In the NAC profile from the Ñacuñán Biosphere Reserve in the
643 Andean piedmont, Argentina (Ringham et al., 2016), $\delta^{18}\text{O}_{\text{rsw}}$ values are constant with depth and
644 resemble $\delta^{18}\text{O}_{\text{ann}}$, suggesting minor to no evaporation (Figure 6). In contrast, the $\Delta^{17}\text{O}_{\text{rsw}}$ values
645 at both depths are lower than typical $\Delta^{17}\text{O}_{\text{mw}}$ values, and the 50 cm sample has a value that is 17
646 per meg lower than the 100 cm sample, suggesting that evaporation could have played a role. We
647 hypothesize that the soil carbonate near the surface and at depths formed at different times of the

648 year as precipitation events from different seasons percolated to different depths, resulting in a
649 complex isotopic profile (Peters et al., 2013; Ringham et al., 2016).

650 From this dataset, it is not clear which conditions allow for evaporation to be preserved in
651 pedogenic carbonate depth profiles. The four sites with clear evidence for near-surface
652 evaporation in their pedogenic carbonates represent disparate climates, latitudes, and elevations
653 (Figure 6; 20MOJrighthand, cp3, GON07, CAN01) (Table 1). One similarity might be relatively
654 coarse soil texture (presence of gravel) that enables evaporation. Surprisingly, the NAC and
655 CAN01 sites yield different results with respect to apparent evaporation recorded in $\delta^{18}\text{O}_{\text{rsw}}$ and
656 $\Delta^{17}\text{O}_{\text{rsw}}$ but are only about ~200 km apart and formed under similar climates. Possible
657 differences are increased plant productivity/density at NAC (Ringham et al., 2016) or carbonate
658 morphology (the NAC sample is a from a profile developed in a sandy substrate with early
659 stage carbonate nodule formation while CAN01 is a clast undercoating from a conglomeratic
660 substrate). We hypothesize that various factors including soil texture, plant water redistribution,
661 precipitation regime, and the timing of pedogenic carbonate formation relative to recharge events
662 will converge to produce a simple, evaporation-driven profile vs. a more complex, or un-
663 evaporated pedogenic profile (e.g., Cerling and Quade, 1993; Ringham et al., 2016; Kelson et al.,
664 2020).

665 Next, we turn to the question of whether paleoclimate workers can rely on soil carbonates
666 collected at depths > 40 cm to record unevaporated meteoric water values. A comparison
667 between $\Delta^{17}\text{O}_{\text{rsw}}$ and typical $\Delta^{17}\text{O}_{\text{mw}}$ values of the pedogenic carbonates at depths > 50 cm
668 suggest that evaporation has modified the isotopic composition of 'deep' soil water in all but one
669 soil profile. In five of the six profiles, $\Delta^{17}\text{O}_{\text{rsw}}$ is lower than typical $\Delta^{17}\text{O}_{\text{mw}}$ values at all depths
670 (Figure 6). It is plausible that differences between $\Delta^{17}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{mw}}$ that are on the order of 20

671 per meg could be eliminated if local $\Delta^{17}\text{O}_{\text{mw}}$ is much lower than typical values and/or if $\lambda_{\text{cc-w}}$ is
672 lower than we estimate, potentially reducing the apparent commonality of evaporated soil waters
673 at depths below 40 cm. Even with this uncertainty, our soil profile data suggest that evaporation
674 can be recorded in pedogenic carbonates from depths > 40 cm. Furthermore, evaporative
675 modification might be difficult to detect with $\delta^{18}\text{O}$ alone because evaporation can modify soil
676 waters at all depths, leaving little depth variation in $\delta^{18}\text{O}$ (NAC profile, Figure 6G). In this
677 regard, our observations do not match the steady-state model predictions of minimal evaporation
678 at depths typical of calcite horizon formation (i.e., minimal evaporation below 30 to 40 cm)
679 (Barnes and Allison 1983) – highlighting that steady-state conditions are not representative of
680 natural soils. Our observation is consistent with other evidence for evaporation in 'deep' soil pore
681 waters (DePaolo et al., 2004). We hypothesize that shallower soil water and/or pre-evaporated
682 surface water percolates to depths below 40 cm in these calcic soils, perhaps after mixing with
683 newly infiltrated waters (Gazis and Feng, 2004; Sprenger et al., 2018). A better understanding of
684 how evaporated soil water is transmitted to typical Bk horizon depths and recorded by carbonates
685 could be achieved with a model of the isotopic composition of soil water that considers vapor
686 flux, non-steady state (time-varying) conditions (Mathieu and Bariac, 1996; Zhou et al., 2021),
687 and calcite solubility (Meyer et al., 2014; Huth et al., 2019; Domínguez-Villar et al., 2022).

688

689 *4.4 A threshold relationship between aridity and $\Delta^{17}\text{O}$ of pedogenic carbonates on a global* 690 *scale*

691 We expected to find a relationship between $\Delta^{17}\text{O}$ of pedogenic carbonate and aridity,
692 where aridity would promote soil water evaporation and lower $\Delta^{17}\text{O}$ values of pedogenic
693 carbonates (Amin et al., 2020; Beverly et al., 2021). We find a wedge-like relationship between

694 $\Delta^{17}\text{O}$ and aridity on a global scale (Figure 5). Evaporation (low $\Delta^{17}\text{O}_{\text{carb}}$ values) is more
695 common in arid environments, but pedogenic carbonates that formed from unevaporated pore
696 waters exist even in arid localities (Figure 5). Humid environments are poorly represented in the
697 dataset (in part because soil carbonates are less common in humid compared with drier
698 environments), but the existing samples show uniformly high $\Delta^{17}\text{O}_{\text{carb}}$ values that indicate little
699 to no soil water evaporation. We hypothesize that the variation in $\Delta^{17}\text{O}$ in each aridity class on a
700 global basis is due to differences in input $\Delta^{17}\text{O}$ of local meteoric waters, effects relating to
701 vegetation, the age of the pedogenic carbonates, and the dynamics of pedogenic carbonate
702 formation, as described below.

703 Differences in the input $\Delta^{17}\text{O}_{\text{mw}}$ may complicate the relationship between $\Delta^{17}\text{O}_{\text{carb}}$ and
704 aridity on a global scale (Figure 5, Figure S14). $\Delta^{17}\text{O}_{\text{mw}}$ sets the local starting value from which
705 soil waters will isotopically evolve during evaporation (Figure 1). $\Delta^{17}\text{O}_{\text{mw}}$ of global meteoric
706 waters are relatively invariant, with a mean of 33 per meg and 1 SD of 12 per meg ($n = 1557$,
707 Aron et al., 2021). If we use global meteoric water to guide site-specific estimates of $\Delta^{17}\text{O}_{\text{mw}}$, we
708 find that the difference between $\Delta^{17}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{mw}}$ at the sites has a strong relationship with
709 aridity (Figure S14) (largely because mean $\Delta^{17}\text{O}_{\text{mw}}$ is relatively invariant). However, we caution
710 that $\Delta^{17}\text{O}_{\text{mw}}$ values based on averages could diverge significantly from the true $\Delta^{17}\text{O}_{\text{mw}}$ values.
711 First, $\Delta^{17}\text{O}_{\text{mw}}$ can vary with season (Aron et al., 2023). Second, though atypical, there are
712 examples of rain and tap water with $\Delta^{17}\text{O}$ values < 0 per meg due to raindrop re-evaporation in
713 the sub-cloud (Landais et al., 2010; Risi et al., 2013; Li et al., 2015; Giménez et al., 2021; Aron
714 et al., 2023; Xia et al., 2023). It is possible that input water with very low (< 0 per meg) $\Delta^{17}\text{O}$
715 values could partially contribute to lowering the observed $\Delta^{17}\text{O}_{\text{rsw}}$ values, especially in arid
716 environments, though the extent to which these very low (< 0 per meg) $\Delta^{17}\text{O}$ precipitation events

717 contribute significantly to recharging soil water is unknown. Future work that characterizes input
718 $\Delta^{17}\text{O}_{\text{mfw}}$ is needed to be able to understand $\Delta^{17}\text{O}_{\text{rsw}}$ and its relationship with aridity.

719 Vegetation (or lack thereof) may play a role in the observed pattern between $\Delta^{17}\text{O}_{\text{rsw}}$ and
720 aridity. First, the sparseness of the vegetation at the more arid sites could contribute to higher
721 surface temperatures and increased evaporation from soils. Second, because transpiration does
722 not alter the isotopic composition of soil water (Ehleringer and Dawson, 1992) but evaporation
723 does, an increased ratio of transpiration to evaporation in the soil dewatering that precedes soil
724 carbonate formation could contribute to the higher $\Delta^{17}\text{O}_{\text{rsw}}$ values observed in more humid (more
725 vegetated) environments (Barnes and Allison 1983). Furthermore, plants can redistribute water
726 in the soil profile, as documented through measurements of oxygen and hydrogen isotope ratios,
727 altering the vertical profiles of the isotopic composition of water and the soil moisture content
728 (Caldwell et al., 1998; Oerter and Bowen, 2019). Differing vegetation (e.g., desert shrubs vs.
729 grasses vs. trees) and their water sourcing strategies could account for some of the variation in
730 $\Delta^{17}\text{O}_{\text{rsw}}$ amongst aridity classes. In this dataset, grasslands and shrublands are overrepresented;
731 future workers may wish to investigate $\Delta^{17}\text{O}_{\text{carb}}$ in forested environments where we might expect
732 less evaporation (Railsback, 2021).

733 One limitation of the current dataset is that some of the sites have poor constraints on the
734 age and duration of pedogenic carbonate formation (Supplementary Text Section 2). It is
735 possible that some of the variation in $\Delta^{17}\text{O}_{\text{rsw}}$ within aridity classes is because some of the
736 pedogenic carbonates formed during climate conditions that were different than modern. For
737 example, the CA08-005-1 sample is from the north flank of the San Bernardino Mountains
738 (which delineate the Mojave Desert) and is late Pleistocene to middle Holocene in age (Passey et
739 al., 2010 and references within). In contrast, the MOJ-righthand samples from the Mojave Desert

740 of California are middle Holocene in age based on geomorphic context (Supplementary
741 Material). These sites are both in the Mojave Desert but yield differing $\Delta^{17}\text{O}_{\text{rsw}}$ values, with the
742 MOJ-righthand samples being significantly lower (Table 2). Differences in age might be a factor,
743 especially given that the late Pleistocene was wetter than the Holocene in the Mojave Desert
744 (McDonald et al., 2003). Other factors include geomorphic surface (breccia landslide vs. coarse
745 alluvial fan) or true differences in aridity (CA08-005-1 is at the edge of the Mojave Desert while
746 MOJ-righthand is well within the Mojave Desert).

747 We hypothesize that the dynamics of pedogenic carbonate formation contributes to the
748 wedge-like relationship between $\Delta^{17}\text{O}_{\text{carb}}$ and aridity through factors including depth, timing,
749 and variation in the processes driving crystallization. Variation in the relative depths of
750 pedogenic carbonate formation and the evaporation front could contribute to some of the
751 variability in $\Delta^{17}\text{O}_{\text{carb}}$ (and $\Delta^{17}\text{O}_{\text{rsw}}$) within aridity classes. The depth to which evaporative
752 isotopic fractionation propagates into the soil depends on environmental factors including
753 evaporation rates, relative humidity of the atmosphere, and physical soil characteristics (Figure
754 S1). The depth of carbonate formation is also related to climate and soil texture (Retallack,
755 2005). How these factors combine to create conditions in which pedogenic carbonate forms
756 within versus below the evaporation front may be explored in the future with non-steady state
757 models of soil water and its isotopic composition, models of pedogenic carbonate formation, and
758 careful sampling of pedogenic carbonate from stable land surfaces.

759 The timing and processes driving pedogenic carbonate precipitation will control the
760 isotopic composition of the soil water that is recorded, including $\Delta^{17}\text{O}_{\text{rsw}}$. There could be
761 discrepancies between annual average aridity conditions (i.e., AI) and the actual conditions
762 preceding and during pedogenic carbonate formation (Supplementary Text Section 3, Figures

763 S16, S17, S18) for discussion of seasonal estimates of AI). As a hypothetical example: in an arid
764 environment, pedogenic carbonate could form shortly following rain or infiltration events that
765 reset the isotopic composition of soil water (Snell et al., 2013; Huth et al., 2019). Thus, even if
766 soil water is highly evaporated on average, pedogenic carbonate may form during the initial
767 phases of evaporation, resulting in values of $\Delta^{17}\text{O}_{\text{rsw}}$ and $\delta^{18}\text{O}_{\text{rsw}}$ that closely resemble input
768 precipitation. This mechanism could explain why we observe more variation in $\Delta^{17}\text{O}$ values in
769 arid and semi-arid environments than in sub-humid and humid environments (although this could
770 also be due to under-sampling in humid environments). This hypothesis would predict that
771 rainfall intermittency and the seasonality of rainfall will be important in determining if
772 pedogenic carbonate records evaporative conditions (Peters et al., 2013; Tabor et al., 2013;
773 Gallagher and Sheldon, 2016; Huth et al., 2019).

774 Furthermore, there could be differing modes of pedogenic carbonate formation that relate
775 to aridity and contribute to the wedge-like relationship with $\Delta^{17}\text{O}_{\text{rsw}}$. Pedogenic carbonate
776 formation can be driven by soil dewatering via evaporation or transpiration (e.g., Breecker et al.,
777 2009; Gallagher and Sheldon, 2016) or by fluctuations in biologically respired CO_2 (Mintz et al.,
778 2011; Zamanian et al., 2016). We expect that in more arid environments, evaporation-driven
779 dewatering may drive pedogenic carbonate precipitation, resulting in lower $\Delta^{17}\text{O}_{\text{rsw}}$ values. In
780 more humid environments, fluctuations in soil CO_2 and/or plant dewatering may drive pedogenic
781 carbonate precipitation, resulting in higher $\Delta^{17}\text{O}_{\text{rsw}}$ values. This idea remains to be
782 systematically tested.

783 The pedogenic carbonate from the Atacama Desert (Quade et al., 2007b) illustrates that
784 relatively minimal evaporation can be recorded by pedogenic carbonates in arid environments.
785 The Atacama Desert is one of the driest places in the world, with a mean annual precipitation of

786 < 100 mm/year and sparse vegetation. If the degree of soil water evaporation at the time of
787 pedogenic carbonate formation were solely based on aridity, we would expect the $\Delta^{17}\text{O}_{\text{rsw}}$ value
788 of this sample to be among the lowest observed. However, we measure a $\Delta^{17}\text{O}$ value that is near
789 the median of the $\Delta^{17}\text{O}$ of globally observed values (median $\Delta^{17}\text{O}_{\text{rsw}} = 3$ per meg, Atacama
790 $\Delta^{17}\text{O}_{\text{rsw}} = 9$ per meg). In theory, high input $\Delta^{17}\text{O}_{\text{mw}}$ could mask a high magnitude of
791 evaporation in soil waters (low $\Delta^{17}\text{O}_{\text{rsw}}$). One study shows that in the Andes, $\Delta^{17}\text{O}$ values of
792 precipitation can be as high as 40 to 50 per meg, although most are within the more typical range
793 of 20 to 40 per meg (Aron et al., 2021b). Surma et al. (2018) report groundwater and tap water
794 with $\Delta^{17}\text{O}$ values of +7 and + 11 per meg from the Salar de Llamara, a lower-elevation salt flat
795 in the Atacama Desert. Local constraints on input $\Delta^{17}\text{O}_{\text{mw}}$ is required to fully evaluate if high
796 input $\Delta^{17}\text{O}_{\text{mw}}$ is responsible for the relatively high $\Delta^{17}\text{O}_{\text{rsw}}$ at the Atacama Desert and elsewhere.
797 Another possible explanation is that the soil water evaporation front (z_{ef}) is above the pedogenic
798 carbonate formation (115 cm). In the steady-state model of the isotopic composition of soil water
799 (Section 2.1, Barnes and Allison [1983]), a high evaporation rate results in a large but shallow
800 evaporative signal as unevaporated liquid water is advected upward and counteracts diffusion of
801 evaporated soil water (Figure S1). Another hypothesis is that in this extremely arid environment,
802 pedogenic carbonate forms soon after infiltration events, resulting in pedogenic carbonates that
803 appear only moderately evaporated as rainwater overwhelms the isotopic composition of residual
804 evaporated water. This could be true even if soil water is highly evaporated during most of the
805 year. The climatologic, hydrologic, and soil factors that contribute to the evaporative state of soil
806 water at the depth and time of soil carbonate formation is a topic for future study at well-
807 constrained localities.

808

809 *4.5 Examples for paleoclimate applications: $\Delta^{17}\text{O}$ reveals drivers of $\delta^{18}\text{O}$ variation in*
810 *geographically related samples*

811 In this section, we describe how $\Delta^{17}\text{O}_{\text{carb}}$ can be used to investigate the causes of
812 variation in $\delta^{18}\text{O}$ and can help reconstruct evaporation, precipitation sources, soil hydrologic
813 processes, and elevations in ancient systems. We draw from examples of geographically related
814 pedogenic carbonates in this dataset.

815 First, we demonstrate how to identify evaporation and improve estimates of un-
816 evaporated $\delta^{18}\text{O}$ of meteoric waters using a suite of samples and their $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ covariation
817 across a landscape. As first reported in Beverly et al. (2021), pedogenic carbonates sampled
818 across an aridity gradient in Serengeti, Tanzania, record varying amounts of evaporation in soil
819 water (Figure 7A). The most arid sites have the lowest $\Delta^{17}\text{O}$ values and the highest $\delta^{18}\text{O}$ values.
820 A linear trend between $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of the Serengeti samples yields a change of -7.4 per
821 meg/‰ ($r^2 = 0.78$), corresponding to a $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ slope (λ_{soil}) of 0.5206. This slope is within the
822 range of triple oxygen isotope evaporation slopes predicted in the steady state soils model
823 (Section 3.1). Thus, evaporation can explain the variation in $\delta^{18}\text{O}$ at this location. By extension,
824 we hypothesize that the pedogenic carbonates formed in soil waters with a similar starting $\delta^{18}\text{O}$
825 value that experienced varying degrees of evaporation. The linear regression of $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$
826 points back to a recharge $\delta^{18}\text{O}$ of about -2 to -3 ‰ assuming a $\Delta^{17}\text{O}_{\text{mw}}$ of 30 to 40 per meg
827 (Figure 7A). This approximate recharge $\delta^{18}\text{O}$ value is similar to the reported $\delta^{18}\text{O}$ values from
828 local spring and river water (Beverly et al., 2021). The accuracy of this kind of reconstruction of
829 the recharge water $\delta^{18}\text{O}$ is subject to uncertainties in $\Delta^{17}\text{O}_{\text{mw}}$ and even in the existence of a
830 single source water $\delta^{18}\text{O}$ (Benettin et al., 2018). However, the Serengeti samples hint that such
831 an approach might be possible and could be developed with improved theoretical and empirical

832 constraints on $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ slopes across climate regimes (analogous to the Passey and Ji [2019]
833 approach for lakes). Even with the stated uncertainties, the $\Delta^{17}\text{O}$ -informed estimate of the $\delta^{18}\text{O}$
834 of source water made is much closer to the true value than the 'face value' estimate from $\delta^{18}\text{O}_{\text{carb}}$.
835 Future workers could employ suites of samples and $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ covariation to identify
836 evaporation in the geologic record.

837 We show that $\Delta^{17}\text{O}$ can identify differences in the $\delta^{18}\text{O}$ values of moisture sources, in
838 part by ruling out evaporation. We documented one region where $\Delta^{17}\text{O}$ shows that variation in
839 $\delta^{18}\text{O}$ is not driven by evaporation: pedogenic carbonates from monsoonal, tropical Myanmar
840 (Figure 7B). Pedogenic carbonates were sampled across a rainfall gradient in central "dry" belt of
841 Myanmar, which is in the rain shadow of the Indo-Burman Ranges and has precipitation of
842 <1000 mm/year. The pedogenic carbonates display a range in $\delta^{18}\text{O}_{\text{carb}}$ of -8.6 to -1.5 ‰, all
843 collected from depths > 50 cm. In these samples, lower $\delta^{18}\text{O}$ values occur at the driest localities,
844 leading previous workers to hypothesize that the variation in $\delta^{18}\text{O}$ was due to variation in the
845 seasonal timing of carbonate formation and seasonal variation in parent soil water $\delta^{18}\text{O}$ (Licht et
846 al., 2022). We measured $\Delta^{17}\text{O}$ of the carbonates from the driest and wettest locality based on
847 MAP (1100 mm/year and 760 mm/year for 19ND04 and 20ND03 respectively, $\delta^{18}\text{O}_{\text{rsw}}$ of -1.3
848 and -5.8 ‰). We observe no variation in $\Delta^{17}\text{O}$ in the two measured samples within our precision
849 ($\Delta^{17}\text{O}_{\text{rsw}}$ of $+6$ and $+4$ per meg). The lack of variation in $\Delta^{17}\text{O}_{\text{rsw}}$ in the two samples supports the
850 idea that $\delta^{18}\text{O}$ variation is not due to evaporation. Instead, $\delta^{18}\text{O}$ variation in this setting could be
851 due to a difference in the timing of pedogenic carbonate formation and seasonal variation in
852 recharge water $\delta^{18}\text{O}$, which should be driven by distillation-type processes and result in no
853 variation in $\Delta^{17}\text{O}_{\text{rsw}}$ in resulting carbonate.

854 In some soils, $\Delta^{17}\text{O}$ values can be used to test hypotheses about hydrologic processes,
855 like soil water mixing with depth. Amongst the samples from Vertisols in a chronosequence of
856 terraces along the Brazos River in Texas, we observed uniformity in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ (Figure 7C).
857 Vertisols are defined by their high clay content and vertical cracks that propagate from the
858 surface downward (Nordt et al., 2004; Kovda, 2020). The large cracks might suggest a high
859 proportion of evaporative soil-dewatering given the large porosity and small tortuosity allowing
860 for rapid vapor transport, which would result in low $\Delta^{17}\text{O}_{\text{sw}}$ values and high $\delta^{18}\text{O}_{\text{sw}}$ values, but
861 they may also lead to rapid down-profile transit of meteoric waters with minimal evaporation
862 (Kovda et al., 2006; Kovda, 2020). The $\Delta^{17}\text{O}_{\text{rsw}}$ values of the group of soils from Texas suggests
863 only minor evaporation compared to meteoric waters ($\Delta^{17}\text{O}_{\text{rsw}}$ of -2 to + 10 per meg), in line
864 with other studies of Vertisols from Texas that have invariant $\delta^{18}\text{O}$ values that are similar to
865 meteoric water $\delta^{18}\text{O}$ (Kovda et al., 2006; Miller et al., 2007). In this group of samples, the lack of
866 variation in $\Delta^{17}\text{O}_{\text{rsw}}$ and $\delta^{18}\text{O}_{\text{rsw}}$ suggests that moderately evaporated soil waters are well-mixed
867 in a Vertisol or that pedogenic carbonate is physically mixed during pedoturbation. $\Delta^{17}\text{O}_{\text{rsw}}$ lends
868 credibility to the interpretation that $\delta^{18}\text{O}_{\text{rsw}}$ values are only slightly evaporated and provides
869 insights into soil water hydrology in Vertisols.

870 The soil carbonate samples from the Iranian plateau demonstrate that $\Delta^{17}\text{O}_{\text{rsw}}$ can be used
871 to better understand $\delta^{18}\text{O}$ -elevation relationships but that complexities persist in using $\delta^{18}\text{O}$
872 values for paleoaltimetry. $\delta^{18}\text{O}$ -based paleoaltimetry uses the depletion of ^{18}O during rain-out of
873 uplifting air masses, as recorded in authigenic minerals, to reconstruct past elevations (Poage and
874 Chamberlain, 2001; Rowley, 2007; Mulch, 2016). However, in arid plateaus this framework is
875 invalidated if rainfall is recycled or if moisture source varies regionally, resulting in $\delta^{18}\text{O}$ that
876 remains constant or even increases with elevation up and across a plateau (Bershaw et al., 2012;

877 Li and Garzione, 2017; Cassel et al., 2018; Caves Rügenstein and Chamberlain, 2018; Aron et
878 al., 2021b). Indeed, we observe that the soil carbonates from the Iranian plateau that are
879 separated by 1.5 km in elevation have $\delta^{18}\text{O}_{\text{rsw}}$ values within 1 ‰ of each other (Figure 7D), a
880 lapse rate that is far lower than a typical 3‰/km driven by uplift and distillation of air masses
881 (Rowley, 2007). The soil carbonate samples have $\Delta^{17}\text{O}_{\text{rsw}}$ that are the same within current
882 precision and are moderately evaporated compared to typical $\Delta^{17}\text{O}_{\text{mw}}$ values (Figure 7D). The
883 similarity in $\delta^{18}\text{O}_{\text{rsw}}$ and $\Delta^{17}\text{O}_{\text{rsw}}$ indicate that the isotopic composition of the higher elevation
884 sample could be a result from recycling of the same moisture source as the lower elevation
885 sample, which would lead to a slight increase in $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ (Bershaw et al., 2012; Surma et
886 al., 2021; Xia et al., 2023). It is also possible that the soil carbonates formed from distinct
887 moisture sources with similar isotopic compositions and similar degree of evaporation, given that
888 both the Caspian Sea and Mediterranean Sea source rainfall in this topographically complex
889 region (Evans et al., 2004). Information on the isotopic composition of various air masses and
890 trajectories is needed to fully understand the $\delta^{18}\text{O}$ -elevation relationships in the soil carbonates of
891 the Iranian plateau. We remain optimistic that $\Delta^{17}\text{O}_{\text{rsw}}$ could be used to identify moisture
892 recycling in the interior of high plateaus and thus better constrain paleo-elevation estimates.

893

894 *4.6 Implications for pedogenic carbonates in paleoclimate studies and recommendations for the* 895 *use and development of $\Delta^{17}\text{O}$ in future studies*

896 Foremost, our data demonstrate that pedogenic carbonate in arid environments is likely to
897 form from water that is evaporatively enriched in ^{18}O by about 1–5 ‰, even at depths > 40 cm in
898 the soil profile. This finding may seem unsettling for terrestrial paleoclimate research that centers
899 around using pedogenic carbonate as a faithful record of meteoric water $\delta^{18}\text{O}$. For example,

900 ignoring evaporation could result in a misattribution of the moisture source of a region. One
901 could underestimate the elevation of ancient mountains by 0.5–2 km, assuming a typical lapse
902 rate of about 0.3 ‰/km (Poage and Chamberlain, 2001). Fortunately, $\Delta^{17}\text{O}$ can be used to
903 identify evaporation, and workers can leverage that information to improve estimates of pristine
904 $\delta^{18}\text{O}$ and/or to infer environmental conditions and carbonate formation processes. Workers may
905 not have to exhaustively analyze all samples in a $\delta^{18}\text{O}$ -based paleoclimate record for $\Delta^{17}\text{O}$,
906 which is not feasible given that measuring $\Delta^{17}\text{O}$ of carbonate is resource-intensive at the time of
907 writing. Instead, workers may use $\delta^{18}\text{O}$ variations to target a subset of samples for $\Delta^{17}\text{O}$ analysis.
908 Choosing the samples that represent the observed minimum and maximum $\delta^{18}\text{O}$ values will most
909 likely maximize the possible range in $\Delta^{17}\text{O}$ and will allow workers to answer specific questions
910 about the factors that drive variation in $\delta^{18}\text{O}$.

911 Future studies could use $\Delta^{17}\text{O}$ to improve estimates of meteoric water $\delta^{18}\text{O}$ reconstructed
912 from pedogenic carbonate. First, $\Delta^{17}\text{O}_{\text{rsw}}$ can be compared to typical or site-specific $\Delta^{17}\text{O}_{\text{mw}}$
913 values to determine if evaporation is likely. If $\Delta^{17}\text{O}_{\text{rsw}}$ is well within range of $\Delta^{17}\text{O}_{\text{mw}}$, one could
914 deem evaporation unlikely and confidently interpret $\delta^{18}\text{O}_{\text{rsw}}$ as indicative of $\delta^{18}\text{O}_{\text{mw}}$. If
915 evaporation has occurred, $\Delta^{17}\text{O}_{\text{rsw}} - \delta^{18}\text{O}_{\text{rsw}}$ trajectories could be used to reconstruct the $\delta^{18}\text{O}$ of
916 the source waters and to estimate the magnitude of evaporation, similar to approaches in lakes
917 (Passey and Ji, 2019; Katz et al., 2023), the example from the Serengeti soils in this paper, and
918 source water determinations from $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (Bowen et al., 2018). This type of reconstruction
919 of unevaporated soil water $\delta^{18}\text{O}$ would require an estimate of unevaporated $\Delta^{17}\text{O}_{\text{mw}}$, which sets
920 the intersection with the meteoric water line, and could be determined via "unevaporated"
921 sedimentary carbonates (i.e., flow-through lake carbonates, tufas, or speleothems, which may
922 record similar $\Delta^{17}\text{O}_{\text{mw}}$ but distinct $\delta^{18}\text{O}_{\text{mw}}$ from soils due to differences in proxy biases), or via

923 modern rainfall. Reconstructing unevaporated $\delta^{18}\text{O}$ and the magnitude of evaporation would also
924 require a determination of the slope of the evaporation line from either a suite of samples that
925 represent increasing evaporation (similar to the Serengeti samples of Beverly et al., 2021) and/or
926 from theory, analogous to slopes in $\delta^{18}\text{O}$ - $\delta^2\text{H}$ space (Benettin et al., 2018; Bowen et al., 2018).

927 Workers could use $\Delta^{17}\text{O}_{\text{carb}}$ to place broad constraints on aridity for past climates if the
928 present pattern of low $\Delta^{17}\text{O}_{\text{carb}}$ values being common in semi-arid, arid, and hyper arid
929 environments and uncommon in sub-humid and humid climates holds up with additional
930 sampling. For example, if low $\Delta^{17}\text{O}_{\text{carb}}$ values are observed ($\Delta^{17}\text{O}_{\text{carb}} < -110$ per meg), there
931 would be high confidence that climates were semi-arid to hyper-arid. However, the observation
932 of high $\Delta^{17}\text{O}_{\text{carb}}$ values would place less of a constraint on aridity, because these appear to be
933 possible across the full range of aridity. Workers who wish to use $\Delta^{17}\text{O}_{\text{carb}}$ to track ancient
934 aridity in a more quantitative fashion might be able to do so on a regional basis by studying its
935 pattern in modern analog environments as in Beverly et al. (2021).

936 As we learn more about $\Delta^{17}\text{O}_{\text{carb}}$, we may discover links between it and $\delta^{13}\text{C}$. The
937 dominant control on $\delta^{13}\text{C}$ of pedogenic carbonate is the photosynthetic pathway of overlying
938 vegetation (i.e., C_3 vs C_4) (Cerling and Quade, 1993). The type of vegetation (recorded by $\delta^{13}\text{C}$)
939 may have indirect effects on $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of soil water via plant water use and/or shading.
940 Within a certain vegetation class, the availability of water can influence the $\delta^{13}\text{C}_{\text{carb}}$ and might be
941 reflected in $\Delta^{17}\text{O}_{\text{carb}}$. For example, we might expect to find higher $\delta^{13}\text{C}$ and lower $\Delta^{17}\text{O}_{\text{carb}}$
942 values during dry periods where microbial respiration is reduced (Conant et al., 2004), which
943 could lead to an decreased component of respired CO_2 in the soil (Cerling, 1984). In contrast,
944 low $\delta^{13}\text{C}$ and high $\Delta^{17}\text{O}$ values might be associated with higher soil respiration rates, as soil
945 carbonate may be formed via biotic-driven fluctuations in CO_2 rates rather than soil drying. If

946 this relationship between $\Delta^{17}\text{O}_{\text{carb}}$ and soil respiration rates proves to be robust, it could greatly
947 improve $\delta^{13}\text{C}$ -based reconstructions of ancient atmospheric concentrations CO_2 that require an
948 assumption of soil respiration rate during pedogenic carbonate formation (Cerling, 1984), as
949 ancient soil respiration rates can be difficult to constrain (Breecker et al., 2010; Cotton and
950 Sheldon, 2012; Montañez, 2013; Fischer-Femal and Bowen, 2021).

951 Soil carbonates are a rich but complex archive, and we need to leverage every isotope
952 system we have to decipher environmental signals. Ultimately, the utility of $\Delta^{17}\text{O}$ may be to
953 yield insights into soil carbonate formation processes and to will help build a proxy system
954 model for soil carbonates (Evans et al., 2013; Dee et al., 2016; Bowen et al., 2020; Fischer-
955 Femal and Bowen, 2021). To this end, future studies of $\Delta^{17}\text{O}$ at well-studied modern soil
956 localities may seek to understand the environmental conditions that promote the presence of
957 evaporatively dominated soil waters during pedogenic carbonate formation. Integrating water
958 content data with data on the isotopic composition of meteoric and soil waters will allow workers
959 to separate the effects of mixing, transpiration, and evaporation to understand the source of soil
960 water. For example, the two Fish Lake Valley (FLV), Nevada, sites have distinct seasonal
961 patterns in soil water content that help explain the $\Delta^{17}\text{O}_{\text{rsw}}$ and $\delta^{18}\text{O}_{\text{rsw}}$ (Oerter and Amundson,
962 2016). Site B has high variability in water content at depths < 40 cm, likely reflecting
963 evapotranspiration fluxes, possibly allowing for recharge and mixing of various generations of
964 water at shallower depths that are transmitted to greater depths. At this site, $\delta^{18}\text{O}_{\text{rsw}}$ (-8 ‰)
965 resembles summer rain, but might also represent a mix summer recharge and antecedent pore
966 water based on the relatively low $\Delta^{17}\text{O}_{\text{rsw}}$ (-14 per meg) (Table 2). In comparison, site C had a
967 more consistent water content with a minimum at a depth of 50 cm that was attributed to plant
968 uptake (Oerter and Amundson, 2016). Site C had a $\delta^{18}\text{O}_{\text{rsw}}$ value that resembles winter rain (-13

969 ‰) and a slightly less evaporated $\Delta^{17}\text{O}_{\text{rsw}}$ value (-7 per meg) (Table 2). At site C, the soil water
970 at depth might reflect winter storm events that percolate to at least 80 cm that were not observed
971 during the monitoring period. Process-based studies are key to understanding how and when soil
972 carbonate forms, the evaporation trajectory of parent waters, and the ultimate source of soil water
973 from which pedogenic carbonates form.

974

975 **5. Conclusions**

976 $\Delta^{17}\text{O}_{\text{carb}}$ records the evaporative state of the soil water at the time of pedogenic carbonate
977 formation. We find that evaporative modification of $\Delta^{17}\text{O}_{\text{rsw}}$ values is commonly recorded by
978 pedogenic carbonates, implying that evaporation is a concern for $\delta^{18}\text{O}_{\text{carb}}$ -based paleoclimate
979 interpretations, especially from arid and/or sparsely vegetated settings. Paleoclimate workers
980 may use $\Delta^{17}\text{O}$ to test for evaporation where a robust reconstruction of meteoric water $\delta^{18}\text{O}$ is
981 required (i.e., to reconstruct moisture recycling, paleo-elevations, air mass interactions, and
982 isotope gradients). This will enable more quantitative comparisons with isotope-enabled climate
983 models (Poage and Chamberlain, 2001; Winnick et al., 2014; van Dijk et al., 2020; Zhu et al.,
984 2020). While $\Delta^{17}\text{O}_{\text{carb}}$ values are generally lower and more variable in more arid environments,
985 similar to the 'wedge' observed in mammal teeth (Lehmann et al., 2022), $\Delta^{17}\text{O}_{\text{carb}}$ falls short as a
986 simple indicator of aridity across geographic regions. We suggest that $\Delta^{17}\text{O}_{\text{carb}}$ will be most
987 useful in identifying when variation in $\delta^{18}\text{O}_{\text{carb}}$ is due to increased evaporation (i.e., in the
988 modern Serengeti samples) versus when variation in $\delta^{18}\text{O}_{\text{carb}}$ is due to a difference in recharge
989 $\delta^{18}\text{O}$ (i.e., in the modern Myanmar samples). In theory, a suite of a related samples with
990 evaporatively driven covariation in $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ could be used to reconstruct unevaporated
991 $\delta^{18}\text{O}$, although this approach remains to be validated in natural soil pore waters and carbonates.

992 This work reveals an incomplete understanding of the environmental factors, in addition to
993 aridity, that control the evaporative state of soil water that is ultimately recorded by pedogenic
994 carbonates. There remains uncertainty in how an evaporation signal is propagated downward in
995 the soil profile, how the depth of the evaporation relates to the depth of calcic horizons in soils,
996 and how the timing of evaporation relates to the timing of carbonate precipitation. $\Delta^{17}\text{O}$ is
997 poised to aid workers in studies of well-constrained localities to better understand the
998 circumstances of pedogenic carbonate formation, which will ultimately improve our ability to
999 understand the paleoclimate information that is recorded in their stable isotopes.

1000

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1012

1013 **Appendix A: Supplementary Material**

1014 The supplementary material to this article includes text, figures, and tables that give additional
1015 details regarding the Barnes and Allison (1983) soil physics model, the soil sites, and the
1016 methods for estimating the AI and $\delta^{18}\text{O}$ of precipitation during soil carbonate formation season.
1017 The supplementary material can be found online at (doi provided by GCA).

1018

1019 **Research Data**

1020 Research Data associated with this article, including individual measurements of triple oxygen
1021 and clumped isotope measurements of samples and standard materials, is accessible via
1022 EarthChem (<https://doi.org/10.26022/IEDA/112737>).

1023

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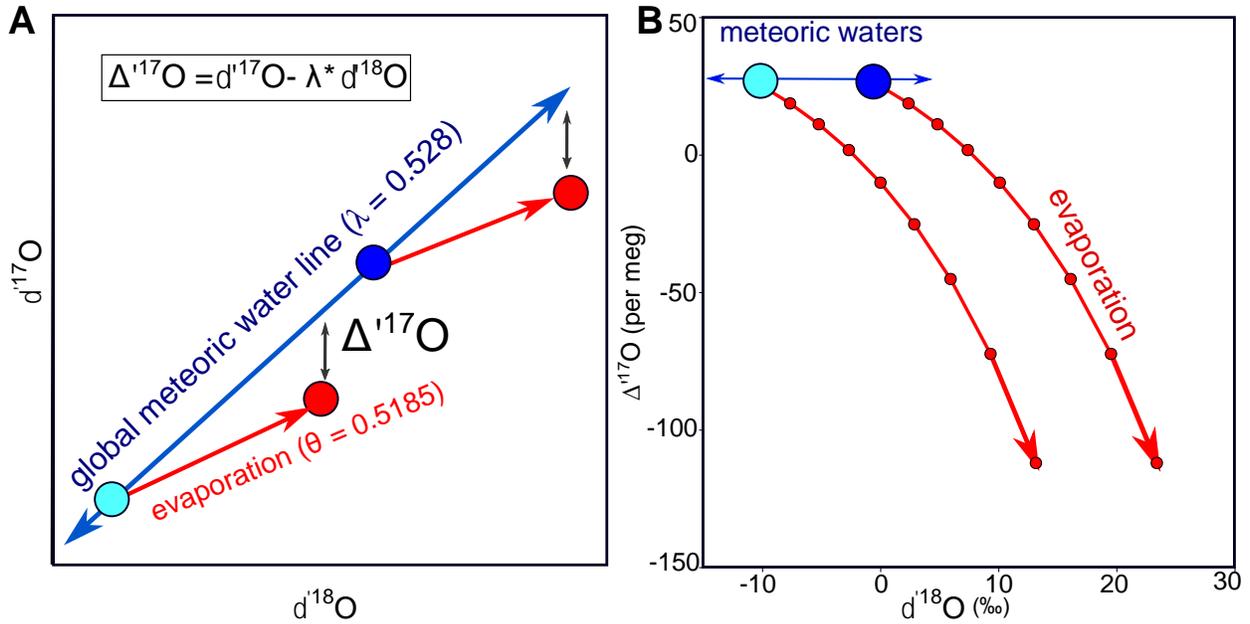
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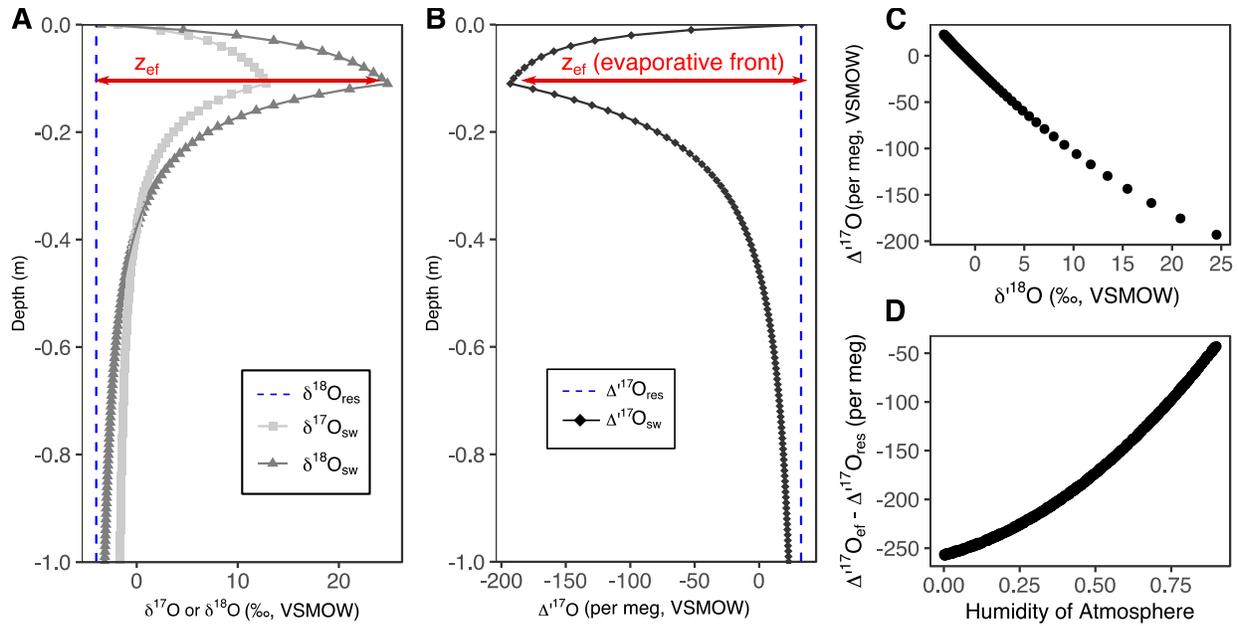
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1562 **Figures**



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Figure 1: Schematic representation of the definition of $\Delta^{17}\text{O}$ and the evolution of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ during evaporation. A) Schematic of $\delta^{18}\text{O}$ vs $\delta^{17}\text{O}$ visually defining $\Delta^{17}\text{O}$. Progressive evaporation, a kinetic process, will cause $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ to evolve along a shallower slope than the reference slope, which is defined by typical meteoric waters. B) Evaporation leads to higher $\delta^{18}\text{O}$ values and lower $\Delta^{17}\text{O}$ values in remaining water. The red lines represent progressive evaporation from waters that start with distinct $\delta^{18}\text{O}$ values. $\Delta^{17}\text{O}$ is not sensitive to the initial $\delta^{18}\text{O}$ value. The evaporation trajectory shown is for the water remaining during pan evaporation at a relative humidity of 0.4, $^{18}\alpha_{diff}$ of 1.0142, with the fraction of remaining water marked in

1572 increments of 0.1 (modified from example in Passey and Levin, (2021), equations of Criss,
 1573 (1999)).



1574

1575 **Figure 2: Predicted isotopic composition of soil water in steady state.**

1576 A and B) Predicted $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ of soil water with depth in a steady-state soil profile,
 1577 calculated using a single set of typical parameters (given in Table S1) ($\theta_{\text{diff}} = 0.5185$). Vertical
 1578 blue dashed line indicates the isotopic composition of the water in the soil pores, the 'reservoir.'

1579 C) The $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ relationship for the same set of typical parameters. This set of parameters
 1580 yields a $\delta^{18}\text{O}$ - $\Delta^{17}\text{O}$ trend of -8.7 per meg/‰, equivalent to a slope in $\delta^{18}\text{O}$ - $\delta^{17}\text{O}$ of 0.5193 (i.e.,

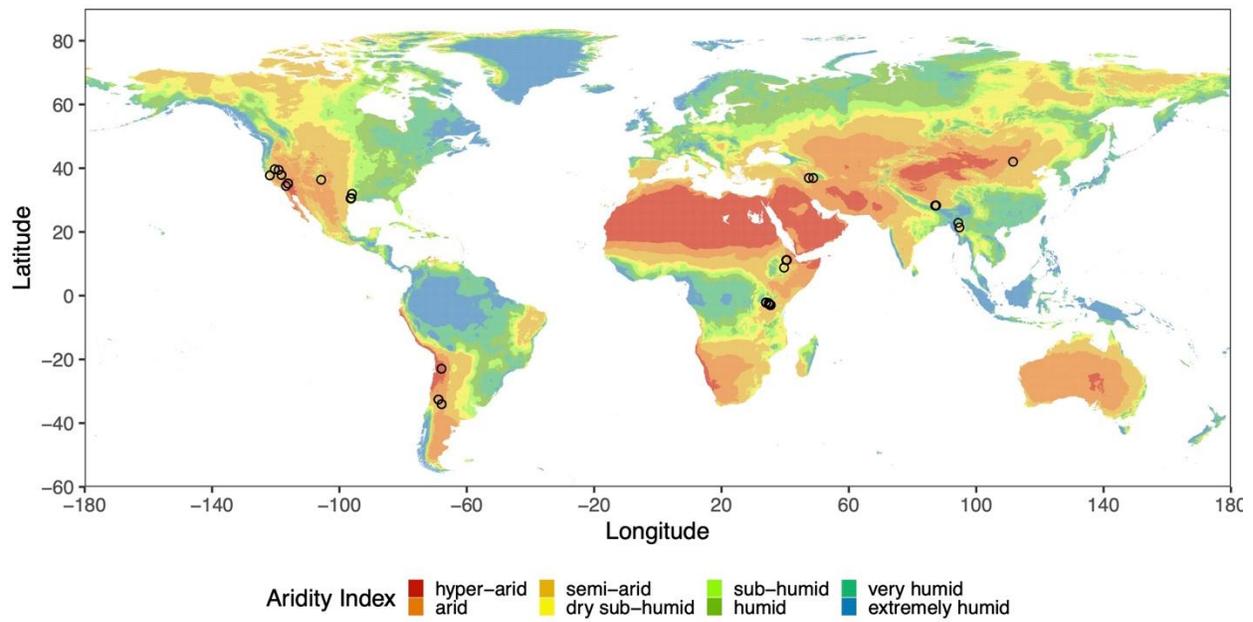
1581 λ_{soil}) D) Possible values of the isotopic offset between $\Delta^{17}\text{O}$ at the evaporative front and the

1582 reservoir water, varying model parameters in 1000 simulations. The humidity of the overlying

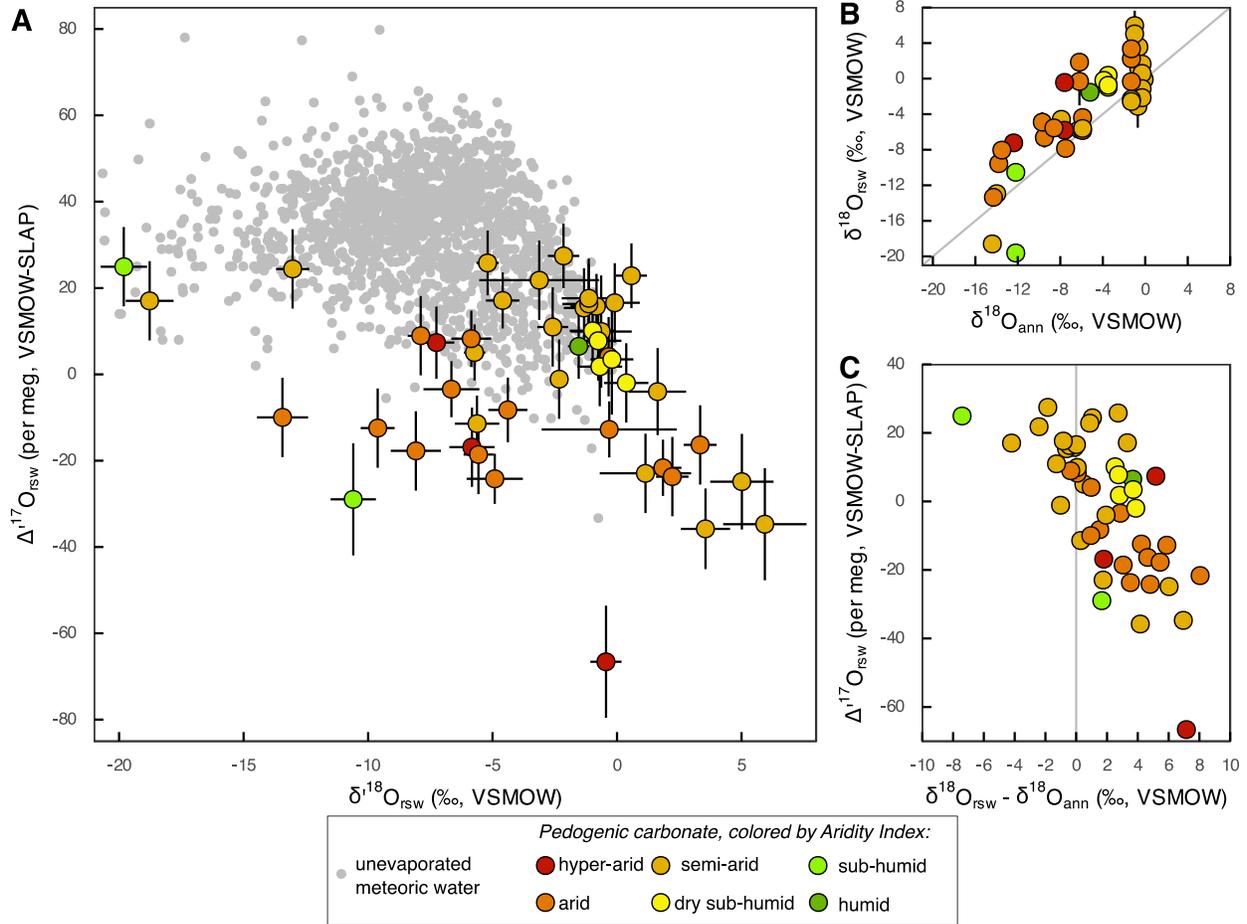
1583 atmosphere is a strong control on the maximum isotopic offset. The sensitivity of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$

1584 to other variables is described in the Supplementary Material (Figures S1-S3).

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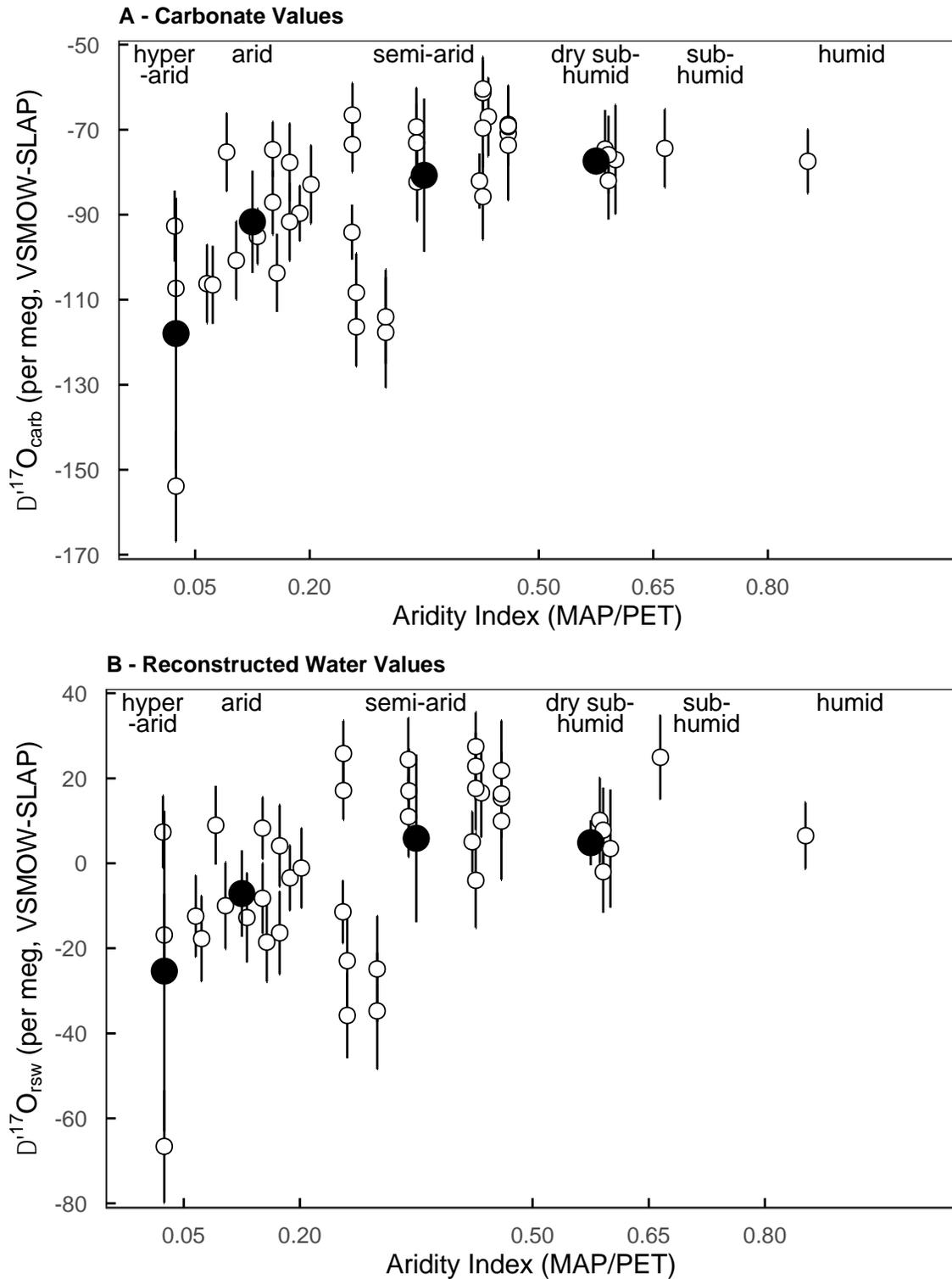


1586
 1587 **Figure 3: Locations of pedogenic carbonate samples considered in this study.** Study sites are
 1588 indicated with unfilled black circles. The AI is from World Clim 2 Data (Fick and Hijmans,
 1589 2017); down sampled from 30 arc second data.
 1590



1591
 1592 **Figure 4. Triple oxygen isotopes of soil waters reconstructed from pedogenic carbonate and**
 1593 **of global meteoric waters. A)** Data from all pedogenic carbonate samples ($\Delta^{17}\text{O}_{\text{rsw}}$ and $\delta^{18}\text{O}_{\text{rsw}}$)
 1594 (colored dots) and global unevaporated meteoric waters (gray dots). This figure shows data from
 1595 all soil depths, unlike Figure 5 which is restricted to depths > 30 cm. The global meteoric water
 1596 data were compiled by Aron et al. (2021) and have been filtered to include only 'unevaporated'
 1597 waters: tap, spring, river or stream, precipitation, and groundwater. **B)** Mean annual $\delta^{18}\text{O}$ values
 1598 of precipitation ($\delta^{18}\text{O}_{\text{ann}}$) and $\delta^{18}\text{O}_{\text{rsw}}$ values calculated from pedogenic carbonates in this study.
 1599 The gray line is the 1:1 line. $\delta^{18}\text{O}_{\text{ann}}$ is from the OIPC or GNIP (see methods in Section 2.1). **C)**
 1600 The difference between $\delta^{18}\text{O}_{\text{rsw}}$ and $\delta^{18}\text{O}_{\text{ann}}$ in ‰ and its correlation to $\Delta^{17}\text{O}_{\text{rsw}}$. The vertical line
 1601 indicates a $\delta^{18}\text{O}_{\text{rsw}} - \delta^{18}\text{O}_{\text{ann}}$ difference of 0 ‰, equivalent to the 1:1 line in panel B.

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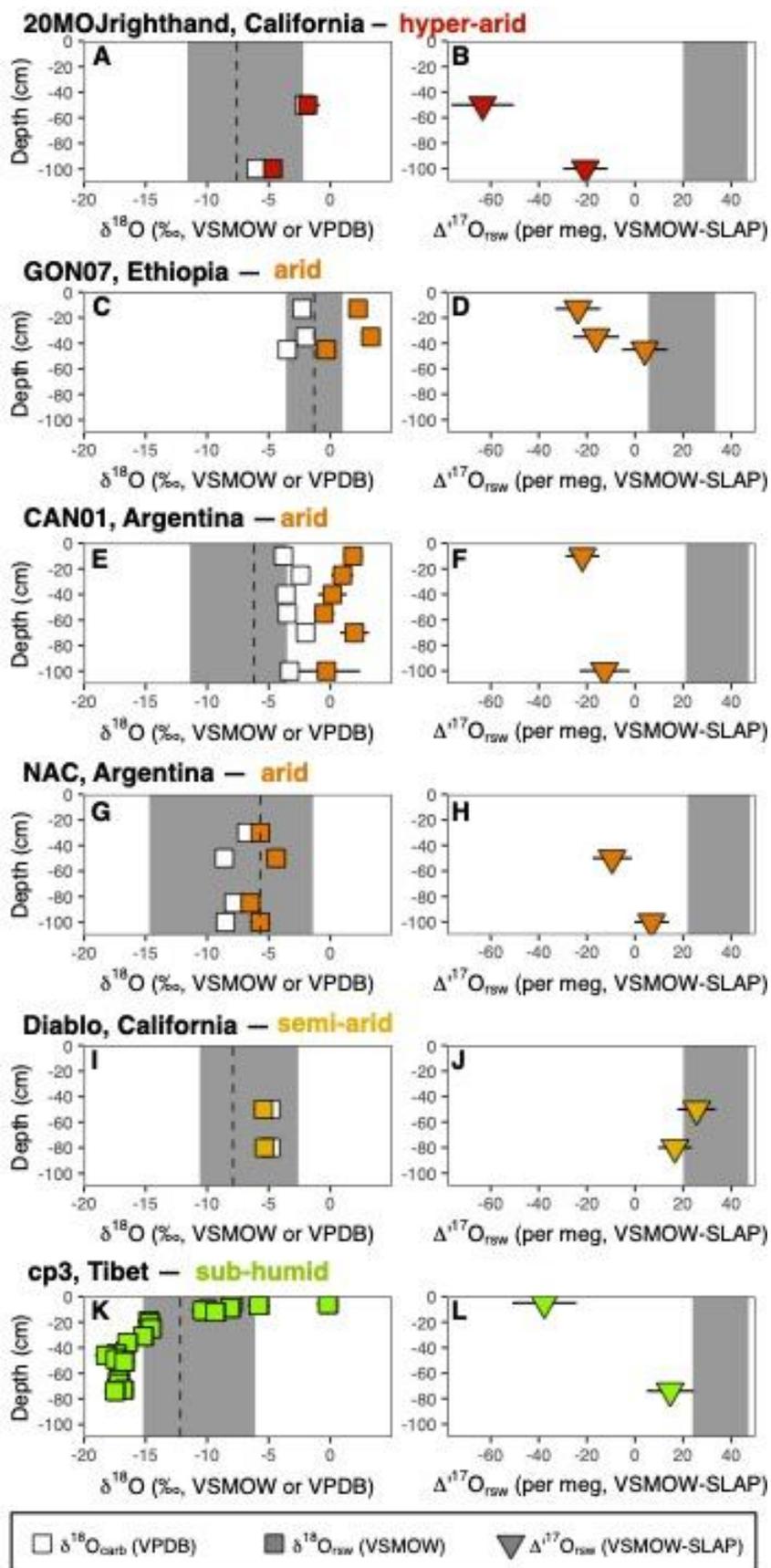


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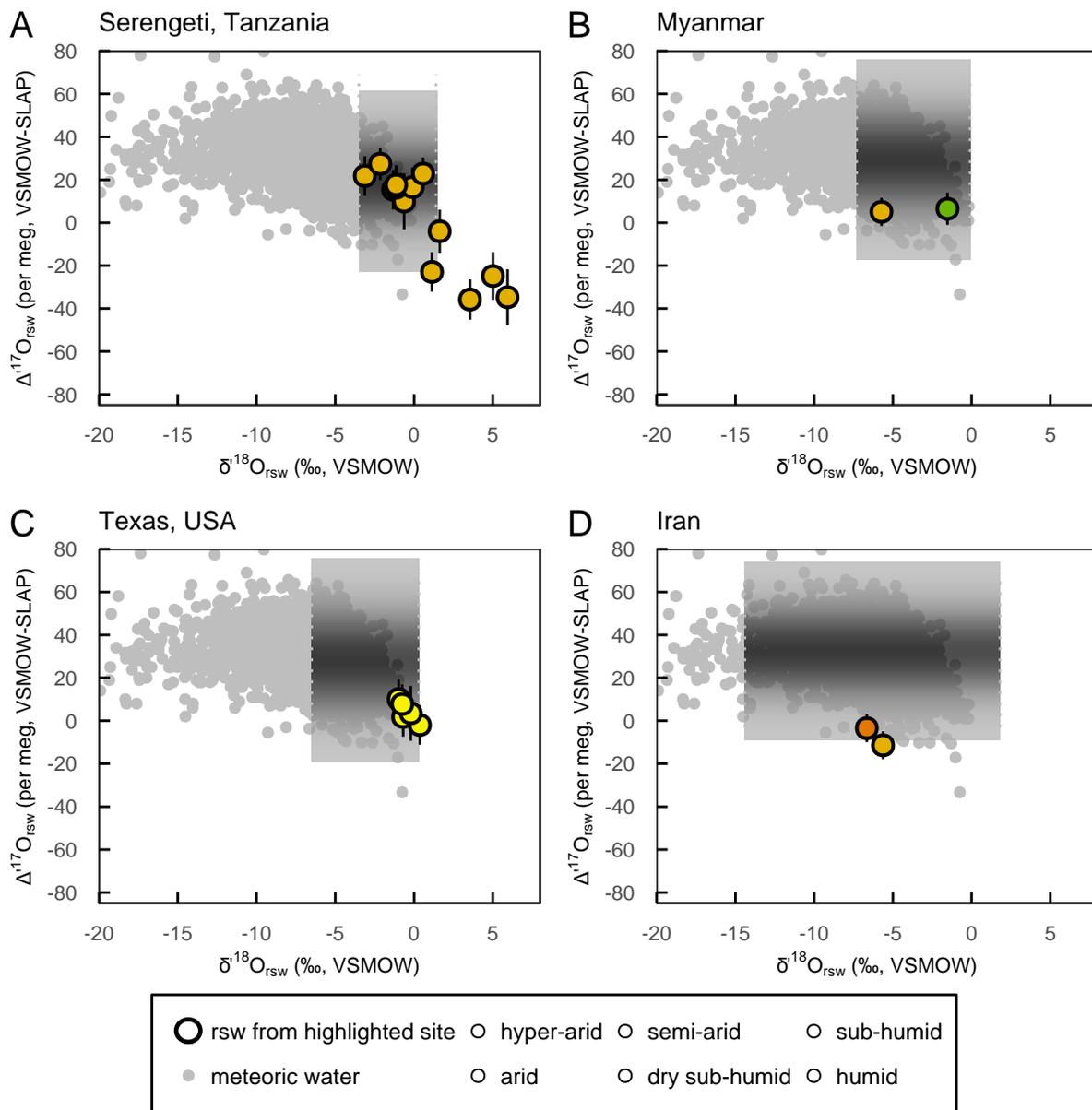
1604 **Figure 5: Triple oxygen isotope composition of pedogenic carbonate vs aridity. A)** Results

1605 presented for carbonate mineral, $\Delta^{17}\text{O}_{\text{carb}}$. **B)** Results presented as $\Delta^{17}\text{O}_{\text{rsw}}$ values, which are

1606 calculated from $\Delta^{17}\text{O}_{\text{carb}}$, $\lambda_{cc-w} = 0.5250$, and mineral growth temperatures (based on Δ_{47} for all
1607 but four samples, see Table 3). Samples that are <30 cm in depth are not shown. Error bars are
1608 external errors propagated from 1 S.E. of replicates and uncertainty in the mineral-water
1609 fractionation. Small white dots indicate individual pedogenic carbonate samples (each with 1–4
1610 replicate measurements). Large black dots show the mean $\Delta^{17}\text{O}$ value for each AI class, the error
1611 is 1 S.D. (no mean shown for the sub-humid and humid classes that each have one sample).
1612



1614 **Figure 6:** Stable isotope depth profiles for soil sites with measurements at multiple depths.
1615 Reconstructed water values ($\delta^{18}\text{O}_{\text{rsw}}$, $\Delta^{17}\text{O}_{\text{rsw}}$) are colored by aridity and $\delta^{18}\text{O}_{\text{carb}}$ is in white. **Left**
1616 **Panels (A, C, E, G, I, K)** show $\delta^{18}\text{O}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{rsw}}$. Gray shading indicates the possible range of
1617 $\delta^{18}\text{O}$ of precipitation at each site. The dashed vertical line is mean annual $\delta^{18}\text{O}$ of precipitation
1618 weighted by amount ($\delta^{18}\text{O}_{\text{ann}}$), derived from the OIPC or GNIP (Section 2.3). Error bars for
1619 $\delta^{18}\text{O}_{\text{rsw}}$ are propagated error from the Δ_{47} temperature and error in $\delta^{18}\text{O}_{\text{carb}}$; if they are not visible,
1620 they are smaller than the symbol. **Right Panels (B, D, F, H, J, L)** show $\Delta^{17}\text{O}_{\text{rsw}}$. The gray
1621 rectangle shows a likely range of $\Delta^{17}\text{O}_{\text{mw}}$ that is estimated using the mean of $\Delta^{17}\text{O}$ values of
1622 global, unevaporated meteoric waters within the range of precipitation $\delta^{18}\text{O}$ values at each site
1623 (water data from Aron et al., 2021, as in Figure 4).



1624

1625 **Figure 7: Triple oxygen isotope compositions of geographically related samples.**

1626 The reconstructed water values from pedogenic carbonate samples of interest are shown as large
1627 dots with thick outline. All other pedogenic carbonate samples are shown for context (colored
1628 dots, same as Figure 4). Unevaporated global meteoric waters are also shown for context (gray
1629 dots, same as Figure 4). The typical isotopic composition of precipitation in each region is
1630 illustrated with the faded gray rectangles. The width of the rectangle is determined by the range
1631 in precipitation $\delta^{18}\text{O}$ at each site. The darkness of the shading of the rectangle illustrates the
1632 likelihood of a $\Delta^{17}\text{O}$ value, as determined by the Gaussian distribution of the $\Delta^{17}\text{O}$ values of the
1633 global meteoric water data within the range of $\delta^{18}\text{O}$ values at that site.

1634

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1636

1637 **Table 1:** Location and climate information for pedogenic carbonates in this study

1638

Sample Name	Depth (cm)	Latitude ^a	Longitude	Elevation (m)	Location	Relevant publications	MAAT °C ^b	MAP (mm/year) ^b	PET (mm/year) ^b	Aridity Index (MAP/PET) ^b	$\delta^{18}\text{O}_{\text{ann}}$ ^c
GONJQ-305-1	50	11.1481	40.3357	694	Afar, Ethiopia	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	26	461	2284	0.2018	-1.3
GON07-4.3.1	13	11.1653	40.4950	637	Afar, Ethiopia	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	27	403	2318	0.1738	-1.3
GON07-4.6.2	35	11.1653	40.4950	637	Afar, Ethiopia	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	27	403	2318	0.1738	-1.3
GON07-4.7.1	45	11.1653	40.4950	637	Afar, Ethiopia	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	27	403	2318	0.1738	-1.3
CN2008-DM-164-130-1	130	42.0153	111.5743	1306	Inner Mongolia	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	4	227	1444	0.1571	-8.6
CA08-005-1	140	34.4212	-116.7890	982	California, USA	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	17	238	2604	0.0913	-7.5
ET05-AWSH-48-1	130	8.7884	39.6617	1259	Afar, Ethiopia	Passey et al. 2014 ($\Delta^{17}\text{O}$); Passey et al. 2010 (Δ_{47})	23	726	2134	0.34	-1.3
BUR MH 30 Buff	30	30.4909	-96.4677	70	Texas, USA	Ji 2016 ($\Delta^{17}\text{O}$)	20	1010	1721	0.5868	-3.5
SHP 80 XTLN	80	30.6174	-96.3000	90	Texas, USA	Ji 2016 ($\Delta^{17}\text{O}$)	20	1022	1728	0.5912	-3.5
RCWMA LD 129-140E	130	31.9458	-96.0563	90	Texas, USA	Ji 2016 ($\Delta^{17}\text{O}$); Michel et al., 2013	19	1015	1689	0.6006	-3.9
BUR MH 70 White	70	30.4909	-96.4677	70	Texas, USA	Ji 2016 ($\Delta^{17}\text{O}$)	20	1010	1721	0.5868	-3.5
SHP 100 Buff	100	30.6174	-96.3000	90	Texas, USA	Ji 2016 ($\Delta^{17}\text{O}$); Robinson et al., 2002	20	1022	1728	0.5912	-3.5
CAN01-10	10	-32.5919	-68.9053	1000	Mendoza, Argentina	Ringham et al., 2016 (Δ_{47})	16	245	1861	0.1316	-6.2

CAN01-100	100	-32.5919	-68.9053	1000	Mendoza, Argentina	Ringham et al., 2016 (Δ_{47})	16	245	1861	0.1316	-6.2
NAC-50	50	-34.0500	-67.9028	600	Mendoza, Argentina	Ringham et al., 2016 (Δ_{47})	16	271	1787	0.1516	-5.9
NAC-100	100	-34.0500	-67.9028	600	Mendoza, Argentina	Ringham et al., 2016 (Δ_{47})	16	271	1787	0.1516	-5.9
Diablo 50	50	37.7397	-121.8370	180	California, USA	this work	15	442	1726	0.256	-7.9
Diablo 80	80	37.7397	-121.8370	180	California, USA	this work	15	442	1726	0.256	-7.9
LH2-40	40	39.4373	-119.0663	1274	Nevada, USA	this work	12	131	1998	0.0655	-13.8
Loyalton2-40	40	39.6631	-120.3155	1500	California, USA	this work	9	565	1662	0.3398	-14
20MOJ-righthand-100	100	35.1914	-116.1401	380	California, USA	this work	22	79	3162	0.0249	-7.6
20MOJ-righthand-50	50	35.1914	-116.1401	380	California, USA	this work	22	79	3162	0.0249	-7.6
TB1701	50	36.9088	48.8046	2190	Zanjan Province, Iran	this work; Paolo Ballato pers. Comm	14	371	1452	0.2554	-5.9
AN1702	110	36.9124	47.4441	695	Zanjan Province, Iran	this work; Paolo Ballato pers. Comm	11	305	1629	0.1871	-9.5
19NOD04	90	22.8508	94.3559	120	Myanmar	Licht et al., 2022 (Δ_{47})	25	1414	1658	0.8524	-5.2
20ND03	170	21.4107	94.7243	300	Myanmar	Licht et al., 2022 (Δ_{47})	26	751	1778	0.4223	-6.2
NM140809-1B	NA	36.3567	-105.7338	2053	New Mexico, USA	Hudson et al., in prep (Δ_{47})	9	295	1770	0.1666	-9.7
PDJ 4055 115a	115	-22.9386	-67.9482	4055	Atacama Desert, Chile	Quade et al., 2007	9	49	2104	0.0232	-12.4
cp3 5-7	5	28.2850	87.3847	3741	Tibet	Breecker 2008	6	893	1342	0.665	-12.2
cp3 65-68	65	28.2850	87.3847	3741	Tibet	Breecker 2008	6	893	1342	0.665	-12.2
cp4-75	75	28.2556	87.0838	4825	Tibet	Breecker 2008	0	385	1130	0.3406	-14.4
FLV-Site-B-84-94cm	84 to 94	37.8812	-118.1804	1745	Nevada, USA	Oerter & Amundson 2016	11	156	2136	0.073	-13.5

FLV-Site-C-74-100cm	74 to 100	37.8554	-118.2301	2140	Nevada, USA	Oerter & Amundson 2016	8	204	1965	0.1038	-14.3
18-SS-215A	80	-2.9603	35.4363	1354	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	21	499	1911	0.261	-0.6
18-SS-215(D-G)	80	-2.9603	35.4363	1354	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	21	499	1911	0.261	-0.6
18-SS-235	50	-2.9355	35.2473	1549	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	20	558	1862	0.2995	-1
18-SS-236(A-C)	50	-2.9355	35.2473	1549	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	20	558	1862	0.2995	-1
18-SS-69A	60	-2.6169	34.8966	1637	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	19	805	1749	0.46	-0.7
18-SS-70A	80	-2.6169	34.8966	1637	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	19	805	1749	0.46	-0.7
18-SS-71A	100	-2.6169	34.8966	1637	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	19	805	1749	0.46	-0.7
18-SS-72B	120	-2.6169	34.8966	1637	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	19	805	1749	0.46	-0.7
18-SS-73B	140	-2.6169	34.8966	1637	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	19	805	1749	0.46	-0.7
18-SS-49A	60	-2.3290	34.8478	1425	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	21	819	1886	0.434	-0.1
18-SS-78B	70	-2.1654	33.9734	1153	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	23	846	1982	0.4268	-0.3
18-SS-79A	90	-2.1654	33.9734	1153	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	23	846	1982	0.4268	-0.3
18-SS-80B	100	-2.1654	33.9734	1153	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	23	846	1982	0.4268	-0.3
18-SS-81A	130	-2.1654	33.9734	1153	Serengeti, Tanzania	Beverly et al., 2021 ($\Delta^{17}\text{O}$)	23	846	1982	0.4268	-0.3

1639 ^aDatum WGS 1984.

1640 ^bMAAT is Mean Annual Air Temperature, MAP is Mean Annual Precipitation, PET is potential evapotranspiration. All climate data are from World Clim 2 and Version 3 of the Global Aridity Index and Potential Evapotranspiration Database (30 arc-second grid resolution) (Fick and Hijmans, 2017; Zomer et al., 2022)

1641 ^cAnnual weighted mean of precipitation $\delta^{18}\text{O}$ from the Oxygen Isotopes in Precipitation Calculator (OIPC) (Bowen and Revenaugh, 2003), except for samples from Ethiopia and NAC samples from Argentina where values from the Global Network of Isotopes in Precipitation values are used instead (see text 2.3).

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Table 2: Triple oxygen isotope data (average values) for pedogenic carbonate samples

Sample Name	number of analyses via O ₂	$\delta^{17}\text{O}_{\text{carb}} \pm 1\sigma$ (‰, VSMOW-SLAP)	$\delta^{18}\text{O}_{\text{carb}} \pm 1\sigma$ (‰, VSMOW-SLAP)	$\Delta^{17}\text{O}_{\text{carb}} \pm \text{ERR}$ (O ₂ /CaCO ₃) (per meg, VSMOW-SLAP) ^a	$\Delta^{17}\text{O}_{\text{rsw}} \pm \text{ERR}$ ³ (O ₂ /CaCO ₃) (per meg, VSMOW-SLAP) ^b	$\delta^{18}\text{O}_{\text{rsw}} \pm \text{ERR}$ (‰, VSMOW) ^c	Reference for $\Delta^{17}\text{O}$ values ^d
GONJQ-305-1	2	13.078 ± 0.086	24.927 ± 0.168	-83 ± 9	-1 ± 9	-2 ± 0	Passey et al. (2014)
GON07-4.3-1	2	14.756 ± 0.428	28.139 ± 0.817	-101 ± 9	-24 ± 10	2 ± 1	Passey et al. (2014)
GON07-4.6 -2	2	14.925 ± 0.008	28.44 ± 0.02	-92 ± 9	-16 ± 10	3 ± 1	Passey et al. (2014)
GON07-4.7 -1	2	14.144 ± 0.268	26.936 ± 0.511	-78 ± 9	4 ± 10	0 ± 0	Passey et al. (2014)
CN2008 -DM -164-130 -1	2	11.941 ± 0.962	22.813 ± 1.824	-104 ± 9	-19 ± 10	-6 ± 1	Passey et al. (2014)
CA08-005-1	2	10.585 ± 0.199	20.19 ± 0.368	-75 ± 9	9 ± 9	-8 ± 1	Passey et al. (2014)
ET05-AWSH-48-1	2	13.354 ± 0.106	25.429 ± 0.182	-73 ± 9	11 ± 10	-3 ± 1	Passey et al. (2014)
BUR MH 30Buff	2	14.299 ± 1.127	27.237 ± 2.135	-82 ± 9	2 ± 9	-1 ± 1	Ji (2016)
SHP 80 XTLN	2	14.193 ± 0.072	27.036 ± 0.142	-82 ± 9	-2 ± 10	0 ± 1	Ji (2016)
RCWMA LD 129-140E	2	13.986 ± 0.251	26.635 ± 0.442	-77 ± 13	3 ± 13	0 ± 1	Ji (2016)
BUR MH 70 White	2	14.306 ± 0.43	27.237 ± 0.823	-75 ± 9	10 ± 10	-1 ± 1	Ji (2016)
SHP 100 Buff	2	14.252 ± 0.522	27.136 ± 0.99	-76 ± 9	8 ± 10	-1 ± 1	Ji (2016)
CAN01 -10	4	13.967 ± 0.268	26.635 ± 0.508	-96 ± 7	-22 ± 7	2 ± 1	this work
CAN01 -100	4	14.233 ± 0.593	27.136 ± 1.122	-95 ± 7	-13 ± 11	0 ± 3	this work
NAC-50	3	11.474 ± 0.56	21.895 ± 1.065	-87 ± 8	-8 ± 8	-4 ± 1	this work
NAC-100	4	11.433 ± 0.165	21.795 ± 0.292	-75 ± 7	8 ± 7	-6 ± 1	this work
Diablo 50	3	13.445 ± 0.487	25.59 ± 0.918	-67 ± 8	26 ± 8	-5 ± 0	this work
Diablo 80	4	13.443 ± 0.768	25.6 ± 1.445	-73 ± 7	17 ± 7	-5 ± 1	this work
LH2-40	2	11.321 ± 0.034	21.643 ± 0.067	-106 ± 9	-12 ± 9	-10 ± 1	this work
Loyalton2-40	2	9.555 ± 0.291	18.228 ± 0.56	-69 ± 9	24 ± 10	-13 ± 1	this work
MOJ-righthand-100	1	14.968 ± NA	28.64 ± NA	-154 ± 13	-67 ± 14	0 ± 1	this work
MOJ-righthand-50	2	12.735 ± 0.009	24.323 ± 0.019	-107 ± 9	-17 ± 10	-6 ± 1	this work
TB1701	4	11.493 ± 0.498	21.946 ± 0.942	-94 ± 7	-11 ± 7	-6 ± 1	this work

AN1702	4	11.578 ± 0.485	22.097 ± 0.915	-90 ± 7	-3 ± 8	-7 ± 1	this work
19ND04	3	13.88 ± 0.098	26.434 ± 0.167	-77 ± 8	6 ± 8	-2 ± 0	this work
20ND03	4	12.229 ± 0.459	23.317 ± 0.854	-82 ± 7	5 ± 7	-6 ± 0	this work
NM140809-1B	5	12.762 ± 0.632	24.384 ± 1.181	-112 ± 6	-24 ± 7	-5 ± 1	this work
PDJ 4055 115a	3	13.684 ± 0.496	26.092 ± 0.952	-93 ± 8	7 ± 9	-7 ± 1	this work
cp3 5-7	1	11.757 ± NA	22.511 ± NA	-128 ± 13	-29 ± 14	-11 ± 1	this work
cp3 65-68	2	6.946 ± 0.184	13.296 ± 0.34	-74 ± 9	25 ± 10	-20 ± 1	this work
cp4 75	2	7.485 ± 0.326	14.333 ± 0.61	-82 ± 9	17 ± 10	-19 ± 1	this work
FLV-Site-B-84-94cm	2	11.252 ± 0.105	21.512 ± 0.182	-107 ± 9	-18 ± 10	-8 ± 1	this work
FLV-Site-C-74-100cm	2	8.78 ± 0.081	16.82 ± 0.167	-101 ± 9	-10 ± 10	-13 ± 1	this work
18-SS-215A	2	15.521 ± 1.179	29.602 ± 2.227	-108 ± 9	-23 ± 11	1 ± 2	Beverly et al. (2021)
18-SS-215(D-G)	3	15.941 ± 0.691	30.412 ± 1.338	-116 ± 9	-36 ± 10	4 ± 1	Beverly et al. (2021)
18-SS-235	1	17.616 ± NA	33.587 ± NA	-118 ± 13	-35 ± 14	6 ± 2	Beverly et al. (2021)
18-SS-236(A-C)	4	18.225 ± 0.408	34.733 ± 0.777	-114 ± 11	-25 ± 12	5 ± 1	Beverly et al. (2021)
18-SS-69A	3	14.739 ± 0.623	28.049 ± 1.176	-71 ± 8	16 ± 9	-1 ± 1	Beverly et al. (2021)
18-SS-70A	2	14.042 ± 0.700	26.725 ± 1.329	-69 ± 9	15 ± 10	-1 ± 1	Beverly et al. (2021)
18-SS-71A	2	14.317 ± 0.776	27.247 ± 1.49	-69 ± 9	22 ± 12	-3 ± 2	Beverly et al. (2021)
18-SS-72B	1	14.297 ± NA	27.217 ± NA	-74 ± 13	10 ± 14	-1 ± 1	Beverly et al. (2021)
18-SS-73B	2	14.36 ± 0.325	27.327 ± 0.623	-69 ± 9	16 ± 10	-1 ± 1	Beverly et al. (2021)
18-SS-49A	2	14.589 ± 0.353	27.758 ± 0.676	-67 ± 9	17 ± 9	0 ± 1	Beverly et al. (2021)
18-SS-78B	3	15.163 ± 0.057	28.881 ± 0.079	-86 ± 10	-4 ± 11	2 ± 1	Beverly et al. (2021)
18-SS-79A	3	15.055 ± 0.299	28.63 ± 0.547	-61 ± 8	23 ± 8	1 ± 1	Beverly et al. (2021)
18-SS-80B	2	14.687 ± 0.210	27.949 ± 0.394	-70 ± 9	18 ± 10	-1 ± 1	Beverly et al. (2021)
18-SS-81A	3	14.273 ± 0.710	27.146 ± 1.351	-60 ± 8	27 ± 8	-2 ± 1	Beverly et al. (2021)

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^a $\Delta^{17}\text{O}$ is reported as a carbonate mineral value (i.e., O_2/CaCO_3 , normalized to IAEA 603 and IAEA C1 = -100 per meg (Wostbrock et al., 2020) and calculated using $\lambda_{\text{ref}} = 0.528$. $\Delta^{17}\text{O}$ ERR of the carbonate mineral value is 1 standard error (S.E.). S.E. is calculated using whichever is larger, the standard deviation of the sample replicate values or the long-term standard deviation of the carbonate standard 102GCAZ01 (13 per meg).

^b $\Delta^{17}\text{O}$ of water reconstructed from carbonate. Calculated using $\lambda_{\text{ref}} = 0.528$ and the carbonate-water triple oxygen isotope exponent value of $\lambda_{\text{cc-w}} = 0.5250$.

Error in the $\Delta^{17}\text{O}_{\text{rsw}}$ values is calculated using the external error in the $\Delta^{17}\text{O}_{\text{carb}}$ value, external error in the growth temperature estimate, and uncertainty in the carbonate-water fractionation factors. Error is calculated with Monte Carlo resampling.

^c Reconstructed $\delta^{18}\text{O}$ values are calculated using the $\delta^{18}\text{O}$ of carbonate measured via CO_2 which can be found in Table 3. Error is calculated with Monte Carlo resampling considering external error in the growth temperature estimate and uncertainty in the carbonate-water fractionation factors.

1656 ^d Samples originally reported in Beverly et al. (2021), Passey et al. (2014), and Ji (2016) are recalculated in this study to report the values as carbonate mineral
1657 values via Wostbrock et al. (2020).
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1663 **Table 3:** Clumped isotope data and alternate growth temperature data for pedogenic carbonate samples
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Sample Name	number of analyses via CO ₂	δ ¹³ C (‰, VPDB)	δ ¹⁸ O (via CO ₂) (‰, VPDB)	Δ ₄₇ ICDES25 ± ERR (‰) ^a	TΔ ₄₇ ± ERR °C	Other Growth Temp.	Reference for Δ ₄₇ /Temp.
GONJQ-305-1	2	-2.5	-5.5	0.628 ± 0.008	29 ± 1.8	-	Passey et al. (2010)
GON07-4.3.1	1	-0.2	-2.3	0.600 ± 0.013	35.9 ± 3.4	-	Passey et al. (2010)
GON07-4.6.2	1	-2.9	-2.0	0.582 ± 0.013	40.3 ± 3.5	-	Passey et al. (2010)
GON07-4.7.1	2	-1.5	-3.5	0.629 ± 0.009	28.9 ± 2.4	-	Passey et al. (2010)
CN2008-DM-164-130-1	1	-3.0	-7.6	0.653 ± 0.013	23.4 ± 3	-	Passey et al. (2010)
CA08-005-1	2	-3.4	-10.2	0.646 ± 0.009	24.9 ± 2.5	-	Passey et al. (2010)
ET05-AWSH-48-1	1	0.5	-5.0	0.645 ± 0.013	25.2 ± 3.1	-	Passey et al. (2010)
BUR MH 30 Buff	1	-3.4	-3.2	0.69 ± 0.013	25.6 ± 4.5	-	Ji (2016)
SHP 80 XTLN	1	-10.5	-3.4	0.671 ± 0.013	32 ± 4.5	-	Ji (2016)
RCWMA LD 129-140E	1	-3.9	-3.8	0.674 ± 0.013	31.1 ± 4.5	-	Ji (2016)
BUR MH 70 White	1	-2.4	-3.2	0.694 ± 0.013	24.2 ± 4.5	-	Ji (2016)
SHP 100 Buff	1	-10.1	-3.3	0.688 ± 0.013	25.8 ± 4.5	-	Ji (2016)
CAN01-10	3	-1.88	-3.80	0.646 ± 0.011	42 ± 4.1	-	Ringham et al. (2016), reprocessed in Kelson et al. (2020)
CAN01-100	3	-2.66	-3.30	0.687 ± 0.045	28 ± 13.7	-	Ringham et al. (2016), reprocessed in Kelson et al. (2020)
NAC-50	4	-5.83	-8.61	0.668 ± 0.012	34 ± 4.1	-	Ringham et al. (2016), reprocessed in Kelson et al. (2020)
NAC-100	2	-5.51	-8.51	0.69 ± 0.013	27 ± 4.1	-	Ringham et al. (2016), reprocessed in Kelson et al. (2020)
Diablo 50	3	-8.91	-4.84	0.724 ± 0.008	11.7 ± 2.2	-	this work; SCIPP at UM
Diablo 80	2	-9.91	-4.83	0.713 ± 0.01	15 ± 2.8	-	this work; SCIPP at UM
LH2-40	3	-3.19	-8.76	0.724 ± 0.008	11.7 ± 2.5	-	this work; IPL lab at UM
Loyalton2-40	4	-8.41	-12.14	0.728 ± 0.011	10.6 ± 3.3	-	this work; IPL lab at UM
20MOJ-righthand-50	1	-2.35	-1.80	0.712 ± 0.013	15.3 ± 4	-	this work; SCIPP at UM
20MOJ-righthand-100	2	-3.94	-6.10	0.696 ± 0.009	20.4 ± 3	-	this work; SCIPP at UM
TB1701	-	-7.21	-8.46	-	-	27.4 ± 4.5	Mean warm quarter air temperature (Jun, Jul, Aug, Sep) from Takab climate station; Islamic

AN1702	-	-6.95	-8.31	-	-	21.6 ± 5.5	Republic of Iran Meteorological Organization Mean warm quarter air temperature (Jun, Jul, Aug, Sep) from Abbar climate station
19NOD04	4	-13.9	-4.0	0.68 ± 0.007	25.7 ± 2.2	-	Licht et al. (2022) (SCIPP at UM)
20ND03	4	-9.2	-7.1	0.696 ± 0.007	20.5 ± 2.3	-	Licht et al. (2022) (SCIPP at UM)
NM140809-1B	-	-3.17	-6.04	-	-	19.5	Mean warm quarter air temperature from NOAA climate normals in Taos (USC00298668)
PDJ 4055 115a	2	-3.63	-4.34	0.761 ± 0.01	1 ± 2.6	-	this work; IPL lab at UM
cp3 5-7	-	0.55	-7.9	-	-	2.3 ± 2.8	Δ47-Temp from cp4
cp3 65-68	-	1.5	-17	-	-	2.3 ± 2.8	Δ47-Temp from cp4
cp4-75	4	-6.78	-17.39	0.758 ± 0.011	2.3 ± 2.8	-	this work; IPL lab at UM
FLV-Site-B-84-94cm	-	-2.72	-8.89	-	-	17.6 ± 5	average of soil temperatures measured in May, August, and April
FLV-Site-C-74-100cm	-	-2.71	-13.53	-	-	14.5 ± 5	average of soil temperatures measured in May, Aug., and Apr.
18-SS-215A	4	-0.07	-0.84	0.69 ± 0.028	23 ± 9	-	Beverly et al. (2021)
18-SS-215(D-G)	2	2.12	-0.03	0.665 ± 0.002	31 ± 4.9	-	Beverly et al. (2021)
18-SS-235	5	1.89	3.15	0.677 ± 0.024	27 ± 8	-	Beverly et al. (2021)
18-SS-236(A-C)	5	1.75	4.3	0.708 ± 0.02	17 ± 6	-	Beverly et al. (2021)
18-SS-69A	3	0.91	-2.39	0.694 ± 0.008	21 ± 5.2	-	Beverly et al. (2021)
18-SS-70A	2	1.16	-3.71	0.685 ± 0.002	25 ± 4.1	-	Beverly et al. (2021)
18-SS-71A	4	0.83	-3.19	0.718 ± 0.017	14 ± 10.7	-	Beverly et al. (2021)
18-SS-72B	3	0.94	-3.22	0.68 ± 0.011	26 ± 6.5	-	Beverly et al. (2021)
18-SS-73B	3	1.22	-3.11	0.689 ± 0.008	23 ± 4.8	-	Beverly et al. (2021)
18-SS-49A	2	0.66	-2.68	0.68 ± 0.002	26 ± 4.8	-	Beverly et al. (2021)
18-SS-78B	3	1.47	-1.56	0.669 ± 0.01	29 ± 5.5	-	Beverly et al. (2021)
18-SS-79A	3	1.02	-1.81	0.684 ± 0.011	25 ± 3.2	-	Beverly et al. (2021)
18-SS-80B	3	1.12	-2.49	0.699 ± 0.014	20 ± 4.7	-	Beverly et al. (2021)
18-SS-81A	3	0.37	-3.29	0.703 ± 0.011	19 ± 3.2	-	Beverly et al. (2021)

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^aAll Δ₄₇ values are corrected to acid digestion at 25 °C. Data new to this work (the SCIPP lab and IPL) are in the ICDES-25 framework and temperature was calculated using the calibration of Anderson et al. (2021) (note: the Anderson calibration is reported in ICDES-90; the intercept must be adjusted with an acid

1668 fractionation factor (i.e., 0.088) to calculate temperatures from ICDES-25 values). Data from Passey et al. (2010) are reported in the 'HG' reference frame of
1669 Caltech. Samples were reacted at 90°C and corrected with an acid fractionation factor of 0.081. Mineral growth temperatures were calculated using the
1670 calibration of Ghosh et al. (2006). Samples from Ji (2016) are in the CDES of Dennis et al. (2011) and temperatures were calculated with Equation 5 from Passey
1671 and Henkes (2012). The samples were reacted in acid held at 90 °C and are corrected with an acid fractionation factor of 0.082 (Defliese et al., 2015). The
1672 samples from Beverly et al. (2021) are reported in the CDES of Dennis et al. (2011) (using gas standards). Raw Δ_{47} values were corrected with the ^{17}O correction
1673 parameters of Brand et al. (2010). Samples Δ_{47} values were adjusted by +0.082 to correct for acid digestion at 90 °C (Defliese et al., 2015). Temperatures were
1674 calculated using the calibration of Bonifacie et al. (2017).
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