The $\delta^{13}C$, $\delta^{18}O$ and $\Delta_{47}$ records in biogenic, pedogenic and geogenic carbonate types from paleosol-loess sequence and their paleoenvironmental meaning

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Abstract

Paleoenvironmental reconstructions are commonly based on isotopic signatures of a variety of carbonate types, including rhizoliths and land-snail shells, present in paleosol-loess sequences. However, various carbonate types are formed through distinct biotic and abiotic processes over various periods, and therefore may record diverging environmental information in the same sedimentological layer. Here, we investigate the effects of carbonate type on $\delta^{13}C$, $\delta^{18}O$, and clumped isotope-derived paleotemperature [$T(\Delta_{47})$] from the Quaternary Nussloch paleosol-loess sequence (Rhine Valley, SW Germany). $\delta^{13}C$, $\delta^{18}O$, and $T(\Delta_{47})$ values of co-occurring rhizoliths (-8.2‰ to -5.8‰, -6.1‰ to -5.9‰, 12–32°C, respectively), loess dolls (-7.0‰ to -6.5‰, 23°C), land-snail shells (-8.1‰ to -3.2‰, -4.0‰ to -2.2‰, 12–38°C), earthworm biospheroliths (-11‰, -4.7‰, 8°C), and “bulk” carbonates (-1.9‰ to -0.5‰, -5.6‰ to -5.3‰, 78–120°C) from three sediment layers depend systematically on the carbonate type, admixture from geogenic carbonate, and the duration of formation periods. Based on these findings, we provide a comprehensive summary for the application of the three isotopic proxies of $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{47}$ in biogenic and pedogenic carbonates present in the same sediment layer to reconstruct paleoenvironments (e.g., local vegetation, evaporative conditions, and temperature). We conclude that bulk carbonates in Nussloch loess should be excluded from paleoenvironmental reconstructions. Instead, pedogenic and biogenic carbonates should be used to provide context for interpreting the isotopic signature for detailed site- and time-specific paleoenvironmental information.

Key words: Rhizoliths; Land-snail shells; Paleosol-loess sequence; Paleosol; Loess; Pedogenic carbonates; Clumped isotopes; Paleoenvironment reconstruction; CaCO$_3$ formation

INTRODUCTION

Paleosol-loess sequences have a long history of use in paleoenvironmental reconstructions for a broad range of paleoclimate, geology, biology, and anthropology investigations (e.g., Riecken, 1950; Fisk, 1951; Kyuma et al., 1985; Wu et al., 2007; Zech et al., 2012; Lechler et al., 2018). The worldwide spatial distribution (Haase et al., 2007; Muhs, 2007; Roberts et al., 2013; Ghafarpour et al., 2016) and high temporal resolution (Frechen et al., 2003; Karimi et al., 2011; Sun et al., 2012; Taheri et al., 2016; Moine et al., 2017) of paleosol-loess sequences make them an important terrestrial archive (Guo et al., 2002). To this end, investigating isotopic compositions of carbon ($\delta^{13}C_{\text{carb}}$) and oxygen ($\delta^{18}O_{\text{carb}}$) of loess materials, and in particular carbonates formed in these sequences, has been a staple of paleoenvironmental reconstructions for decades. Carbonate $\delta^{13}C$ values provide information about paleovegetation (Quade and Cerling, 1995; Liu et al., 1996; Bayat et al., 2016), and $\delta^{18}O$ values are related to the temperature and the isotopic composition of oxygen in the soil water ($\delta^{18}O_{\text{water}}$) from which the carbonates precipitated (Cerling, 1984; Bayat et al., 2016; Lechler et al., 2018).
More recently, carbonate clumped isotope ($\Delta_{c7}$) thermometry has been used in terrestrial paleoclimate reconstructions (e.g., Affek, 2012; Eiler et al., 2014). $\Delta_{c7}$ thermometry is an indicator of carbonate formation temperature independent of $\delta^{13}O_{water}$ through measure of the abundance of “clumped” carbonate molecules containing both $^{13}C$ and $^{18}O$ in excess of the abundance that would be expected if heavy isotopes were distributed randomly (Ghosh et al., 2006; Eiler, 2007). Recent applications of clumped isotope thermometry to study carbonates formed in or associated with paleosols and loess show the potential for using independent (paleo)temperature constraints to extract paleoclimate information from these records (Eagle et al., 2013; VanDeVeld et al., 2013; Garzione et al., 2014; Ji et al., 2018; Lechler et al., 2018; Zhai et al., 2019).

Paleosol-loess sequences contain various carbonate types (e.g., loess dols, nodules, rhizoliths, land-snap shells, and earthworm biospheroliths) that are formed through a variety of processes that occur over different time periods (Zamanian et al., 2016a). All carbonate types that might be found in paleosol-loess sequences can be classified in three groups: (1) geogenic carbonates (i.e., “bulk” loess carbonates), which account for up to 30% of loess material; (2) biogenic carbonates, such as land-snap shells, earthworm biospheroliths, and micro mammal remains such as bones and teeth; and (3) pedogenic carbonates, such as rhizoliths, carbonate pendants, and nodules (Zamanian et al., 2016a). Formation of each carbonate type is governed by the same equilibrium equations:

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (Eq. 1)$$

$$\alpha_{CaCO_3} = \frac{4m^{3}_{Ca^{2+}}}{pCO_2} \left[ \frac{K_2}{K_1K_{cal}K_{CO_2}} \right] \quad (Eq. 2)$$

where calcite activity ($\alpha_{CaCO_3}$) varies as a function of the concentration of calcium ions in aqueous solution ($m_{Ca^{2+}}$), the partial pressure of CO$_2$ in the soil gas ($pCO_2$), and temperature-sensitive equilibrium constants for the dissociation of carbonic acid ($K_1$), bicarbonate ($K_2$), and calcite ($K_{cal}$), and for the hydration of CO$_2$ ($K_{CO_2}$) (Drever, 1982).

For each carbonate type, Equation 1 is driven to the left to cause CaCO$_3$ precipitation via distinct processes that operate over different time spans and locations (Zamanian et al., 2016a). In the case of biogenic carbonates, environmental conditions that promote (or restrict) biological activity, and growth must be considered. The mean lifespan of land-snails (depending on the species) is 3–5 years (Kerney and Cameron, 1979), and snails are more active at temperatures close to their growth optimum (Zaarur et al., 2011; Yanes et al., 2012). For example, the number of active Arianta arbustorum at 8°C is about five times higher than at 0°C and about two times higher than at 22°C (Cameron, 1970). Pupilla muscorum is active during the whole year, while the activity of Succinella oblonga is limited to the warm seasons of May to July (Pokryszko, 2001). In contrast, some pedogenic carbonates (e.g., rhizoliths) may form over a few decades (Gocke et al., 2011). Pedogenic carbonate nodule and pendant formation takes place over hundreds to thousands of years (Gile et al., 1966; Birkeland, 1999) and occurs seasonally (Breecker et al., 2009), leading to clumped isotope temperatures that presumably reflect long-term averaged, and in many cases seasonally biased, environmental temperatures (Peters et al., 2013; Huntington and Lechler, 2015; Burgener et al., 2016; Gallagher and Sheldon, 2016; Gallagher et al., 2019; Huth et al., 2019; Kelson et al., 2020). The origin and time-integration of geogenic carbonate isotopic compositions may be more difficult to ascertain. Geogenic carbonates found in paleosol-loess sequences may record formation temperatures of minerals in the deflation area from which dust was sourced, where the minerals may have been formed through a variety of geological processes, including metamorphism (Catoni et al., 2012; Baez-Hernandez et al., 2019). Therefore, various carbonate types—even located in the same stratigraphic level in a paleosol-loess sequence—may record a mixture, but specific and potentially complementary environmental information based on differences in $\delta^{13}C$, $\delta^{18}O$, and $\Delta_{c7}$ values.

We examine paleoenvironmental information recorded by carbonate types from a well-known paleosol-loess sequence, the Upper Pleistocene Nussloch paleosol-loess in the Rhine Valley of southwestern Germany (Zoller et al., 1988; Hatté et al., 1999; Rousseau et al., 2002, 2017a; Antoine et al., 2009; Prud’homme et al., 2018). Taken together, the $\delta^{18}O$, $\delta^{13}C$, and $\Delta_{c7}$ data for multiple carbonate types enable us to investigate the effects of geogenic carbonate input, pedogenesis, and environmental factors on resulting isotopic variations.

### MATERIALS AND METHODS

#### Study area and sampling

The Nussloch paleosol-loess sequence (49°18.82’N, 8°43.01’E) in southwestern Germany (Fig. 1a) is a well-studied type section of the European paleosol-loess. The Upper Pleniglacial sequence in Nussloch, with a total thickness of 18.5 m, has been dated by $^{14}C$ (Lang et al., 2003; Rousseau et al., 2007; Moine et al., 2017) and infrared-stimulated luminescence (Antoine et al., 2001, 2009), indicating formation throughout the last glacial-interglacial cycle since ~130 ka (Zoller et al., 1988; Hatté et al., 1998; Rousseau et al., 2007, 2017a). We sampled the younger part of the Nussloch sequence, which contains various morphologies of carbonates, including rhizoliths, loess dols, land-snap shells, carbonate coatings, and hypocoatings, as well as concretions and earthworm biospheroliths (Moine et al., 2008, 2017; Gocke et al., 2011; Prud’homme et al., 2016, 2018)

Sampling focused on the most abundant carbonate morphologies (i.e., rhizoliths, loess doll, land-snap shells, and earthworm biospheroliths) from three horizons (Fig. 1b). The sampled horizons are: (1) ca. 20 ka loess unit at 5–6 m below the modern surface (“Upper loess”), (2) the ca. 38 ka paleosol (Lohnes soil) at ~12 m below the modern surface
Paleosol, and (3) the loess unit directly below the paleosol ("Lower loess"). The sampled layers correspond to units 32 and 31, 20 and 19 described by Antoine et al. (2009), respectively. Bulk samples (∼10 kg each) were collected in the field from ~50 cm deep into 1-m-wide outcrops that were freshly cleaned off by the authors. Bulk samples were taken to the lab and the various carbonate types were separated through wet sieving using a 50 μm screen. The following carbonate types were separated from each layer (Fig. 1c–l):

Upper loess: short and thin rhizoliths, < 1 mm in diameter and up to 1 cm long ("Fine-rhizo A," Fig. 1c); short and thick rhizoliths, a few mm in diameter and length ("Fine-rhizo B;" Fig. 1d); large rhizoliths, up to 2 cm in diameter and 10 cm long ("Large-rhizo;" Fig. 1e); earthworm biospheroliths, average ∼1 mm in diameter (Fig. 1f); loess dolls, a few mm in diameter and < 1 cm long with different shapes (e.g., elongated ovals or globules with rounded edges; Fig. 1g); a few small white shell pieces of unidentified taxa with a maximum length of 5 mm ("Up-shell;" Fig. 1h); and bulk loess (26% calcium carbonate equivalent; CCE).

Paleosol: Land-snail shells of Succinella oblonga (Fig. 1i), Pupilla muscorum (Fig. 1j), Trochulus hispidus (Fig. 1k), Arianta arbustorum (Fig. 1l), and bulk paleosol (21% CCE).

Lower loess: Land-snail shells of Succinella oblonga (Fig. 1i), Pupilla muscorum (Fig. 1j), Trochulus hispidus (Fig. 1k), Arianta arbustorum (Fig. 1l), and bulk loess (25% CCE). The land-snail shells observed and sampled in the Lower loess are the same species as those from the paleosol.

**Stable isotope analysis and calculations**

Carbonate samples were ground with a mortar and pestle into homogenized powders prior to stable isotope (δ¹⁸O, δ¹³C, Δ₁⁷) analyses at the University of Washington IsoLab. Sample preparation and analysis followed methods of Burgener et al. (2016) and Schauer et al. (2016). Briefly, 8–20 mg of powdered carbonate was reacted in a common phosphoric acid bath held at 90°C. The released CO₂ was purified cryogenically through an automated nickel and stainless steel vacuum line using an ethanol-dry ice slush trap and liquid N₂ trap, then chromatographically with a helium carrier through a Porapak Q trap (50/80 mesh, 15 cm long, 4.5 mm ID, 0.635 mm OD, held at -20°C). Preparation was completed when the sample CO₂ was frozen into a 6 mm Pyrex tube and flame sealed. The break seal containing purified CO₂ was loaded on the

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**Figure 1.** (color online) (a) The location of the Nussloch paleosol-loess sequence (49°18.82′N, 8°43.01′E) in southwestern Germany. (b) The sampling depths (adapted from Antoine et al., 2009) and (c–l) the types of carbonates collected from each depth. The black scale bar on all images is 1 cm, except (f) earthworm biospheroliths, which is 300 μm.
The results for Upper loess, Paleosol, and Lower loess samples are summarized in Table 1, and full data for samples and standards is provided in Supplementary Table A1.

**Formation temperatures [T(ΔΔ)] of carbonate types**

Measured carbonate ΔΔ values range from 0.754–0.499‰, corresponding to apparent temperatures of 8–120°C (Table 1). The T(ΔΔ) values of the bulk carbonate samples range from ~78–120°C, far exceeding Earth-surface temperature conditions, while T(ΔΔ) values for other carbonate types (i.e., pedogenic and biogenic) range from ~8–38°C and are in the plausible range of Earth-surface temperatures (Fig. 3). The small rhizoliths (Fine-rhizo A and B) in the Upper loess of the Lower loess hordi (12 ± 4 and 15 ± 5°C), pedogenic loess horizons (8–17°C), and Lower loess horizons (8–12°C) are systematically offset relative to δ34C values of the bulk paleosol (~1.1%) and bulk loess from the Lower loess interval (~2.3% and ~4.7% and ~4.7%). The small rhizoliths (Fine-rhizo A and B) have average δ34C values (~11% and ~14%) for bulk loess/paleosol carbonate samples from the Upper loess interval (~0.5% and ~2.3%). The small rhizoliths (Fine-rhizo A and B) have average δ34C values (~11% and ~14%) for bulk loess/paleosol carbonate samples from the Upper loess interval (~0.5% and ~2.3%).
Table 1. Stable isotopes and clumped isotope data for carbonate types collected from three depths at Nussloch paleosol-loess sequence.

<table>
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<tr>
<th>Carbonate materials</th>
<th>Sample ID</th>
<th>Replicate analyses</th>
<th>Sample averages and external error (SE)</th>
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<th>δ¹⁸O water</th>
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<td>δ¹³C %VPDB</td>
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<td>Average δ¹³C SE.</td>
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<td>δ¹³C Std. %VPDB</td>
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<td>Average δ¹⁸O SE.</td>
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<td>δ¹³C Std. %VPDB</td>
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Table 1. Continued.

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* Outliers are noted in italics.
Up-shell (12 ± 6°C), and earthworm biospherolith (8 ± 3°C)
samples. Land-snail shells revealed two distinct temperature
ranges in both the Paleosol and the Lower loess horizons
(Fig. 3). The clumped isotope temperatures for
S. oblonga (38 ± 4 and 36 ± 6°C) and T. hispidus (27 ± 5 and 32 ± 5°C)
are consistently warmer than analyzed P. muscorum (16 ± 6
and 21 ± 4°C) and A. arbustorum (12 ± 4 and 15 ± 3°C)
samples. Similar land-snail species show similar tempera-
tures in the Paleosol and in the Lower loess (Fig. 3).

Figure 3. (color online) Temperature of carbonate formation calculated based on T(ΔT) values of carbonate types present at three depths in the Nussloch paleosol-loess sequence. The inset graph shows the temperatures of carbonate types in the Upper loess horizon. Horizontal bars show standard errors.

The calculated value of reconstructed δ^{18}O_{water}
Calculated apparent δ^{18}O_{water} values vary among carbonate
types (Fig. 4). Apparent δ^{18}O_{water} for bulk loess and paleosol
carbonates are positive values (6–12‰ VSMOW). In contrast, the other carbonate types (i.e. pedogenic and biogenic carbonates) have δ¹⁸O_{water} values in the range of possible paleoenvironmental water values. Reconstructed apparent δ¹⁸O_{water} values for rhizoliths of different sizes (-6.4 to -2.1‰), land-snail shells of different species (-3.8 to +0.3‰) and earthworm biospheroliths (-6.0‰) differ significantly, even at a similar depth. However, similar species of land-snails record similar reconstructed δ¹⁸O_{water} values independent of depth (Fig. 4).

**DISCUSSION**

Stable isotopic compositions vary with carbonate type within a single sedimentological layer within the Nussloch loess-paleosol sequence. T(Δ⁴₇) in excess of 78°C indicates bulk loess and bulk paleosol carbonates are not suitable for paleoenvironmental reconstructions. In contrast, the pedogenic and biogenic carbonate types record distinct paleoenvironmental information, with sample δ¹⁸O, δ¹³C, and Δ⁴₇ values likely reflecting specific formation mechanisms and time periods over which the carbonates precipitated.

**Geogenic carbonates: bulk loess and bulk paleosol samples**

δ¹³C, δ¹⁸O, and T(Δ⁴₇) values suggest carbonates in bulk loess and bulk paleosols of the Nussloch sequence are detrital rather than pedogenic in origin. Apparent T(Δ⁴₇) values of bulk carbonates (~78–120°C) far exceed the range of plausible Earth-surface temperatures (Fig. 3). Additionally, calculated apparent δ¹⁸O_{water} values of bulk carbonates (6.3–12‰; Fig. 4) are inconsistent with formation in situ in the (paleo)soil unit. Instead, the isotopic data point to diagenetic and/or metamorphic sources for these carbonates, which we suggest were likely derived from pre-existing rock through processes of weathering and erosion.

Waters in metamorphic environments are commonly characterized by high δ¹⁸O values (potentially > 0‰ VSMOW) as a result of dehydration processes and water-rock isotopic exchange in deep-crustal environments (Sheppard, 1986), which may explain the positive δ¹⁸O_{water} values calculated for many bulk carbonates in the Nussloch sequence. Diagenetic and metamorphic carbonates are exposed throughout Western Europe, making it difficult to ascertain the exact source(s) of Nussloch detrital carbonate. That said, prevailing westerly and north-westerly winds into the Nussloch region during the last glacial period (Antoine et al., 2013; Rousseau et al., 2014) point to source regions to the west of the Nussloch Basin, possibly marbles exhumed in the Scottish Highlands and abundant limestone throughout the Devon Basin in England. Additional geochemical data (e.g., Sr-Nd isotopes) could potentially help decipher source(s) for Nussloch detrital carbonate. Nevertheless, high apparent T(Δ⁴₇) and δ¹⁸O_{water} values of bulk carbonates indicate that bulk carbonates do not record the local environmental conditions during or following sedimentation and cannot be used as a direct paleoenvironmental proxy.

**Pedogenic carbonates: rhizoliths and loess dolls**

Rhizoliths and loess dolls are pedogenic carbonates formed in situ in the soil (e.g., Gocke et al., 2010, 2011; Li et al., 2015; Gao et al., 2020; Sun et al., 2020). Their δ¹³C values should largely reflect vegetation type, their δ¹⁸O_{water} mirror the values of local soil water, and T(Δ⁴₇) is presumably a measure of the soil temperature during soil drying and CO₂ degassing. The pedogenic carbonate isotopic values are generally

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**Figure 4.** (color online) The estimated isotopic composition of water (δ¹⁸O_{water}), from which the carbonate types were formed. The error bars are smaller than the symbol size for all carbonate types. The solid vertical line at δ¹⁸O_{water} = 0 is shown for reference.
consistent with formation in soil conditions. In the following paragraphs, we examine the pedogenic carbonate data in the context of the range of δ13C, δ18O, and T(Δ47) values expected for Nussloch site paleoenvironmental conditions and discuss implications of distinct seasonality and mechanisms of pedogenic carbonate formation for paleoenvironmental reconstruction.

Multiple lines of evidence place constraints on Nussloch paleoenvironmental conditions relevant to the period of pedogenic carbonate formation. We lack direct constraints on local terrestrial δ18Owater values during this period; however, Sima et al. (2009) assumed that precipitation sources and dominant wind trajectories were similar to modern during the Last Glacial. Such δ18Owater values of precipitation would differ by only ~0.5‰ from modern (-11‰ to -7‰) (Field, 2010; Terzer et al., 2013) due to the ice volume effect (Prud’homme et al., 2016). Today, minimum and maximum monthly mean air temperatures in the study area range from ~0 to ~25°C, and average cold- and warm-season air temperatures are 1.7 ± 0.9°C (DJF) and 18 ± 2°C (JJA), respectively. The mean annual air temperature is 10°C, and modern mean annual soil temperature is therefore likely to be in the range of 10°C to up to 3–5°C higher due to radiative heating of the soil surface (Roxy et al., 2014). Significant elevation of soil surface temperatures via radiative heating is common when the annual precipitation is < 600 mm (Burgener et al., 2019; Gallagher et al., 2019), as it is estimated to have been in Nussloch (Prud’homme et al., 2018). Recent air and soil temperature estimates from earthworm calcite granules at Nussloch suggest similar-to-modern mean warm season air and soil temperatures of 12 ± 4 and 15 ± 5°C, respectively, during paleosol formation (Prud’homme et al., 2016). These temperature estimates were based on measured carbonate δ13C and assumed δ18Owater values for the Nussloch paleosol-loess sequence. Other paleo-temperature estimates suggest comparable-to-modern mean annual air temperatures of 8.5–10°C during paleosol formation in analogous paleosol-loess sequences in Hungary (Schatz et al., 2015).

Within these ranges of temperature, the season over which the rhizoliths are formed and the formation mechanisms of rhizoliths should determine the isotopic values and temperatures recorded. Nussloch rhizolith samples have δ13C values that are dependent on rhizolith size: small rhizoliths have higher δ13C values than large rhizoliths and loess dolls from the same horizon (Fig. 2). We interpret the dependence of the δ13C values with rhizolith size to suggest that these carbonates originate from different plant species or groups, and/or form through specific mechanisms (e.g., root water uptake or soil wetting-drying cycles), motivating hypotheses that can be tested using the suite of δ13C, δ18O and T(Δ47) data.

First, it is possible that rhizolith formation mechanisms vary with time. Water uptake by roots and resulting water flow toward the root is accepted as the main formation mechanism for rhizoliths (Klappa, 1980; Lambers et al., 2009; Gocke et al., 2011). Following root death, water uptake by the root and water flow towards the root is stopped. However, non-biogenic mechanisms (e.g., wetting-drying cycles) can still drive further carbonate dissolution and precipitation. In this way, a rhizolith formed in association with water uptake by roots may subsequently act as a framework for further carbonate precipitation to build on such that increased size of the rhizolith records a longer formation period (Sun et al., 2019a, b, c; Huguet et al., 2020). In this scenario, specific formation mechanisms operating over different time scales would affect the environmental information recorded by rhizoliths larger than a few millimeters compared to smaller rhizoliths that presumably form over a short period of time associated with active root water uptake.

Vegetation type could also cause differences in the isotopic signals recorded by large and small rhizoliths. Indeed, a variety of vegetation species are associated with rhizolith formation (Rodriguez-Aranda and Calvo, 1998; Alonso-Zarza, 1999; Matteucci et al., 2007). If large rhizoliths form along perennial roots that are bigger than the roots of annual grasses, this would lead to continued root-water uptake over many years. In contrast, the morphology of small rhizoliths suggest that they formed along the smaller roots of annual grasses, likely over one growing season. Such a difference in duration of carbonate formation could explain the observed differences in δ13C, δ18O, and T(Δ47) values among large and small rhizoliths. Alternatively, small rhizoliths might have formed when the plant was under water stress, for example at the end of the winter season through the early spring (Tranquillini, 1982), which is most probably the case in glacial times (Yung et al., 1996; Medeiros and Ward, 2013). Under such conditions the plant will close the stomata to reduce water loss, which leads to 13C enrichment by C3 photosynthesis (e.g., Dawson et al., 2002). Observed differences in temperature and δ18Owater values among small versus large rhizoliths could be consistent with small-rhizolith formation under water stress, with fine rhizoliths recording higher formation temperature (Fig. 3) and forming from more evaporative waters (Fig. 4). The δ13C values (Fig. 2) do not show obvious evaporation control, potentially reflecting other factors, such as plant type, that may influence δ13C values.

We suggest that rhizolith formation temperatures (Fig. 3) are consistent with differences in formation duration and mechanisms. We suggest small rhizoliths likely formed over short periods, potentially as short-lived as during a single soil-drying event due to root-water uptake. In contrast, large rhizoliths may have formed over a few years up to a few decades (Gocke et al., 2011; Sun et al., 2019a) integrating several warm seasons, and therefore recording the mean temperature of those seasons. We therefore interpret the clumped isotope temperature for the large rhizoliths (average T(Δ47) = 14 ± 5°C) to represent warm-season soil conditions averaged over up to a few decades.

The clumped isotope warm-season soil temperature reconstruction is consistent with the average mean warm-season soil temperature estimates (13 ± 4°C and 15 ± 3°C) reported for Nussloch (Prud’honne et al., 2016, 2018). Prud’homme et al. (2016) estimated δ18Owater values during last glacial at Nussloch based on a linear equation among modern values of water δ18O (δ18Owater) and modern mean annual air
temperature of the IAEA dataset, and used the $\delta^{18}O_{\text{water}}$ values to calculate temperature from carbonate $\delta^{18}O$. Assuming measured $T(\Delta_{47})$ values record soil carbonate formation temperatures, we can directly calculate the $\delta^{18}O_{\text{water}}$ values during rhizolith formation. The good agreement between temperature results from our study and those of Prud’homme et al. (2016) suggest that the assumptions by Prud’homme et al. (2016) about paleo $\delta^{18}O_{\text{water}}$ values at Nussloch during the last glacial interval were reasonable.

Loess doll formation may occur over centuries or longer depending on size (Zamanian et al., 2016a), rather than during a single vegetation period like small rhizoliths. However, the loess dolls and one of the small rhizolith samples are similar in both formation temperatures and size (Figs. 1, 3). Thus, it is possible that the small loess dolls might also be formed over short periods, although more evidence than just formation temperatures is necessary to substantiate such an argument.

Taken together with the $\delta^{13}C$ and $\delta^{18}O$ data, $T(\Delta_{47})$ values further support interpretation of differences in duration of carbonate growth by carbonate type (Fig. 5). We suggest that small rhizoliths (a few millimeters in diameter) and loess dolls exhibiting large variability in $T(\Delta_{47})$ (19–32°C) record the temperature of one growing season and/or soil-drying event. Such transient growth during peak warm-season events can explain why observed $T(\Delta_{47})$ values are significantly warmer than expected for growth during glacial conditions. In contrast, we interpret average $T(\Delta_{47})$ of ~14°C for large rhizoliths (a few centimeters in diameter) as a more reliable measure of average paleo-temperatures across multiple growing seasons, or over decades (Table 1, Fig. 3).

**Biogenic carbonates: land-snail shells and earthworm biospheroliths**

The $\delta^{13}C$ and $\delta^{18}O$ values of distinct land-snail species (Fig. 2) reflect the specifics in the diet of these organisms (i.e., ingested plants and, to a lesser extent, geogenic carbonate). $\delta^{13}C$ values in shell carbonate depend mainly on the land-snail diet regime (Metref et al., 2003; Balakrishnan et al., 2005; Zhang et al., 2014). The similar shift (~ -1‰) to lower $\delta^{13}C$ values from Lower loess to paleosol in both land-snail shells and bulk carbonates reveals that the land snails *S. oblonga*, *P. muscorum*, and *T. hispidus* were ingesting bulk carbonate (Pigati et al., 2010; Yanes et al., 2012) (Fig. 2). These identified species are all able to ingest carbonates (Fechter et al., 1990; Boschi et al., 2011), which comprise ~5–25% of their diet (Pigati et al., 2010; Yanes et al., 2012). We can estimate the $\delta^{13}C$ of vegetation during paleosol formation and Lower loess deposition using the equation of Yanes et al. (2008) based on shell carbonate $\delta^{13}C$ values. Using this equation, and assuming 0% carbonate ingestion, the range of $\delta^{13}C$ of vegetation is calculated as -22 to -17‰ VPDB; but considering 5–25% carbonate ingestion, the estimated $\delta^{13}C$ values of vegetation range from -25‰ to -20‰ VPDB. The latter calculated $\delta^{13}C$ range of vegetation is consistent with the reported $\delta^{13}C$ values of organic carbon (~24.9 to -23.7‰) for the Nussloch paleosol-loess sequence (Hatté et al., 1999; Prud’homme et al., 2018), supporting our interpretation of significant carbonate ingestion by analyzed snail species. Similar calculations using *A. arbustorum*, which we assume did not ingest carbonate due to the similarity of $\delta^{13}C$ values for co-occurring shell and non-biogenic carbonate in...
paleosol and Lower loess, also gives a Δ13C value of -26‰ for vegetation. Lastly, earthworm biospheroliths also can be used to reconstruct plant Δ13C (Prud’homme et al., 2018). Using an epsilon calculated from Canti (2009) and typical diet estimation equations (Passey et al., 2005), we calculate a Δ13Cplant of -23‰ from the earthworm biospheroliths Δ13C values.

The clumped isotope data and calculated 18Owater values are broadly consistent with the hypothesis that land-snail individuals record seasonal and local changes in atmospheric temperature (Eagle et al., 2013; Wang et al., 2016; Zhang et al., 2018; Zhai et al., 2019) and the isotopic composition of local precipitation modified by evaporation (Zaarur et al., 2011; Dong et al., 2020). Different species grow in seasons with different temperatures (Wang et al., 2016; Zhai et al., 2019), precipitation 18Owater values, and relative humidity. Furthermore, because individual snails are short lived, considerable variation in the temperatures and 18Owater values recorded by land-snail individuals is expected (Eagle et al., 2013). This variability is further exacerbated because the recorded clumped isotope temperatures depend on shell properties such as shell color and morphology, and the ecological behavior of the snail (Zaarur et al., 2011). Accordingly, the observed variability among individual snail-shell T(Δ47) and reconstructed 18Owater values within a single horizon is expected; however, this natural variability can mask and complicate interpretation of environmental shifts in the proxy records.

Land-snail shells, following embedding in loess and paleosol, might also have undergone recrystallization and associated re-equilibration of shell carbonate isotopic values due to dissolution and re-precipitation (Zamanian et al., 2016b, c). Hence, it is possible that recrystallization might have biased the recorded temperatures toward warmer, post-burial environmental conditions. However, we are unable to determine the extent of such effects. Large T(Δ47) uncertainties for some analyzed biogenic carbonate samples (Table 1) further limit our ability to test the hypothesis of land-snail variability rigorously. Future studies, where it is possible to sample a large number of individual shells of each species, could achieve sufficient precision (Eagle et al., 2013).

In contrast to land-snail shells, earthworms seem to not incorporate the ingested carbonates in their biospheroliths (Moine et al., 2017). Thus, the T(Δ47) values (8 ± 2°C) of earthworm biospheroliths likely record the temperature at the soil surface during earthworm activity. Our direct biospheroliths T(Δ47) measurement is within the range, but on the lower side of our average warm-season soil temperature estimate based on large rhizolith clumped isotope measurements (14 ± 5°C), and the warm-season soil (13 ± 4°C to 15 ± 3°C) temperature ranges inferred by Prud’homme et al. (2016) for the Nussloch paleosol-loess sequence. The uncertainties are large enough to permit significant variation in biospherolith-based temperature estimates, which would not be surprising given that the carbonate samples here and in the study of Prud’homme et al. (2016) homogenize a large number of individual earthworm granules, each of which formed in a single day. Soil carbonate formation and earthworm activity were likely both restricted to the warmest periods of year in the Nussloch permafrost environment, so we do not suggest that the low resolution of these thermometry techniques masks a seasonal difference in rhizoliths and biospheroliths formation.

Implications for paleoenvironmental reconstructions from stable isotopes of carbonates in loess and paleosol deposits

Our observations of the Δ13C, Δ18O, and clumped isotope temperatures of carbonate types associated with the Nussloch paleosol-loess sequence suggest several broader implications for paleoenvironmental reconstructions from these and similar deposits (Table 2, Fig. 5).

First, the contribution of detrital carbonate to bulk loess and paleosol carbonate makes these materials unsuitable for paleoenvironmental reconstruction (e.g., interpreting mean annual or seasonal air temperatures), as observed in other recent T(Δ47) investigations of loess-paleosol sequences (Lechler et al., 2018). The contribution of geogenic detrital carbonate was made obvious by the clumped isotope apparent temperatures well in excess of plausible Earth surface conditions. However, it is possible that in the absence of clumped isotope data, the contribution of bulk geogenic carbonate may not be recognized. Geogenic carbonate contribution may be particularly difficult to recognize in deposits where pedogenic grain coatings of carbonate formed in situ also contribute significantly to the isotopic composition of the bulk carbonate samples. In such cases, it may be possible to interpret variations in carbonate Δ13C and Δ18O to document temporal variation in the seasonality of precipitation, in vegetation or in other paleoenvironmental variables, when in reality the carbonate Δ13C and Δ18O variations may document variations in the degree of pedogenic overprinting of detrital carbonate in bulk loess or paleosol deposits. Clumped isotope data would provide a simple test of the interpretation. In addition, isotopic analysis of bulk carbonate in paleosol-loess deposits can be valuable in interpreting isotopic compositions of land-snail shells, given that many of these organisms ingest this carbonate as a significant proportion of their diet.

Second, our findings contribute to a growing body of literature concerning seasonal bias in pedogenic carbonate formation, and the implications of this bias for paleoenvironmental reconstruction (e.g., Burgener et al., 2016; Kelson et al., 2020). Most previous work on this topic has focused on carbonate pendant (clast coating) and nodule formation in modern and Holocene soils (Breecker et al., 2009; Quade et al., 2011; Peters et al., 2013; Burgener et al., 2016; Gallagher and Sheldon, 2016; Ringham et al., 2016). We complement these approaches by examining isotopic values in carbonates of different types in the same temporal horizon. The variations in carbonate Δ13C, Δ18O (Fig. 2), and clumped isotope temperatures (Fig. 3) are consistent with specific mechanisms...
of carbonate formation that integrate environmental information over time periods, which we suggest may range from a single vegetation growth event in small rhizoliths, to decades and centuries of summers in larger rhizoliths. Together, our interpretations provide guidance for sampling strategies, to consider time resolution in future studies. Such studies may target carbonates that grow over short periods to examine seasonal variability and extremes, and carbonates that grow over longer periods to document seasonal average temperatures and representative vegetation and precipitation isotopic values (Burgener et al., 2016; Ringham et al., 2016; Ji et al., 2018; Lechler et al., 2018).

Finally, our results and those of other studies in the Nussloch remind us that pedogenic/biogenic processes as well as seasonal biases must be considered in paleoenvironmental interpretations of paleosol archives. In European paleosol-loess archives alone, reconstructions of Last Glacial paleoenvironmental conditions over the short time periods over which they form. In contrast, large rhizoliths (centimeters in thickness) record mainly summer temperatures averaged over decades. This finding suggests that rhizolith size should be considered for paleoenvironmental reconstructions, with larger rhizoliths being more reliable indicators of average warm season conditions. Earthworm biospheroliths and land-snell shells are suitable materials for paleoenvironment and paleovegetation reconstructions. In the case of land snails, their ecological habit, including the proportion of ingested bulk/geogenic carbonate and the isotopic composition of bulk soil carbonates should be considered. This study highlights that with proper

### CONCLUSIONS

Various carbonate types deposited in the same paleo-horizon or layer of the Nussloch paleosol-loess sequence record specific environmental information because of differences in formation mechanisms and duration. Bulk carbonates in the Nussloch paleosol-loess sequence are detrital materials that record the diageneric conditions of carbonates in the deflation area instead of local environmental conditions. Therefore, bulk carbonates should be excluded from samples taken to reconstruct the local paleoenvironment. We interpret small rhizoliths, loess dolls, land-snell shells, and earthworm biospheroliths as records of temperatures and soil water content that reflect environmental conditions over the short time periods over which they form. In contrast, large rhizoliths (centimeters in thickness) record mainly summer temperatures averaged over decades.
consideration of proxy carbonate type and associated formation mechanisms, integrated stable ($\delta^{13}C$, $\delta^{18}O$) isotopic values of pedogenic and biogenic carbonates can yield robust paleoenvironment reconstructions with decadal and even seasonal temporal resolution.

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SUPPLEMENTARY MATERIAL

The supplementary material for this article can be found at https://doi.org/10.1017/qua.2020.109

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