

RECONSTRUCTING TERRESTRIAL ENVIRONMENTS USING STABLE ISOTOPES IN FOSSIL TEETH AND PALEOSOL CARBONATES

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ABSTRACT.—Carbon isotopes in Neogene-age fossil teeth and paleosol carbonates are commonly interpreted in the context of past distributions of C₃ and C₄ vegetation. These two plant types have very different distributions in relation to climate and ecology, and provide a robust basis for reconstructing terrestrial paleoclimates and paleoenvironments during the Neogene. Carbon isotopes in pre-Neogene fossil teeth are usually interpreted in the context of changes in the $\delta^{13}\text{C}$ value of atmospheric CO₂, and variable climate-dependent carbon-isotope discrimination in C₃ plants. Carbon isotopes in pre-Neogene soil carbonates can be used to estimate past levels of atmospheric CO₂. Oxygen isotopes in fossil teeth and paleosol carbonates primarily are influenced by the oxygen isotopic compositions of ancient rainfall and surface waters. The oxygen isotopic composition of rainfall is has a complex, but tractable, relationship with climate, and variably relates to temperature, elevation, precipitation amount, and other factors. Mammal species that rely on moisture in dietary plant tissues to satisfy their water requirements (rather than surface drinking water) may have oxygen isotopic compositions that track aridity. Thus, oxygen isotopes of fossil mammals can place broad constraints on paleoaridity. Carbonate clumped isotope thermometry allows for reconstruction of soil temperatures at the time of pedogenic carbonate mineralization. The method is unique because it is the only thermodynamically based isotopic paleothermometer that does not require assumptions about the isotopic composition of the fluid in which the archive mineral formed. Soil temperature reflects a complex interplay of air temperature, solar radiative heating, latent heat effects, soil thermal diffusivity, and seasonal variations of these parameters. Because plants and most animals live in and/or near the soil, soil temperature is an important aspect of terrestrial (paleo)climate.

INTRODUCTION

STABLE ISOTOPES are a powerful basis for reconstructing terrestrial paleoclimates and paleoenvironments, but seldom provide simple climate variables such as mean annual temperature and mean annual precipitation. Rather, their effective application and interpretation requires an appreciation of phenomena such as C₃ and C₄ plant ecophysiology, animal dietary ecology, physical and chemical properties of soils, and atmospheric dynamics. Stable-isotope reconstruction of terrestrial environments is most successful when these complexities are embraced and creatively exploited. Practitioners must be content with the kinds of answers that that these methods can provide, even if they are not the answers initially sought.

Studies of the stable isotopic compositions of

fossil teeth and paleosol carbonates largely began in the 1980s, and have provided a wealth of information about paleoclimate and evolution in terrestrial environments. Noteworthy successes of these methods include: the revelation that C₄ grasses, which today account for about 20% of terrestrial primary productivity (Still et al., 2003), only existed in background levels prior to the late Miocene (Cerling et al., 1997); discovery that the Paleocene–Eocene Thermal Maximum (PETM) carbon-isotope excursion, then known only from the marine record, also was reflected in terrestrial food webs (Koch et al., 1992, 1995); reconstruction of rapid late Miocene uplift of the central Andean Plateau (Ghosh et al., 2006a; Garzzone et al., 2008) and antiquity of high elevations on the Tibetan Plateau (Rowley and Currie, 2007); emerging findings that hominids—whose peculiar evolution has long been suspected to relate to ex-

plottation of expanding savanna ecosystems—actually did consume significant quantities of savanna-based (C_4 plant) resources (Ungar and Sponheimer, 2011); and reconstruction of atmospheric CO_2 levels during the Phanerozoic (Cerling, 1991; Ekart et al., 1999; Montañez et al., 2007; Breecker et al., 2010).

This review presents some background information for five different systems based on carbon and oxygen isotopes in teeth and pedogenic carbonates: (1) carbon isotopes in fossil mammal teeth as a record of the isotopic compositions and photosynthetic pathways of plants, and of mammal dietary ecology; (2) carbon isotopes in paleosol carbonates as a record of the isotopic compositions and photosynthetic pathways of dominant plant communities, and of past levels of atmospheric CO_2 ; (3) oxygen isotopes in fossil mammal teeth as a record of climate and animal physiology; (4) oxygen isotopes in paleosol carbonates as a record of climate; and (5) clumped isotopes in paleosol carbonates as recorders of soil temperatures.

Because plants are the foundation of primary productivity in terrestrial ecosystems, this review briefly discusses the ecological significance of C_3 and C_4 plants and of carbon isotope discrimination within C_3 plants. Similarly, given the central role of meteoric water isotopes in terrestrial paleoclimate, the review discusses present-day global variation in the $\delta^{18}O$ of meteoric waters and its relation to climate.

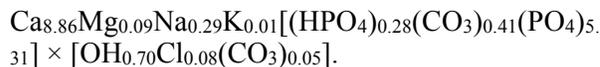
This review is intended as a starting point and source of up-to-date references. The reader is referred to excellent reviews of similar subject matters given by Koch (1998), Kohn and Cerling (2002), and Sheldon and Tabor (2009). References are biased towards recent publications reflecting the state-of-the-art rather than original publications, and many of the examples are drawn from the work of the author's own sphere of colleagues and collaborators. This review does not consider related emerging applications, such as the bioapatite clumped isotope method for inferring body temperatures of animals (Eagle et al., 2010; 2011), or studies of the 'triple' oxygen isotope composition ($^{17}O/^{16}O$, $^{18}O/^{16}O$) of bioapatites (Gehler et al., 2011).

BASIC CONSIDERATIONS

Carbonate and phosphate isotopologues

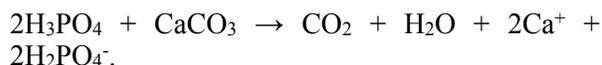
Carbonate (CO_3) is a species of interest both in fossil teeth and soil carbonates. Teeth, which

are composed of bioapatite, contain a few percent CO_3^{2-} ion substituting in phosphate and hydroxyl/halide positions. An approximation of the composition of a pristine bioapatite was given by Elliott (2002):



The mineralogy of soil carbonates is primarily calcite ($CaCO_3$), although dolomitic soil carbonates have been observed in recent soils (Capo et al., 2000; Kohut et al., 2005) as well as fossil soils (Kessler et al., 2001; Sheldon and Tabor, 2009; Kearsley et al., 2012). When considering the measurement of carbon or oxygen isotope ratios of carbonates, what is actually being measured is the relative abundance of different carbonate isotopologues. Of the five most abundant carbonate isotopologues, four are of interest here: $^{12}C^{16}O_3$ [mass 60, 98.2%], $^{13}C^{16}O_3$ [mass 61, 11,000 ppm], $^{12}C^{18}O^{16}O_2$ [mass 62, 6000 ppm], and $^{13}C^{18}O^{16}O_2$ [mass 63, 67 ppm], where the numbers in brackets give the atomic mass and relative abundance (Ghosh et al., 2006) (a useful conversion is 1% = 10,000 ppm). Mass 60 carbonate can be referred to as an unsubstituted isotopologue because it contains no rare isotope substitutions; thus, mass 61 and 62 carbonate are singly substituted and mass 63 is doubly (or multiply) substituted. The carbon isotope ratio of a sample is ultimately related to the ratio of the mass 61 isotopologue to the common mass-60 isotopologue, the oxygen isotope ratio to the mass 62 isotopologue to the common mass 60 isotopologue, and the clumped isotope composition to the ratio of mass 63 to mass 60 carbonate. Note that the existence of ^{17}O gives rise to another mass 61 isotopologue ($^{12}C^{17}O^{16}O_2$, 1100 ppm), and, in practice, the contribution of this isotopologue must be accounted for when calculating the carbon isotope ratio from mass spectrometric data (Brand et al., 2010). ^{17}O also gives rise to two analogous mass 62 isotopologues, but these are of sufficiently low abundance (12 ppm, 405 ppb) that corrections to the apparent $^{18}O/^{16}O$ ratio usually are not necessary.

Stable isotope ratio measurements are made not on these carbonate ions, but on CO_2 that is liberated by reaction of carbonates in anhydrous phosphoric acid. A possible reaction is:



Here, the oxygen in the carbonate is partitioned into CO₂ and H₂O, and there is a resulting oxygen isotopic fractionation that scales as a function of the temperature at which the reaction takes place. For calcite, the acid-liberated CO₂ is enriched in ¹⁸O by about 10.2 ‰ for 25 °C reactions and 8.2 ‰ for 90 °C reactions (Swart et al., 1991). The temperature sensitivity of this fractionation is similar for modern bioapatites, whereas fossil bioapatites may have slightly higher temperature sensitivities (Passey et al., 2007). There is no fractionation of carbon isotopes associated with acid digestion for calcium carbonate or bioapatite because all of the C in carbonate is transferred to C in CO₂, and thus, by mass balance, there can be no fractionation. For clumped isotopes, the CO₂ appears to be about 0.27‰ enriched in ¹³C¹⁸O bonds relative to the carbonate mineral (for 25 °C reactions; Guo et al., 2009; Dennis et al., 2011).

Most of the oxygen in bioapatite occurs as phosphate (PO₄), and this phase can be specifically targeted for oxygen isotope analysis. The relevant isotopologue is ³¹P¹⁸O¹⁶O₃, with a natural abundance of about 8,000 ppm. Phosphate typically is isolated by dissolution of the apatite in acid and re-precipitation of phosphate as silver phosphate (Ag₃PO₄). The oxygen in this phosphate is then converted to O₂ via fluorination or CO via high-temperature reduction (e.g., O’Neil et al., 1994, Vennemann et al., 2002). Mass spectrometry is then performed on these gases.

Stable isotope nomenclature

Isotope distributions are most useful when they are presented as ratios of isotopes, and relative differences in isotope ratios. This stems partly from the fact that ratios of isotopes can be determined with far better precision and accuracy than absolute abundances of isotopes. Additionally, the absolute abundance of an isotope is usually less interesting than the deviation of the abundance from a starting composition or a reference composition. What is given below is a simplification of basic isotopic nomenclature (see Coplen, 2011, for a comprehensive review of accepted and correct ways of reporting isotope data). In addition, Brand and Coplen (2012) have proposed the new unit “Urey” (abbreviated Ur) for isotope delta values, although only time will tell if the unit becomes widely adopted.

The fundamental measures are the isotope ratio R , the fractionation factor α , and the delta value δ . These are defined as follows (using carbon isotopes as an example):

$$^{13}R = ^{13}C/^{12}C$$

Here, ¹³C and ¹²C refer to the abundance of each isotope, although in practice absolute numbers of atoms are not counted, but rather some signal related to the abundance is measured (e.g., the currents of the mass 44 and mass 45 CO₂⁺ ion beams in a mass spectrometer). Also note that it is customary to place the common isotope in the denominator.

The fractionation factor is defined as:

$$\alpha_{a-b} = R_a/R_b$$

where R_a is the isotope ratio of some phase “a”, and R_b is the ratio of some other phase “b.” Phase b usually has a physical relationship with phase a (e.g., phase a could be liquid water, and phase b could be water vapor in isotopic equilibrium with the liquid water).

A close cousin of the fractionation factor is epsilon:

$$\epsilon_{a-b} = \alpha_{a-b} - 1$$

It is customary to multiply epsilon values by 1000, resulting in a per mil value. Epsilon multiplied by 1000 is called a “per mil fractionation factor,” and is a convenient way of talking about fractionations: most α values are numbers close to one, e.g., 1.013 or 0.998, whereas the corresponding per mil epsilons are 13‰ and -2‰. The fractionations discussed in this paper are given as per mil fractionations unless otherwise noted.

Isotopic compositions are most commonly reported as delta values:

$$\delta^{13}C_a = ^{13}R_a/^{13}R_{std} - 1$$

where R_{std} is the isotope ratio of an internationally accepted isotopic reference material. Delta values are almost always multiplied by 1000, resulting in values that represent per mil differences relative to the standard. Delta values discussed in this paper are per mil delta values.

For carbon isotopes in all materials, and for oxygen isotopes in carbonate minerals, the reference standard is PDB (Peedee Belemnite). For oxygen isotopes in all phases, the standard is SMOW (Standard Mean Ocean Water). Because the supply of PDB no longer exists, it has been proposed that PDB be superseded by VPDB (Vienna Peedee Belemnite), where the international

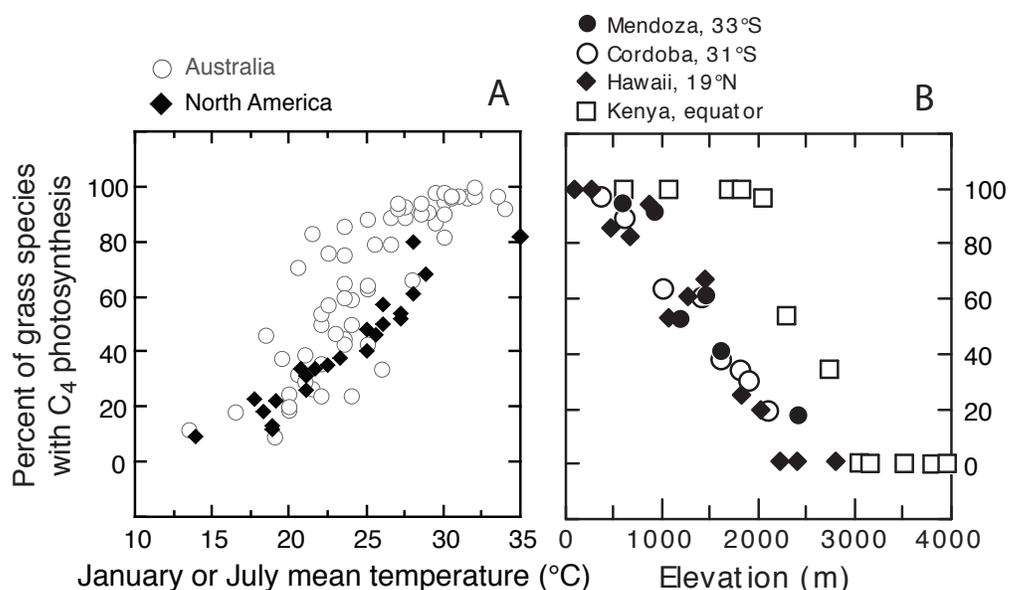


FIGURE 1.—Present-day relationships between C₄ grass dominance and temperature and elevation. A) Correlation between percent grass species with C₄ photosynthesis and warmest month mean temperature for Australia (Hattersley, 1983) and North America (Teeri and Stowe, 1976). B) Correlation with elevation for plant surveys conducted near Mendoza, Argentina (Cavagnaro, 1988), Cordoba, Argentina (Cabido et al., 1997), Hawaii (Rundel, 1980), and Kenya (Tieszen et al., 1979).

standard NBS-19 has a $\delta^{13}\text{C}$ value of 1.95‰ and a $\delta^{18}\text{O}$ value of -2.20‰ relative to VPDB (Coplen, 1995). Similarly, given complexities in the definition of SMOW, it has been proposed that it be replaced by VSMOW (Vienna Standard Mean Ocean Water), where the international standards SLAP (Standard Light Antarctic Precipitation) and SMOW have $\delta^{18}\text{O}$ values of -55.5 ‰ and 0 ‰ relative to VSMOW (Coplen, 1995). However, while these definitions of VPDB and VSMOW are widely accepted, some workers view the addition of the 'V' as unnecessary and potentially confusing, and prefer to report values relative to PDB and SMOW while stating explicitly how data are normalized to those scales (see Sharp, 2007, for an in-depth discussion of the history of isotopic reference materials and proposed reference frames).

Finally, a useful relation for interconverting among δ , α , and ϵ values is:

$$\alpha_{a-b} = (1000 + \delta_a) / (1000 + \delta_b) = (\epsilon_{a-b} / 1000) + 1$$

This equation is valid only when δ and ϵ values have been multiplied by 1000 (i.e., standard per mil δ and ϵ values).

CARBON ISOTOPES

Carbon isotopic compositions of plants and atmospheric CO₂, and their relationship to paleoenvironment

A typical goal of carbon isotope analysis of fossil teeth and paleosol carbonates is the reconstruction of paleovegetation, because the latter is related to climate and largely sets the baseline for the ecology of the fossil ecosystem. Another goal may be the reconstruction of the $\delta^{13}\text{C}$ value of atmospheric CO₂. Plants derive essentially all of their carbon from atmospheric CO₂, so the $\delta^{13}\text{C}$ value of atmospheric CO₂ (currently about -8‰) will exert the first-order control on the $\delta^{13}\text{C}$ of plants. However, plants discriminate strongly against ¹³C (stated differently, they preferentially uptake ¹²C), and the paleoecological carbon-isotope signal reflects differences in the degree of discrimination among different plant types, and within the same plant type for different environmental conditions.

C₃ and C₄ vegetation.—The vast majority of plants use either C₃ or C₄ photosynthesis. C₃ and C₄ plants have very different ecologies, and conveniently have very different carbon isotopic compositions. C₃ plants include virtually all woody vegetation (trees, shrubs) as well as most non-grassy herbs and forbs, and cool growing season grasses. C₄ plants have far less taxonomic diversity than C₃ plants, and primarily are warm

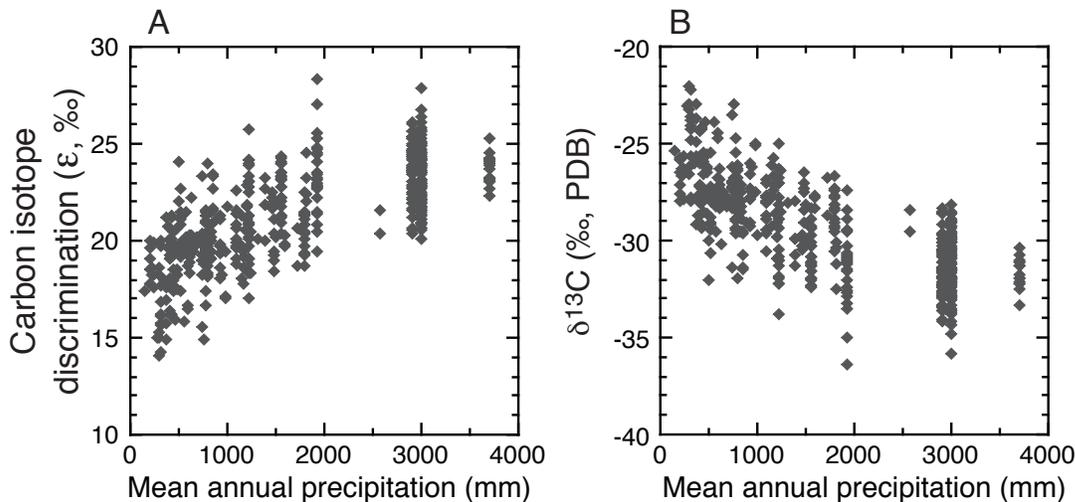


FIGURE 2.— C_3 plant carbon isotopes and mean annual precipitation. A) Carbon isotope discrimination against ^{13}C as a function of mean annual precipitation for a global database of $\delta^{13}C$ values of natural vegetation. B) Equivalent $\delta^{13}C$ values of the same plants, normalized for an atmosphere with a $\delta^{13}C$ value similar to today, -8‰ . All data from Diefendorf et al., 2010.

growing season grasses, yet are responsible for about 20% of gross primary production (Still et al., 2003). A typical $\delta^{13}C$ value for bulk carbon in a C_3 plant is -28‰ (but see below), whereas a typical value for a C_4 plant is -13‰ . Relative to an analytical precision of 0.1‰ or better for $\delta^{13}C$ analysis, the isotopic separation between C_3 and C_4 plants is enormous. Therefore, different ecosystems have easily distinguishable carbon isotope signatures: for example, tropical savannas (C_3 trees and shrubs, C_4 grasses), and Mediterranean climates (C_3 trees and shrubs, C_3 grasses) can be distinguished from temperate semi-arid climates with summer rainfall (C_3 trees and shrubs, C_3 and C_4 grasses).

Useful reviews of the ecology and paleoecology of C_4 grasses include Ehleringer et al. (1997), Tipler and Pagani (2007), and Edwards et al. (2010). C_4 plants have the ability to concentrate CO_2 inside of leaves at the sites of photosynthesis; thus, C_4 plants avoid the deleterious effects of photorespiration brought about by high temperatures, water limitation, and low atmospheric CO_2 levels. The expansion of C_4 vegetation in the Miocene is thought to relate at least in part to decreasing CO_2 levels during the Cenozoic (Cerling et al., 1997; Edwards et al., 2010). Remarkably good positive correlations are observed in the modern environment between percent of grass species with C_4 photosynthesis and growing season temperature (e.g., Teeri and Stowe, 1976;

Hattersley, 1983), and negative correlations between percent C_4 grass species and elevation (Cavagnaro et al., 1988; Cabido et al., 1997; Rundel, 1980; Tieszen et al., 1979). Some of these correlations are shown in Figure 1.

Carbon isotope variation within C_3 plants.— It has long been appreciated that discrimination by C_3 plants against ^{13}C decreases with increasing stress brought on by high temperatures, water limitation, and low CO_2 , and the physiological/biochemical basis of this discrimination is well understood (e.g., Farquhar et al., 1989). Recent global compilations of C_3 plant $\delta^{13}C$ values show a clear relationship with mean annual precipitation (Diefendorf et al., 2010; Kohn, 2010). Figure 2 shows that the $\delta^{13}C$ values of plants from very dry ecosystems (e.g., < 200 mm precipitation/yr.) are, on average, about 5‰ higher than $\delta^{13}C$ values of plants from wet ecosystems (> 1500 mm precipitation/yr.). On this basis, Kohn (2010) proposed that carbon isotopes might be used as a broad indicator of paleoprecipitation, provided that C_4 vegetation is a negligible contributor to the overall carbon isotope signal, and that changes in the $\delta^{13}C$ of ancient atmospheric CO_2 can be accounted for. However, Diefendorf et al. (2010) show that evergreen gymnosperms have lower $\delta^{13}C$ values (by $\sim 1\text{--}3\text{‰}$) than other types of woody plants, a factor that could complicate the use of $\delta^{13}C$ values from fossil plants as precipitation indicators.

Carbon isotopic composition of ancient at-

atmospheric CO_2 .—A brief example shows the importance of accounting for changes in the carbon isotopic composition of atmospheric CO_2 : under current atmospheric conditions with a $\delta^{13}\text{C}$ value of atmospheric CO_2 of about 8‰, a C_3 plant growing under a hypothetical set of conditions might have a 20‰ discrimination against ^{13}C , and therefore, a $\delta^{13}\text{C}$ value of about -28‰. If the atmosphere had a $\delta^{13}\text{C}$ value of 5‰ at some point in the past, the same plant growing under the same conditions would have a $\delta^{13}\text{C}$ value of -25‰. Thus, estimates of $\delta^{13}\text{C}$ values of past atmospheres are necessary for reconstructing (for instance) carbon-isotope discriminations of past vegetation, or the relative abundances of C_3 and C_4 vegetation in ancient ecosystems.

A common method of reconstructing $\delta^{13}\text{C}$ of atmospheric CO_2 during the Phanerozoic is based on the $\delta^{13}\text{C}$ values of marine carbonates (e.g., Ekart et al., 1999), and, specifically for Cenozoic times, $\delta^{13}\text{C}$ values of foraminifera (Passey et al., 2002, 2009; Tipple et al., 2010). Broadly speaking, atmospheric CO_2 is in carbon-isotope equilibrium with dissolved inorganic carbon (DIC) in seawater, and foraminifera precipitate their carbonate shells using this DIC. Therefore, in principle, if the effective fractionation factor between atmospheric CO_2 and foraminiferal carbonate is known, the $\delta^{13}\text{C}$ of ancient atmospheric CO_2 can be calculated based on $\delta^{13}\text{C}$ values of foraminifera. Passey et al. (2002) compiled recent and Holocene data to derive an empirical estimate of the fractionation between atmospheric CO_2 and planktonic foraminifera ($7.9 \text{‰} \pm 1.1 \text{‰}$). They applied this value to a 20-million-year record of planktonic foraminiferal $\delta^{13}\text{C}$ to derive estimates of $\delta^{13}\text{C}$ of atmospheric CO_2 , resolved into 0.5 Myr bins. A similar approach was used by Passey et al. (2009), but based on benthic foraminifera, which have a more complete record than planktonic foraminifera and suffer less from vital effects, including those associated with photosymbiosis. Tipple et al. (2010) used a similar, but more sophisticated approach to reconstruct atmospheric CO_2 $\delta^{13}\text{C}$ values across the entire Cenozoic, and Ekart et al. (1999) present a model for most of the Phanerozoic based on $\delta^{13}\text{C}$ values of brachiopods and other carbonate fossils (Veizer et al., 1999). Figure 3 shows variations in the expected isotopic compositions of C_3 and C_4 plants based on reconstructed variations in atmospheric CO_2 for the past 20 million years. Barring the recent decrease in atmospheric CO_2 $\delta^{13}\text{C}$ of about 1.5 ‰ due to fossil fuel burning, the estimated

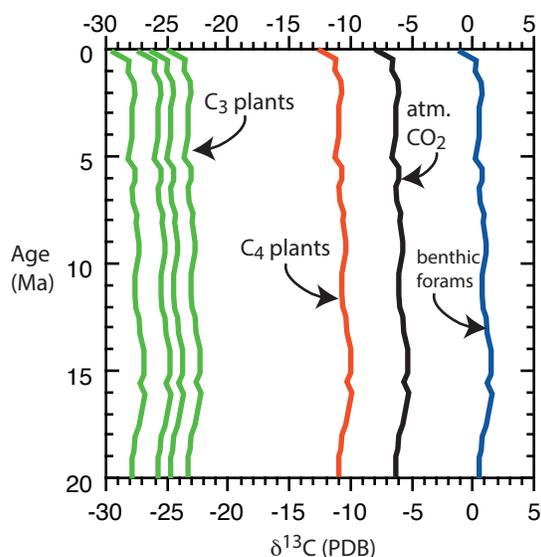


FIGURE 3.—Reconstructed variation in $\delta^{13}\text{C}$ of atmospheric CO_2 based on carbon isotopes of fossil marine benthic foraminifera, and resulting variation in the $\delta^{13}\text{C}$ values of C_3 and C_4 plants. The C_4 curve is calculated using an epsilon (ϵ) value of 4.7‰. The four different C_3 curves show predicted compositions of average C_3 vegetation growing in climates with mean annual precipitation of, from left to right, 2500, 1000, 500, and 100 mm/yr. The ϵ values used to generate these curves were calculated using equation 2 of Kohn (2010), assuming an elevation of 1000 m and an absolute latitude of 40° . Benthic foraminifera data compilation, and calculated $\delta^{13}\text{C}$ of atmospheric CO_2 , are from Passey et al. (2009).

variation in $\delta^{13}\text{C}$ during the past 20 Myr was approximately 2‰, with maximal values during the middle Miocene (about -5‰) and minimal values during the late Pleistocene (about -7‰). Thus, the apparent variation in atmospheric $\delta^{13}\text{C}$ over this time interval is significant: it is relatively small compared to isotopic differences between C_3 and C_4 plants ($\sim 15\text{‰}$), but it is large compared to variation within C_3 plants (e.g., Figure 2), and it can be critical when evaluating whether ancient ecosystems contained small fractions of C_4 vegetation or pure C_3 vegetation growing under water-limited conditions (e.g., Fox et al., 2012).

Carbon isotope compositions of mammalian teeth

Carbon isotope fractionation between diet and teeth.—The adage, ‘you are what you eat’ sums up the basis of this method for reconstructing the diets of fossil mammals. Herbivores eat plants and respire plant organic carbon to CO_2 and

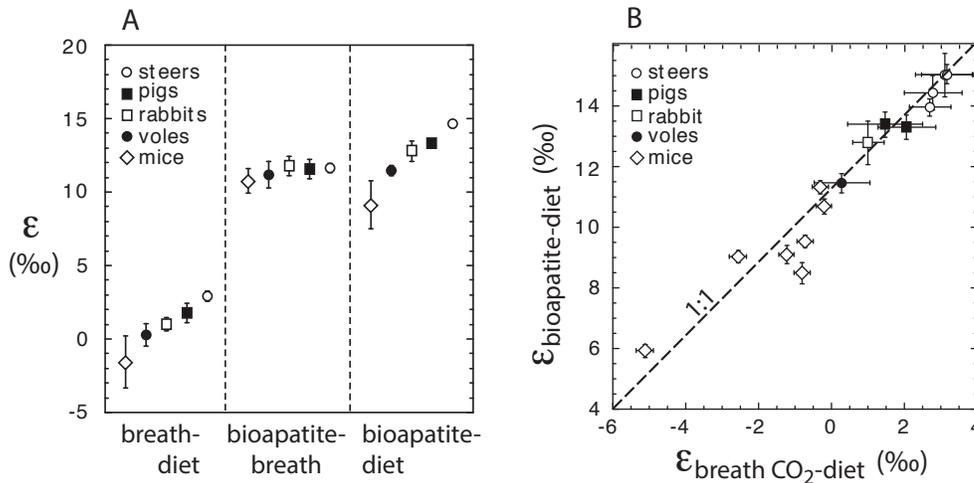


FIGURE 4.—Carbon isotope fractionation in different mammals. A) Carbon isotope fractionation between breath and diet, bioapatite and breath, and bioapatite and diet. B) Relationship between bioapatite-diet and breath-diet fractionation. The results of this study suggest that taxonomic variation in bioapatite-diet fractionation is a result of differences in digestive physiology, as traced by the breath-diet fractionation. Data are from Passey et al., 2005.

H₂O. The CO₂ then becomes part of dissolved inorganic carbon in the blood and other body fluids. As teeth form, they incorporate some of this inorganic carbon, which ultimately ends up as CO₃ locked into the bioapatite lattice. The magnitude of carbon isotopic fractionation between dietary carbon and tooth carbon is broadly similar within similar classes of mammals. For example, large mammalian herbivores have fractionations typically around 14–15‰, such that the δ¹³C value of teeth is 14–15‰ higher than that of the plant diet (Cerling and Harris, 1999; Passey et al., 2005; Zazzo et al., 2010). Small mammals such as rodents appear to have smaller fractionations, around 11‰ (Figure 4A).

Passey et al. (2005) studied carbon isotope fractionations between diet, breath CO₂, and tooth enamel in a range of mammal species (voles, rabbits, pigs, and cows). They found that the isotopic fractionation between breath CO₂ and tooth enamel was broadly similar across these species, whereas the fractionations between diet and breath, and between diet and tooth enamel, varied significantly across these species. Furthermore, the diet-breath and diet-tooth enamel fractionations tracked each other in a 1:1 relationship (Figure 4B). This suggests that the difference in diet to enamel fractionation in different species arises in the digestion step (as traced by the diet to breath fractionation) rather than in the mineralization step (as traced by the breath to enamel fractionation, because breath should track the isotopic

composition of the DIC pool from which tooth enamel derives its inorganic carbon). An important difference in the digestive physiology across these organisms may be the amount of methane produced by microbes in the digestive tract. Methane is strongly depleted in ¹³C, and, by mass balance, production in the digestive tract of ¹³C-depleted methane and its subsequent loss via eructation and flatulence will lead to a corresponding enrichment in the δ¹³C value of the remaining carbon in the animal. In this model, cows, having the largest diet to enamel fractionation in the study of Passey et al. (2005), have the highest relative amount of methane production, and voles, having the lowest diet to enamel fractionation, have the lowest relative methane production, with rabbits and pigs having intermediate degrees of production. This is broadly consistent with the current understanding of methane production in different taxa (Hackstein and van Alen, 1996).

Time integration.—Mammalian teeth mineralize over timescales of weeks to years, thus leading to time averaging of isotopic signals. Evergrowing rodent incisors, for example, can be completely replaced in a few weeks owing to continual wear at the tip and growth at the base. A high-crowned horse molar, on the other hand, may take 1–2 years to fully form. Tooth enamel, when initially deposited by specialized cells called ameloblasts, is a soft, mineral-poor, organic-rich substance that, by volume, contains only about 25% of the mineral content of fully mineralized

enamel. The increase in mineral content during enamel maturation is gradual and spatially diffuse. Therefore, the isotopic composition of a small volume of enamel does not record one short instant (e.g., a day) in the animal's isotopic composition, but rather reflects a time-average of the isotopic composition of the animal across the time period that the enamel cured from mineral-poor matrix to fully mineralized enamel (Passey and Cerling, 2002), which can be weeks to months depending on species and tooth position.

Most teeth have a directional sense of formation, beginning at the crown and proceeding towards the root, and consequently, teeth will preserve a time-series of variation in the isotopic composition of animals. Meaningful signals have been recovered despite the time averaging resulting from the process of enamel maturation, and such time series may be used to investigate seasonality in different aspects of the animal's behavior or environment (Koch et al., 1989). Using a controlled feeding study, Balasse et al. (2002) first showed that tooth enamel isotope profiles—a series of samples taken in chronological order from the crown to root of a tooth—are indeed time-averaged compared to the pattern of dietary variation in the animal. Passey and Cerling (2002) developed a mathematical forward model to predict how a given time series of isotopic variation in an animal's diet would appear as isotopic variation along the length of a tooth. In another controlled feeding study, Zazzo et al. (2010) showed that the predicted tooth enamel signal based on forward modeling of the known dietary variation closely matched the observed pattern of variation in teeth.

Dietary paleoecology.—Ecology and behavior exert a strong control on the isotopic compositions of animals. Extant large-mammal herbivores largely partition as browsers and grazers, with very few mixed feeders, and the carbon isotopic compositions of extant herbivores reflect this (e.g., Cerling et al., 2003; Sponheimer et al., 2003). It is not clear how long this sharp dichotomy extends back into the fossil record, and it is possible that there were more mixed feeders in the past. Carbon isotopes in tooth enamel can be used to study this kind of dietary paleoecology and have been used to study niche partitioning in ancient ecosystems (e.g., Feranec et al., 2008; MacFadden, 2008). Uno et al. (2011) were able to document how, in East Africa, different taxa responded to (or interacted with) newly available C₄ grasses in the late Miocene and Pliocene. Fossil horses were the earliest and most sustained con-

sumers of C₄ grass, switching over to C₄-dominated diets by about 9 Myr ago. Gomphothere and elephantid proboscideans showed a more gradual transition, but became dedicated C₄ feeders by about 6 Myr ago, whereas rhinos, bovids, and hippos showed variable responses, with some individuals adopting C₄ diets early on, and others retaining C₃ or mixed C₃/C₄ diets. Suids showed a remarkably protracted increase in C₄ grazing spanning several million years, and Harris and Cerling (2002) used carbon isotopes to show that this increase in grazing was accompanied by an increase in the length of third molars, presumably an adaptation to the more abrasive grazing diets.

Diagenesis.—Fossil teeth must preserve their original isotopic compositions in order to be useful for paleoecology. Bone, dentine, and cementum are highly susceptible to post-mortem alteration, in part because they are highly porous, contain a large fraction of organic compounds, and have very small and poorly ordered bioapatite crystallites. On the other hand, tooth enamel is dense, contains very little organic carbon, and has larger, more stable bioapatite crystals. Figure 5 shows a comparison of carbon and oxygen isotope preservation between enamel and bone + dentine + cementum (BDC) in an assemblage of late Miocene fossil mammals from Baode, northern China. The ecology of the mammals was such that there was a wide initial range of carbon and oxygen isotopic compositions of bioapatite. Isotopic diagenesis has caused BDC to converge towards a common value, with carbon isotopic composition similar to paleosol carbonate in the same sediments. The most compelling evidence that carbon isotopes in tooth enamel are generally primary comes from observations of patterns that would be impossible to explain as artifacts of diagenesis. For example, a global increase in the amount of C₄ vegetation in diet is documented in grazing herbivores during the late Miocene (Cerling et al., 1997). The simultaneity of this event on several continents would be difficult to explain by diagenesis alone, or, from another perspective, if diagenesis were pervasive, it would smear out such an event. Furthermore, browsing (leaf-eating) herbivores do not increase in $\delta^{13}\text{C}$ during this time. Since browsers do not eat grass, their carbon isotopic compositions should not record the C₄ grass expansion, and this is borne out by the data.

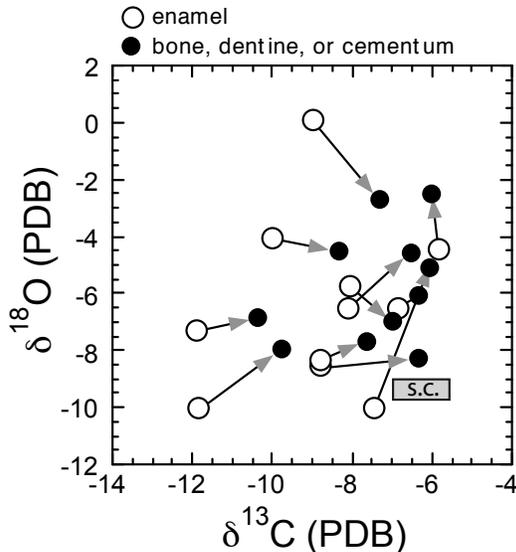


FIGURE 5.—Carbon and oxygen isotopic compositions of coexisting pairs of fossilized tooth enamel (open circles) and bone/dentine/cementum (BDC) (filled circles) from the late Miocene Baode Formation, China. Each pair comes from a unique fossil, and the two points represent tooth enamel and BDC sampled from the same fossil. The BDC values converge towards a diagenetic isotopic composition with a carbon isotopic composition similar to paleosol carbonate that is ubiquitous in these strata (box labeled S.C.).

Carbon isotope compositions of pedogenic carbonate

The term ‘pedogenic carbonate’ refers to carbonate that precipitates *in situ* in soils. The term ‘paleosol carbonate’ as used in this paper refers strictly to fossil pedogenic carbonate. Pedogenic carbonate is authigenic, therefore, carbonate inherited from parent material or deposited by wind is not pedogenic carbonate. Pedogenic carbonate can form when soil waters become saturated with respect to calcium carbonate, which may be caused by evaporation of water and water removal by plant roots, and decreasing partial pressure of soil CO₂ owing to slowdown of plant respiration, itself often a response to soil dewatering. Pedogenic carbonates are most common in regions with dry climates (< ~750 mm precipitation/yr., Royer, 1999), but can occur in regions with more rainfall, especially if there is pronounced seasonality in rainfall.

The carbon in pedogenic carbonate ultimately comes from CO₂, and the carbon isotopic composition of pedogenic carbonate reflects the carbon isotopic composition of this CO₂. The CO₂, in

turn, has two primary sources: biological and atmospheric. The biological CO₂ comes from respiration by living, below-ground plant biomass (primarily roots), or respiration by heterotrophs of dead biomass. Since plants are the ultimate source of biomass, the carbon isotopic composition of the biological CO₂ reflects that of the prevailing plants. On the other hand, atmospheric CO₂ has a globally uniform isotopic composition and concentration (currently about -8‰ and 390 ppm), and the isotopic composition of soil CO₂ reflects a kind of diffusion-controlled mixing between biological CO₂ produced in the soil and atmospheric CO₂ that mixes in from the surface (Figure 6) (Cerling, 1984).

Cerling’s (1984) soil-diffusion model has been successful in predicting carbon isotopic compositions of soil CO₂ and pedogenic carbonate in a wide variety of environments, and is in wide use today. In practice, the Cerling soil-diffusion model is used in two different ways, largely depending on the time period in which fossil paleosol carbonates were formed. For pre-Neogene times when atmospheric CO₂ levels may have been high and C₄ plants were uncommon, paleosol carbonate δ¹³C values are usually interpreted in the context of past levels of atmospheric CO₂. For Cenozoic time, and especially Neogene time (including present-day), paleosol carbonate δ¹³C values are usually interpreted in the context of the δ¹³C of prevailing vegetation, and especially in terms of relative abundances of C₃ and C₄ vegetation.

The paleosol carbonate CO₂ barometer.—A thorough review of the soil CO₂ diffusion model is beyond the scope of this review, and the reader is referred to Cerling (1984), Cerling and Quade (1993), and Cerling (1999). However, Cerling (1999) presents a straightforward solution to the soil CO₂ model that relates atmospheric CO₂ concentration (C_a^*) to the δ¹³C values of soil CO₂ (δ_s), soil-respired CO₂ (δ_r), and atmospheric CO₂ (δ_a):

$$C_a^* = S(z) \frac{\delta_s - 1.0044\delta_r - 4.4}{\delta_a - \delta_s}$$

Here, soil CO₂ is the total CO₂ in the soil, reflecting a mixture of atmospheric CO₂ and soil-respired CO₂ (i.e., the biological CO₂ discussed above). The term $S(z)$ is the specific solution to the soil CO₂ diffusion equation that depends on parameters such as depth, soil porosity, soil respi-

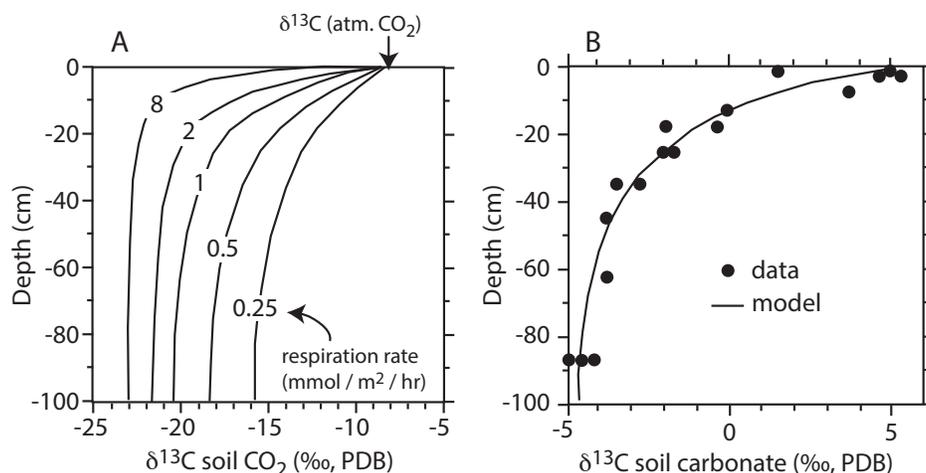


FIGURE 6.—Soil CO₂ diffusion model. A) Modeled carbon isotopic composition of CO₂ for uniform ‘C₃’ source isotopic composition, but different rates of production (respiration rate). Values converge at the surface to the isotopic composition of atmospheric CO₂. B). Measured δ¹³C values for soil carbonate from a soil profile near Las Vegas, Nevada, USA. Figures modified from Cerling and Quade, 1993.

ration rate, and characteristic depth of CO₂ production. $S(z)$ is the component of soil CO₂ that is contributed by respiration in the soil. To use the above equation to reconstruct past levels of atmospheric CO₂, estimates or proxy measurements of $S(z)$, δ_s , δ_r , and δ_a are necessary. Also, inspection of the equation shows that higher levels of atmospheric CO₂ (C_a^*) give rise to smaller differences between the isotopic compositions of the atmosphere (δ_a) and soil CO₂ (δ_s); alternatively, high CO₂ gives rise to larger isotopic differences between soil CO₂ (δ_s) and soil-respired CO₂ (δ_r).

The paleosol carbonate δ¹³C value is the proxy for δ_s . The latter is calculated based on the former using a temperature-dependent equilibrium fractionation factor (e.g., Romanek et al., 1992), with an assumed value for temperature that commonly is selected to approximate past mean annual temperature (Ekart et al., 1999). However, in light of recent findings about the seasonal timing of pedogenic carbonate growth (Breecker et al., 2009) and results from carbonate clumped isotope thermometry (see below for discussion), it may be more appropriate to use a value reflective of summer maximum soil temperature, and furthermore, clumped isotope analyses may permit direct determination of this temperature.

The parameter δ_r is determined by the carbon isotopic composition of respirable biomass in the soil (including respirable carbon in living plants and biomass), and can be estimated based on δ¹³C values of fossilized organic carbon extracted from the same soils from which paleosol carbonates are

collected. However, it is typical that most of the original soil carbon is lost after soils become inactive and during burial and fossilization, and there can be attendant changes in δ¹³C values of soil organic carbon (e.g., Wynn, 2007). To sidestep this problem, Ekart et al. (1999) used an approach whereby the carbon isotopic composition of atmospheric CO₂ (δ_a) is calculated based on δ¹³C values of marine carbonates (as described previously), and representative values of δ¹³C for C₃ plants (and hence δ_r) are calculated from δ_a by assuming a representative fractionation factor between C₃ plants and atmospheric CO₂ (Figure 2). Ekart et al. (1999) showed that using this approach, calculated δ_r values are similar to measured fossil organic carbon δ¹³C values when a C₃ plant – atmospheric CO₂ discrimination of about 18‰ is used in the calculations.

The parameter $S(z)$ has no direct proxy and must be assumed based on analogy with Recent soils. In productive soils, $S(z)$ is essentially invariant below depths of about 50 cm, and because most paleosol carbonates are collected from depths of 50 cm or greater below the preserved top of the soil horizon, the value of $S(z)$ is usually assumed to be constant for any given soil. $S(z)$ values for high productivity soils may be 5,000–8,000 ppm, and those from arid zone soils 3,000–5,000 ppm (Cerling, 1999). However, based on evidence that pedogenic carbonate mineralizes primarily during the hottest times of the year when soil moisture and soil productivity are low, Breecker et al. (2010) argue that $S(z)$ values of

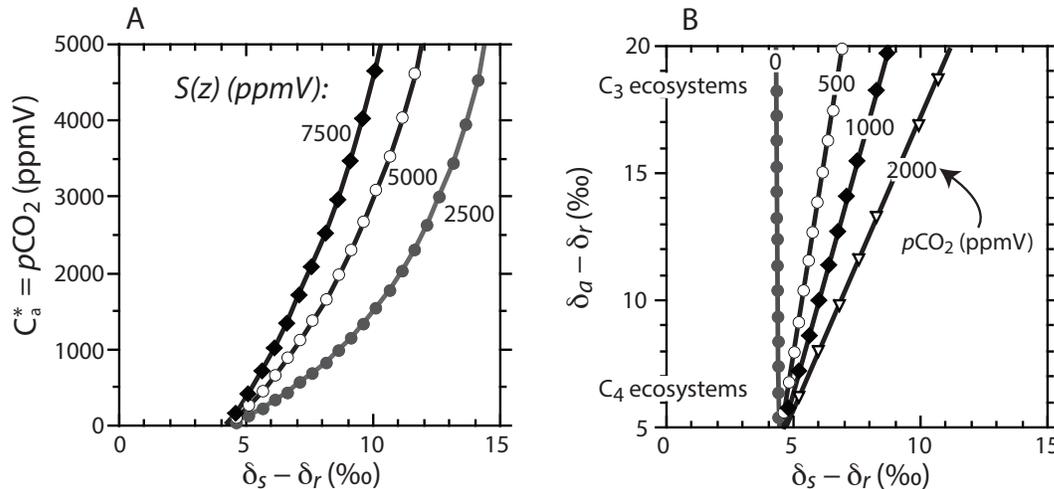


FIGURE 7.—Illustrations of the sensitivity of the paleosol CO₂ barometer (equation 1) to different parameters. A) Estimated partial pressure of CO₂ ($p\text{CO}_2$) as a function of the carbon isotopic difference between soil CO₂ (δ_s) and soil respired CO₂ (δ_r), solved for different values of $S(z)$, the soil-derived component of total CO₂ in the soil. In practice, δ_s is determined based on the carbon isotopic composition of paleosol carbonate, and δ_r is determined directly by the carbon isotopic composition of soil organic matter or indirectly by modeling of paleo-atmospheric CO₂ $\delta^{13}\text{C}$ and paleo-plant $\delta^{13}\text{C}$, whereas $S(z)$ is an assumed value that is informed by values observed in modern soils. Figure is after Cerling, 1999, fig. 10. B) Influence of CO₂ levels on the isotopic difference between soil CO₂ (δ_s) and soil-respired CO₂ (δ_r) in ecosystems ranging from pure C₄ ecosystems ($\delta_a - \delta_r \approx 6$ ‰) to pure C₃ ecosystems ($\delta_a - \delta_r \approx 18$ ‰). In pure C₄ ecosystems, atmospheric CO₂ has little influence on values of $\delta_s - \delta_r$. Figure after Ekart et al., 1999, fig. 7.

~2,500 ppm are more appropriate for most soils. Figure 7A shows how the inferred paleoatmospheric CO₂ concentration varies as a function of the difference between δ_s and δ_r , solved for a range of values of $S(z)$. The uncertainty in the CO₂ estimates is large, but as Cerling (1999, p. 55) remarks, "...the paleosol CO₂ barometer, in spite of this uncertainty, is more promising than searching for Mesozoic ice!"

The paleosol CO₂ barometer is most sensitive when there is a large difference between plant carbon isotopic composition, which determines δ_r , and atmospheric CO₂ carbon isotopic composition (δ_a). C₄ plants have carbon isotopic compositions that are only ~ 4–7‰ lower than atmospheric CO₂, whereas C₃ plants are typically > 18‰ lower than atmospheric CO₂. Thus, the paleosol CO₂ barometer is ineffective in ecosystems with abundant C₄ vegetation (Figure 7B), and for this reason, the paleosol CO₂ barometer is essentially restricted to pre-Neogene time, when C₄ plants appear to have been uncommon.

Application of the paleosol CO₂ barometer to Phanerozoic soil carbonates suggests that CO₂ levels during the Mesozoic were generally much higher than today, with estimates of ~1,000 ppm

using the lower $S(z)$ value (2,500 ppm) preferred by Breecker et al. (2010), and possibly up to 3,000 ppm using higher $S(z)$ values (Ekart et al., 1999). Early Paleozoic CO₂ levels appear to have been similarly high, whereas late Paleozoic CO₂ levels were variable, and may have approached values similar to Recent during Carboniferous–Permian glacial intervals (Montañez et al., 2007).

Paleosol carbonates as recorders of plant $\delta^{13}\text{C}$.—Soils typically have far higher CO₂ concentrations than the atmosphere owing to continual production of biological CO₂, which sets up a net flux of CO₂ out of the soil. Thus, unless atmospheric CO₂ levels are very high ($\approx > 1000$ ppm) biological CO₂ dominates the isotopic composition of soil CO₂ for all but the lowest rates of biological CO₂ production (the soil respiration rate; Figure 6A). At present levels, atmospheric CO₂ dominates only in the shallow part of the soil, and when soil respiration rates are less than ~1 mmol/m²/hr. Such low respiration rates only occur in soils with very little vegetation, and most soils have sufficient vegetation and respiration rates that soil CO₂ (and pedogenic carbonate) below approximately 20–30 cm primarily reflects

the isotopic composition of the prevailing plant biomass (Figure 6B). For normal respiration rates and a known level of atmospheric CO₂ (and ideally a low level), the $\delta^{13}\text{C}$ value of pedogenic carbonate can be interpreted in terms of a mixing model between C₃ and C₄ vegetation (e.g., lines for 0 and 500 ppmV CO₂, Figure 7B).

Pedogenic carbonate in modern soils below depths of 20–30 cm is typically 14–17‰ enriched in ¹³C over coexisting plant biomass. This enrichment reflects many different factors, including the contribution of atmospheric CO₂ as described above, fractionation owing to diffusion of CO₂ from the soil, and equilibrium fractionation between carbonate mineral and dissolved inorganic carbon in soil waters, the magnitude of which is temperature dependent (e.g., Romanek et al., 1992).

Identification of paleosol carbonates in the field.—Identifying paleosol carbonates in the field and distinguishing them from non-paleosol carbonates often is not straightforward. Put differently, it can be very difficult to prove that a sedimentary carbonate is, in fact, primary pedogenic carbonate. Marine carbonates have $\delta^{13}\text{C}$ values near 0‰, similar to pedogenic carbonates forming in pure C₄ ecosystems, so the error in paleoecological interpretation can be profound when pedogenic carbonates are not properly identified. There is no single diagnostic criterion for pedogenic carbonate, but a suite of features, including association with other soil features such as weathering horizons, bioturbation, and ped structure (or conversely lack of association with non-soil features such as distinct sedimentary bedding), and shapes and textures such as clast coatings, filamentous wisps, and nodules can aid in identification. In addition, primary pedogenic carbonates are micritic, not sparry. Coatings often preferentially form on the undersides of large clasts in soils, and a consistent directionality of these coatings may indicate that the carbonates were not reworked from older deposits. Nodules often occur in discrete horizons, and have a popcorn-like appearance.

Combined records of $\delta^{13}\text{C}$ in tooth enamel and paleosol carbonate

Overall, the fractionation between plant carbon and soil carbonate is of similar magnitude and direction as the fractionation in mammals between tooth enamel and plant diet, so records of tooth enamel and soil carbonate are broadly comparable. However, there are some important dif-

ferences between pedogenic carbonate and tooth enamel that should be considered when making paleoenvironmental inferences. Two of the most important are discussed below.

1) Timescale of formation. Whereas teeth mineralize over periods of weeks to months, pedogenic carbonates may form over decades to millennia. Thus, the carbon isotopic compositions of teeth are essentially snapshots of an environment integrating over weeks to months, whereas those of pedogenic carbonates may reflect time-integrated averages over decades to millennia.

2) Representation of biomass. Mammalian herbivores are selective in their diets, and thus the carbon isotopic composition of tooth enamel does not reflect that of average ecosystem biomass, but rather that of the biomass the animal prefers to eat. Pedogenic carbonates are better integrators of the prevailing vegetation.

It is often useful to use both types of data together. Tooth enamel can reveal the full spectrum of vegetation available in the ecosystem, provided that multiple taxa with multiple dietary preferences are sampled, and soil carbonate reveals the dominant type of vegetation. Using both kinds of data from the Great Plains during the late Miocene, tooth enamel $\delta^{13}\text{C}$ values show that, at least at times, C₄ vegetation was available in enough quantity to comprise the majority of an animal's diet over several months (Passey et al., 2002), whereas soil carbonates show that C₄ vegetation was still a minor fraction of overall vegetation (Fox and Koch, 2003; Fox et al., 2012). Thus, the mammal data provide a glimpse into the early history of C₄ vegetation that would be largely invisible to the soil carbonate method, while the soil carbonate method gives an impression of the overall ecological importance of C₄ plants that would be difficult to infer from tooth enamel alone.

OXYGEN ISOTOPES

Oxygen isotopic variations in meteoric waters and plants

Meteoric water (rainfall, snow, and other atmosphere-sourced water) is the ultimate source of oxygen to pedogenic carbonates and mammalian body water, and its isotopic composition varies broadly with certain climatic and meteorological variables. The $\delta^{18}\text{O}$ value of meteoric water is the end result of a complex series of isotopic fractionation and mixing processes influencing water from the time that it enters the atmosphere

through evaporation or transpiration to the time that it falls back to the surface as precipitation. Dansgaard's (1964) classic paper clearly illustrated the temperature effect in meteoric waters, whereby the $\delta^{18}\text{O}$ value correlates strongly with mean annual temperature at the point where precipitation reaches the surface, and can be described by the relationship $\delta^{18}\text{O} = 0.695 \cdot \text{MAT} - 13.6\text{‰}$. Dansgaard (1964) developed a Rayleigh distillation model to explain this trend, and the model is widely accepted today as explaining the first-order variation in $\delta^{18}\text{O}$ of meteoric waters. This temperature effect sets up a meteoric water oxygen-isotope thermometer that, along with an analogous hydrogen isotope thermometer, continues to be the primary basis of paleothermometry using polar ice-core records.

However, in most temperate and tropical environments, the meteoric water oxygen isotope thermometer constitutes a somewhat poor paleotemperature proxy. Why is it a reasonably good paleothermometer in high latitudes, but a poor thermometer in temperate and tropical latitudes? The reason is that the excellent correlation between meteoric water $\delta^{18}\text{O}$ and MAT observed at high latitudes breaks down in temperate and tropical latitudes (Figure 8). The majority of $\delta^{18}\text{O}$ data in Dansgaard's original 1964 compilation were from locations with MAT less than 0°C , so Dansgaard's original equation (given above) is not really applicable to temperate and tropical environments. Since 1964, an enormous amount of meteoric water $\delta^{18}\text{O}$ data has been published, and many studies have examined the relationship between meteoric water $\delta^{18}\text{O}$ and different climatic variables. An analysis by Fricke and O'Neil (1999) shows that there is a clear correlation between temperature and $\delta^{18}\text{O}$ in the midlatitudes, but that there also is a fair amount of scatter about the trend, and summer and winter precipitation define separate and unique trends (Figure 8).

Fitting all meteoric water $\delta^{18}\text{O}$ data into a single temperature-effect model is unsatisfactory, and it turns out that there are many other effects, each of which in some way relates back to temperature, but not necessarily mean annual temperature at the point where precipitation reaches the surface. Three of these effects are:

1) Elevation effect. In many regions, there is a strong correlation between $\delta^{18}\text{O}$ and surface elevation such that $\delta^{18}\text{O}$ decreases as elevation increases. This effect is widely exploited by the tectonics/geomorphology community as a means of reconstructing paleoelevation, where the $\delta^{18}\text{O}$

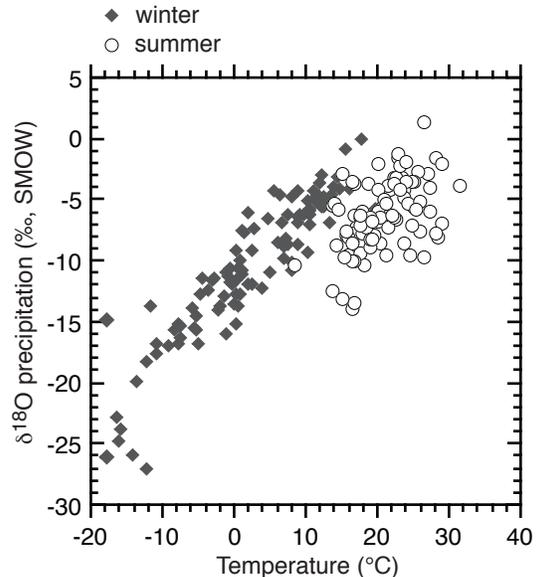


FIGURE 8.—Oxygen isotopic compositions of temperate latitude meteoric waters ($25^\circ - 60^\circ$ latitude), averaged for summer and winter seasons. Data are from IAEA/WMO (International Atomic Energy Agency/World Meteorological Organization), as compiled by Fricke and O'Neil, 1999.

value of ancient meteoric waters is recorded in the $\delta^{18}\text{O}$ compositions of paleosol carbonates, fossil teeth, shells, lacustrine carbonates, and other materials (e.g., Garzzone et al., 2000; Rowley and Currie, 2006; Bershaw et al., 2010; Quade et al., 2011).

2) Amount effect. In the tropics and in places where a monsoon climate dominates, there may be a negative correlation between $\delta^{18}\text{O}$ and the amount of precipitation (Dansgaard, 1964). Monsoon systems often have deep convective circulation, meaning that there is strong, vertical transport of moist air masses. Thus, in the simplest view, amount effects result from *in-situ* Rayleigh distillation of an ascending, and hence cooling, air mass. In actuality, the origins of amount effects may be more complex, as discussed below.

3) Seasonality effect. In many regions, the $\delta^{18}\text{O}$ value of precipitation varies seasonally (Figure 9). The effect is most pronounced in regions with a large seasonal range in temperature, where a positive correlation is usually observed between temperature and $\delta^{18}\text{O}$ of precipitation.

Other meteoric water $\delta^{18}\text{O}$ effects include a continentality effect ($\delta^{18}\text{O}$ generally is higher near the coasts and lower inland), and a storm trajectory effect. Meteoric water sourced from different regions can have different $\delta^{18}\text{O}$ values (e.g., Arc-

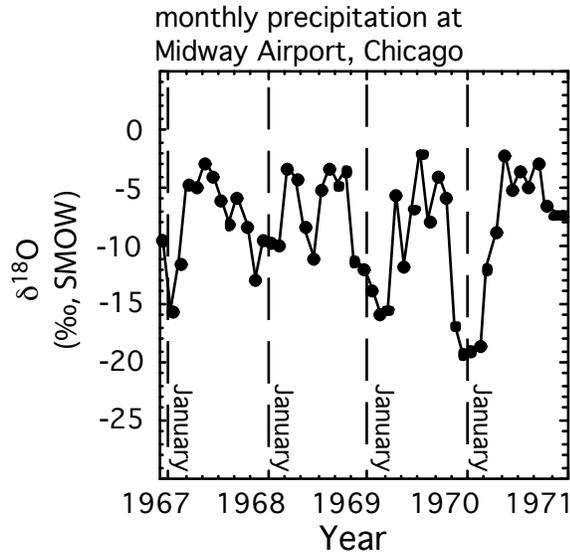


FIGURE 9.—Seasonal variation in oxygen isotopic composition of precipitation at Midway Airport, Chicago, from 1967–1970. Data are from the International Atomic Energy Association (<http://isohis.iaea.org>).

tic- versus Gulf of Mexico-sourced weather systems reaching the central United States). In addition, water vapor is depleted in ^{18}O relative to liquid water, so significant evaporation will leave residual waters (e.g., lake water, soil water, virga) enriched in ^{18}O compared to the original precipitation. Therefore, the paleoenvironmental significance of $\delta^{18}\text{O}$ is not limited to single variables, such as temperature or precipitation amount, and paleo $\delta^{18}\text{O}$ data must be interpreted accordingly.

One promising way forward is the use of isotope-enabled GCMs to aid in interpretation of paleo $\delta^{18}\text{O}$ data. For example, the study of Pausata et al. (2010) allows for a refined interpretation of East Asian speleothem $\delta^{18}\text{O}$ records beyond the conventional amount effect-based idea that higher $\delta^{18}\text{O}$ equals weaker summer monsoons. Using isotope-enabled GCMs, these workers suggest that increased $\delta^{18}\text{O}$ values seen in East Asian speleothems during Heinrich events are a result of weakened Indian summer monsoons, and this in turn is ultimately related to increased sea-ice extent in the North Atlantic. This kind of nuanced interpretation would be impossible without a GCM approach.

Oxygen isotope compositions of teeth

The oxygen isotope composition of meteoric water exerts the first-order control on the oxygen isotope composition of mammalian body water,

which determines the isotope composition of bioapatite. Other sources of oxygen to body water include atmospheric O_2 , oxygen bound in food, and free water in food. Major oxygen outputs from an animal include oxygen in urinary water, fecal water, sweat, and transcutaneous water vapor, as well as oxygen in exhaled CO_2 and water vapor. Several models have been developed for predicting body water $\delta^{18}\text{O}$ based on these and other oxygen inputs and outputs (e.g., Luz et al., 1984; Bryant and Froelich, 1995; Kohn 1996; Podlesak et al., 2007). Oxygen isotope data collected from modern mammals over the past ~25 years, interpreted in the context of such models, show that mammal species can be separated into two broad categories: those whose isotopic compositions faithfully track the isotopic composition of meteoric water, and those whose compositions deviate from meteoric water in response to environmental aridity (Ayliffe and Chivas, 1990; Luz et al., 1990; Kohn et al., 1996; Levin et al., 2006). The isotopic compositions of the former, termed ‘evaporation insensitive’ (EI) taxa by Levin et al. (2006), may show taxon-specific relationships to the isotopic composition of meteoric water, and taxon-specific equations have been developed describing these relationships (Tütken et al., 2006 give a summary of such equations).

The isotopic compositions of the latter, termed ‘evaporation sensitive’ (ES) by Levin et al. (2006), correlate with measures of aridity such as relative humidity (Ayliffe and Chivas, 1990) (Figure 10) and water deficit (= precipitation minus potential evapotranspiration; Levin et al., 2006) (Figure 11). The mechanism of an aridity oxygen-isotope effect lies in the evaporation of water, which leaves residual waters enriched in ^{18}O . The major source of evaporated water available to animals is leaf water, and both observations and theory show a strong correlation between $\delta^{18}\text{O}$ of leaf water and relative humidity (Roden and Ehleringer, 1999; Helliker and Ehleringer, 2001). Evaporated surface waters may also contribute to the ES effect in mammals. ES taxa tend to be those capable of surviving with little or no drinking water, deriving most or all water needs from their diet. In Africa, ES taxa identified by Levin et al. (2006) are exclusively ruminants, a group known for efficient water use, whereas EI taxa include ruminant and non-ruminant species, such as hippopotamus, buffalo, zebra, warthogs, and others that are more dependent on drinking water. Levin et al. (2006) also observed that the $\delta^{18}\text{O}$ values of ES taxa conform to a single relationship

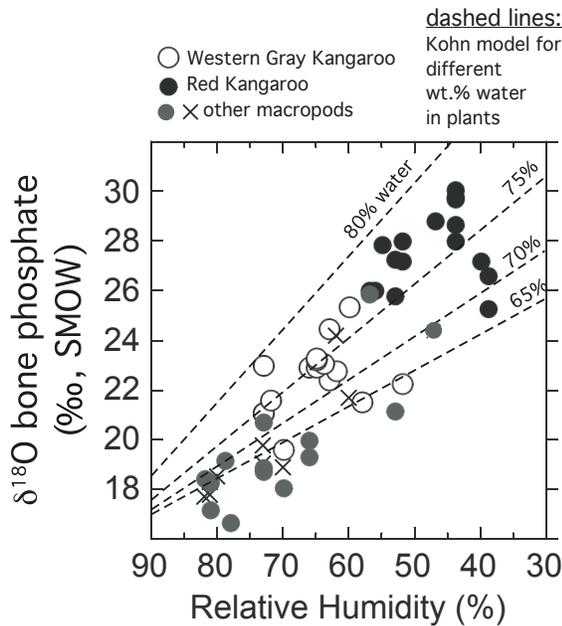


FIGURE 10.—Oxygen isotopic compositions of modern kangaroos plotted as a function of relative humidity. Data are from Ayliffe and Chivas, 1990. Dashed lines are modeled isotopic compositions using the model of Kohn (1996), solved for a range of free-water contents of leaves.

with water deficit, while EI taxa show species-specific offsets from the $\delta^{18}\text{O}$ of meteoric waters. They proposed an ‘aridity index’ scheme whereby paleoaridity can be inferred based on the isotopic separation between pairs of ES and EI taxa, with greater separation implying greater aridity. In effect, the use of such an approach corrects for potential secular variation in the $\delta^{18}\text{O}$ of meteoric waters, and makes it insensitive to factors such as the temperature effect or amount effect described above.

Oxygen isotopic compositions of pedogenic carbonates

Pedogenic carbonates are generally thought to precipitate in oxygen isotopic equilibrium with soil waters (Quade et al., 1989), therefore, the $\delta^{18}\text{O}$ value of the carbonate is a function of both the $\delta^{18}\text{O}$ value of soil water, and the soil temperature when the carbonate precipitated. This kind of temperature effect is very different from the meteoric water temperature effect discussed above (the ‘meteoric water oxygen-isotope thermometer’), and arises because the isotopic fractionation between carbonate and water is temperature dependent, with a sensitivity of about 0.2‰ per 1 °C (e.g., Kim and O’Neil, 1997). In order to use

pedogenic carbonates to estimate paleo-soil water $\delta^{18}\text{O}$, an independent estimate of temperature is needed. Carbonate clumped isotope thermometry (see below) is one means of providing this estimate, but prior to the advent of this method (or in the absence of clumped isotope data), it was common to use an assumed temperature, such as present-day mean annual temperature. In most soils, meteoric water is the source of soil water, and soil water may be enriched in ^{18}O relative to the original meteoric water due to evaporation. Thus, reconstructed soil water $\delta^{18}\text{O}$ puts an upper bound on meteoric water $\delta^{18}\text{O}$. In most circumstances, the temperature uncertainty leads to a 1–3‰ uncertainty in reconstructed soil water $\delta^{18}\text{O}$, and the evaporation effect is on the order of a few per mil or less for most soils, but higher values have been observed (e.g., Quade et al., 1989; Quade et al., 2011). A comprehensive compilation and evaluation of published data could help place much needed constraints on typical evaporation effects in soil carbonates and how these effects relate to climatic and ecological variables. Nevertheless, in many cases, these temperature- and evaporation-related uncertainties are relatively small compared to the regional climate signal in the $\delta^{18}\text{O}$ of meteoric water, and they have not prevented the widespread use of pedogenic carbonate $\delta^{18}\text{O}$ in reconstructing paleoclimate and paleo- evaporation.

CLUMPED ISOTOPES IN PEDOGENIC CARBONATES

Carbonate clumped isotope thermometry (Ghosh et al., 2006a; Affek, 2012) is a relatively new method that examines the enrichments of multiply substituted isotopologues beyond levels predicted by probability. As an example of enrichment beyond probability, consider that when rolling a die twice, the probability of getting two sixes in a row is $1/6 * 1/6 = 0.0278$. If, in numerous, repeated two-roll experiments, we find that we get the two sixes as a result significantly more than 2.78% of the time, we can conclude that the dice are weighted to give a preferred outcome of rolling a six. Isotopologues are similarly weighted: multiply substituted isotopologues are thermodynamically preferred over singly- and non-substituted isotopologues. For carbonates forming at Earth-surface temperatures, this preference is about 0.5‰ relative to the abundance predicted by probability theory. In addition, this preference increases with decreasing temperature, thus giv-

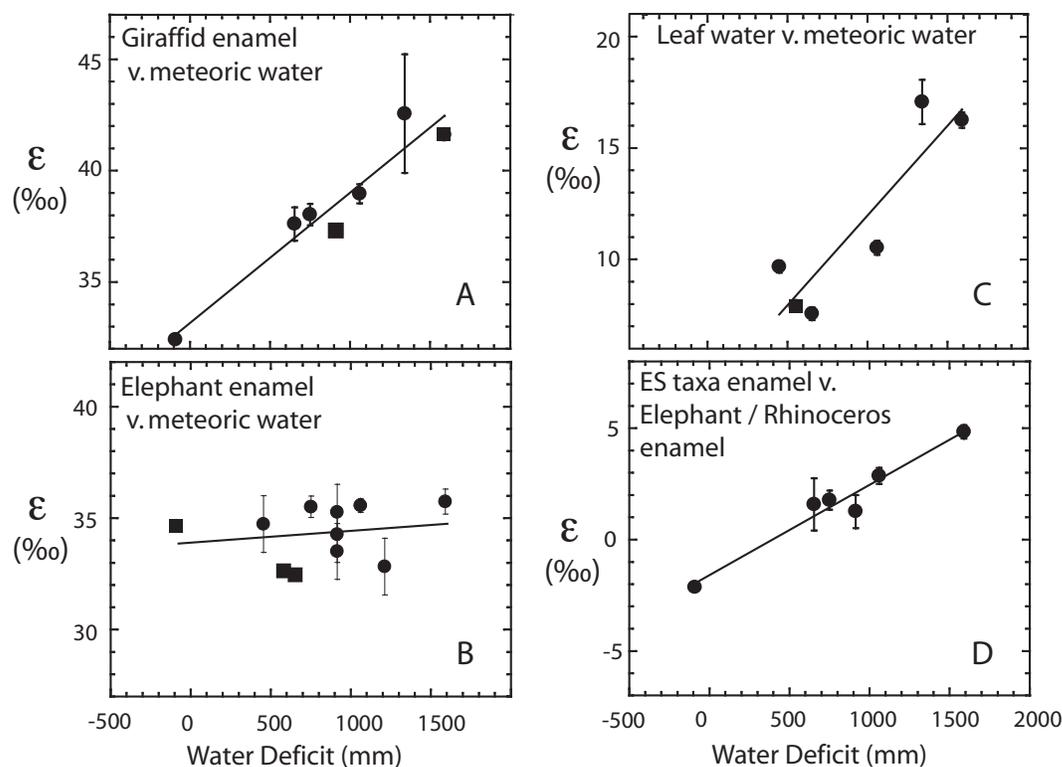


FIGURE 11.—Oxygen isotopic compositions of East African mammals in relation to water deficit (= mean annual precipitation minus potential evapotranspiration). A) Oxygen isotopic difference between giraffid tooth enamel and meteoric water. B) Oxygen isotopic difference between elephant tooth enamel and meteoric water. C) Modeled oxygen isotopic difference between leaf water and meteoric water using climate data from specific localities in East Africa. D) Oxygen isotopic difference between giraffe tooth enamel and elephant or rhinoceros tooth enamel. Data from Levin et al., 2006.

ing rise to the clumped isotope thermometer. Afek (this volume) provides a description of the theoretical basis of clumped isotope thermometry, as well as an explanation of the nomenclature specific to the method.

Most isotopic paleothermometers are under-constrained because they feature three interrelated variables: fluid isotopic composition, mineral isotopic composition, and temperature. Temperature determines the isotopic fractionation between the mineral and the fluid from which it precipitates. Thus, to determine paleotemperature, one must know the isotopic compositions of both mineral and the fluid. Minerals are preserved in the geological record, whereas fluids typically are not. An assumption must therefore be made about the isotopic composition of the fluid in order to calculate temperature. The clumped isotope thermometer, in contrast, is independent of the fluid isotopic composition. The mineral itself provides all of the information necessary to calculate temperature. In

the case of carbonate clumped isotope thermometry, the $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the carbonate are measured, allowing prediction of the stochastic (predicted by probability) abundance of mass 63 clumped carbonate ($\text{Ca}^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$, $\text{Ca}^{12}\text{C}^{17}\text{O}^{18}\text{O}^{16}\text{O}$). The actual abundance of mass 63 carbonate is measured and compared to the calculated stochastic abundance. The difference between these values is directly related to the temperature of mineralization (Schauble et al., 2006; Ghosh et al., 2006b).

Only a handful of papers have presented clumped isotope results for pedogenic carbonates (Ghosh et al., 2006b; Quade et al., 2007; Passey et al., 2010; Quade et al., 2011; Suarez et al., 2011), so the field is nascent and general patterns are still emerging (e.g., Peters et al., 2010; Quade et al., 2011; VanDeVelde et al., 2010). Several studies are nearing completion, with more publications expected within the next year.

Clumped isotope thermometry measures the

soil temperature at the time of carbonate mineralization, so it is important to first consider how soil temperatures relate to climate. The first-order factor to affect the soil temperature is air temperature. However, the key factor influencing soil temperature at depth is not the air temperature, but rather the temperature of the surface layer of the soil. Solar heating can elevate this temperature far above air temperatures (surface temperatures in excess of 60 °C are not uncommon for exposed soils under sunny conditions), so soil temperatures are commonly higher than air temperature. Thus, for example, soil temperatures in forested ecosystems are lower than soil temperatures in open ecosystems (Figure 12).

Soils have significant thermal inertia, so temporal variation in soil temperature at depth reflects a damped version of temporal variation at the surface. Some estimated figures for this damping are as follows. Diurnal temperature variations are typically damped to less than ~3 °C below about 20–30 cm depth. In temperate climates, soil temperatures at ~50–100 cm depth reflect seasonally averaged temperature. Annual temperature variations are damped to a few degrees or less below depths of a few meters. Time series of temperature variation over several months at a tropical site (Turkana Basin, Kenya) and a temperate site (Mojave Desert, California) show this effect (Figure 13). A host of variables influence temporal variation of temperature at depth, including the magnitude of temperature variation at the surface, the thermal conductivity and diffusivity of the soil, advection of heat owing to seepage of rainfall or natural barometric pumping of gas in and out of soils, and latent heat effects, such as evaporation of water or melting of snow and ice. The physics of soil temperature variation are well understood (e.g., Jury and Horton, 2004), as are the unique microclimates near the ground surface (e.g., Geiger et al., 2009). Thus, soil temperatures are predictable given information about climate and vegetation. Inasmuch as plants and most animals live in and near the ground, it can be argued that a proxy for ground temperature is just as relevant to terrestrial paleoclimate as a proxy for air temperature.

Based on the limited clumped isotope data from recent pedogenic carbonates, it appears that clumped isotope temperatures of pedogenic carbonates are similar to warm season temperatures in temperate climates, and are similar to mean annual temperature in tropical climates with little seasonality in air temperature (Figure 14). The

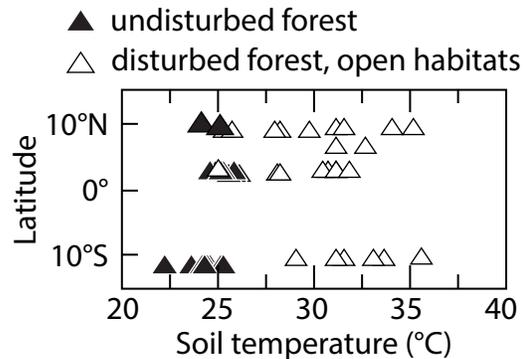


FIGURE 12.—Soil temperatures below primary forest (filled triangles) and below disturbed forest and open ecosystems (open triangles). All data are from latitudes between 12°S and 12°N, and were compiled from primary literature references given in Passey et al., 2010.

implication for temperate climates is that pedogenic carbonates form primarily during the warm season, and this warm-season bias has been suggested for pedogenic carbonates forming in the arid southwestern United States, based on independent lines of evidence (Breecker et al., 2009). The author is aware of three additional (currently unpublished) clumped isotope datasets, two of which appear to show a warm season bias, and another with temperatures closer to mean annual temperature. Thus, over the next few years, understanding of the relationship between carbonate clumped isotope compositions of pedogenic carbonates and climate should increase considerably.

Clumped isotope thermometry also allows for reconstruction of the $\delta^{18}\text{O}$ of paleo-soil waters because it provides both carbonate $\delta^{18}\text{O}$ and temperature, two of the three variables in the carbonate-water oxygen isotope paleothermometer. Ghosh et al. (2006b) used estimates of paleo-soil water $\delta^{18}\text{O}$ in conjunction with clumped isotope temperatures to place constraints on the timing of uplift of the Bolivian Altiplano. Suarez et al. (2011) used clumped isotope thermometry primarily as a means of reconstructing $\delta^{18}\text{O}$ of soil water for late Miocene and Pliocene pedogenic carbonates from northern China. They found that carbonates had clumped isotope temperatures consistent with mineralization primarily during the warm season, and thus treated the reconstructed soil water $\delta^{18}\text{O}$ values as a proxy for the $\delta^{18}\text{O}$ of ancient summer monsoon precipitation. The paleo-monsoon $\delta^{18}\text{O}$ values were indistinguishable from modern monsoon $\delta^{18}\text{O}$ values, a

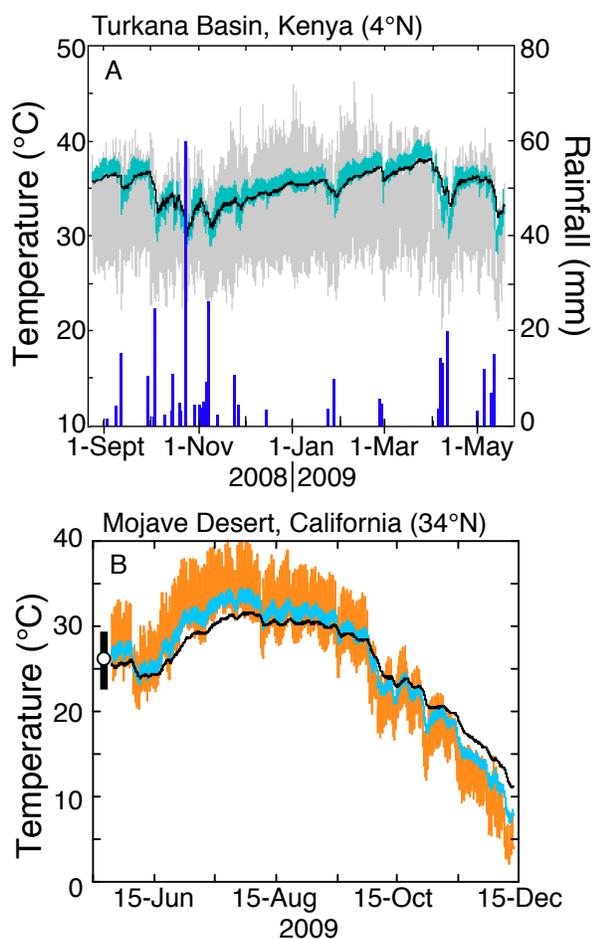


FIGURE 13.—Soil temperatures in arid, open environments. A) Nine-month temperature record from Ileret, Turkana Basin, northern Kenya. Light gray field is air temperature, turquoise is soil temperature 26 cm below the surface, and black is soil temperature 50 cm below the surface. Blue bars show rainfall amounts. B) Seven-month temperature record from the Blackhawk Slide, Lucerne Valley, California. Orange field is soil temperature 15 cm below the surface, turquoise is 30 cm below the surface, and black is 50 cm below the surface. Circle and error bar on right hand side show the carbonate clumped isotope temperature mean and standard deviation of soil carbonates collected nearby. After Passey et al., 2010.

finding that is consistent with similar-to-present monsoon dynamics extending back to the late Miocene.

Preservation of original clumped isotope signatures

For the carbonate clumped isotope thermometer, temperature information is contained not in

the bulk isotopic composition of the mineral, but in the preferential clumping of ^{13}C and ^{18}O into bonds with each other. While this feature lends the method great promise for solving long-standing questions in paleoclimate, the same feature also leads to an inconvenient truth about preservation of the original isotopic signal: it is far easier, chemically and kinetically, for the abundances of ^{13}C - ^{18}O bonds to be altered during burial than it is for the bulk carbon- or oxygen-isotopic composition to be altered. The abundances of ^{13}C - ^{18}O bonds can be altered by simple burial heating of the mineral, which causes carbon and oxygen atoms to migrate through the mineral lattice through a process called solid-state diffusion. Additionally, recrystallization of carbonates via solution precipitation under closed-system conditions (i.e., without mass exchange between the mineral and surrounding fluids) will not change the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the carbonate, but it will reset ^{13}C - ^{18}O clumping to a level reflecting the temperature of recrystallization. Thus, gauging preservation state is a critical aspect of the use of the carbonate clumped isotope thermometer.

Analyses of carbonatites (igneous carbonate rocks) and marbles (metamorphosed carbonates) show that these materials can retain their original high-temperature signals over geological time, demonstrating that long-term preservation of clumped isotope signals is possible (Dennis and Schrag, 2010; Schmidt and Bernasconi, 2010). Paleosol carbonates buried up to ~1 km (Passey et al., 2010) and 4–5 km (Eiler et al., 2006) show no clear increase in clumped isotope temperature with depth (i.e., they do not track geothermal gradients), a pattern consistent with preservation of original clumping signals. Additional, new datasets and experimental work will help to refine estimates of upper temperature limits and burial depths for clumped isotope preservation. Based on what the author has seen in these yet-to-be published datasets, these values will be close to ~100 °C and 3 km for many situations. In addition, most well-preserved hand specimens of paleosol carbonate contain discrete veins and pockets of secondary carbonate, the clumped isotopic compositions of which will reflect their temperatures of mineralization. Thus, these secondary carbonates must be avoided during sampling. Huntington et al. (2011) show how petrography and cathodoluminescence can be used to distinguish primary from secondary carbonates, and illustrate how different generations of secondary

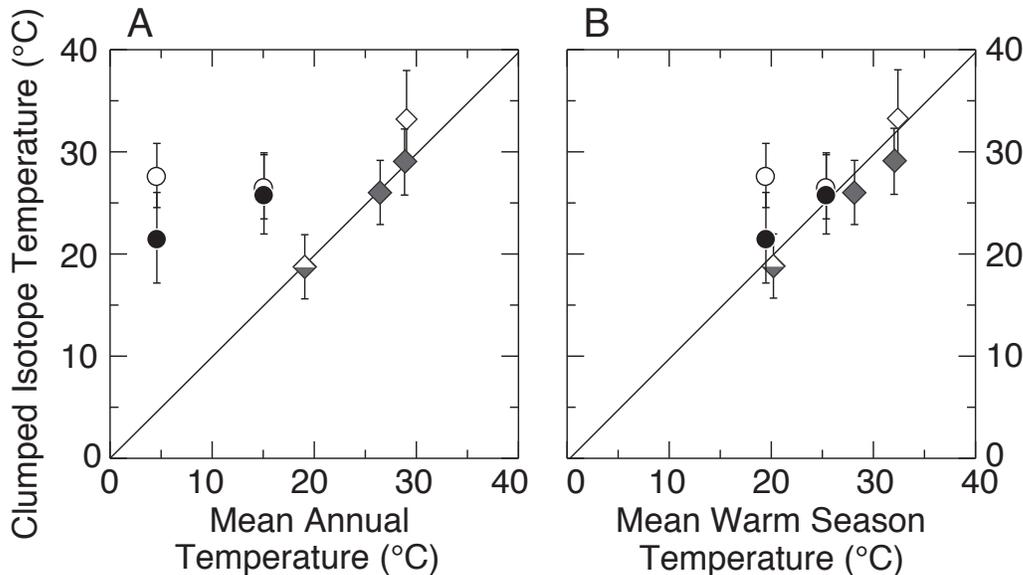


FIGURE 14.—Carbonate clumped isotope temperatures of recent soil carbonates. A) Plotted versus mean annual temperature. Circles are samples from temperate latitudes, diamonds are samples from tropical latitudes. Filled symbols represent samples collected from 40 cm or deeper below the surface, open circles are shallower samples, and mixed symbols are samples with undocumented depths. B). Same data, but plotted versus mean warm season temperature (= mean temperature of the three warmest consecutive months). After Passey et al., 2010.

carbonate can be used to reveal the thermal histories of rock units. See Grossman (2012) for an extensive discussion of screening techniques to recognize diagenetically altered carbonate.

CONCLUDING REMARKS

As a way of concluding this paper, I will comment on the strengths and weaknesses of the different methods discussed above, discuss aspects that need to be developed, and touch on best uses of the methods and exciting future prospects. I will take a somewhat unconventional (and perhaps risky) approach, and rank different aspects of each method using the US National Science Foundation merit-review scale of ‘excellent, very good, good, fair, poor.’ These rankings and comments, of course, will be based on my own perspectives and experiences, and other workers will probably have different assessments. My hope is to encourage realistic discussion of how good the different methods are, and what can and cannot be determined using them.

The aspects to be ranked are: ‘simplicity,’ ‘value,’ ‘preservation potential, and ‘applicability.’ Simplicity is a measure of how straightforward and robust the link is between the isotopic data and some real aspect of past climates or envi-

ronments. As an example, a radiometric age of a mineral has ‘excellent’ simplicity—there is no ambiguity in the meaning or significance of, for example, a 10.5 million year age-date of a mineral. Provided the geochronology was done correctly and the mineral cooled quickly, it simply means that the mineral is 10.5 million years old. On the other hand, the oxygen isotopic composition of pedogenic carbonate has a much lower simplicity ranking. What is the meaning of, for example, a -10.6‰ $\delta^{18}\text{O}$ value of a pedogenic carbonate? To what extent does this isotopic composition reflect soil temperature, evaporation of soil water, seasonality of precipitation, and changes in prevailing moisture tracks? There is no straightforward, simple interpretation of isolated $\delta^{18}\text{O}$ values of pedogenic carbonates, and such data require a broad context for meaningful interpretation. If you cannot explain the significance of the data you are using to your parents or undergraduate students, it probably does not have a high simplicity ranking!

‘Value’ is a measure, not surprisingly, of the value of a paleo-measurement. A radiometric age has great value, as does an absolute temperature measurement. The carbon isotopic composition of an ancient herbivore’s diet could be argued to have lower value in terms of paleoenvironmental

interpretation – the animal could be selectively feeding on a plant type not representative of the dominant vegetation, and even if the diet is representative of vegetation, how does vegetation relate to climate? However, if the goal is reconstruction of feeding ecology of extinct species, then the carbon isotopic composition of an herbivore's diet has great value.

'Preservation potential' is straightforward. How robust is the mineral and isotopic system against diagenesis? 'Applicability' refers to how widely in space and time the method can be used. Fossil teeth are surprisingly common in terrestrial sediments, and so fossil-tooth-based methods have very good applicability (and they would have greater applicability if thick tooth enamel were more common in Mesozoic reptiles). Bone, even more common than tooth enamel, has 'excellent' applicability, but unfortunately, it has poor preservation potential. An example from the marine realm is the alkenone unsaturation index (U_{37}^K) paleotemperature method: it has excellent applicability because of the near ubiquity of alkenones in marine sediments. The mammal oxygen isotope aridity-index approach discussed earlier has lower applicability, because it requires sampling of multiple individuals of multiple taxa that lived at the same time. Only the best fossil localities permit this kind of analysis, and these are essentially restricted to the Cenozoic, when mammals were common.

Carbon isotopes in fossil tooth enamel

Simplicity: Excellent. 'You are what you eat' works very well. There is some variation (and for some taxa, ambiguity) in the carbon isotopic fractionation between diet and tooth enamel, but often this is minor compared the full isotopic range of possible diets. With very little equivocation, the carbon isotopic composition of tooth enamel reflects the carbon isotopic composition of diet and little else.

Value: Good (for purposes of paleoenvironmental reconstruction); Excellent (for studying dietary ecology of extinct mammal species). For paleoenvironmental reconstruction, the method is most valuable when many taxa are analyzed, potentially overcoming artifacts related to narrow dietary preferences of some individual species. Value is enhanced because of the strong theoretical and observational basis of how plant carbon isotopic compositions relate to conditions during photosynthesis (e.g., Farquhar et al., 1989; Diefendorf et al., 2010), and how C_3 and C_4 plant

distributions relate to climate variables such as growing season temperature, and physical variables such as elevation.

Preservation Potential: Excellent. Having analyzed the carbon isotopic compositions of many hundreds of fossil tooth-enamel samples, the author cannot recall an instance when carbon isotopes were clearly altered (that is, when the carbon isotopic composition made absolutely no sense in the framework of C_3 and C_4 vegetation). This, of course, is predicated upon sampling only well-preserved portions of enamel samples. If a tooth enamel sample is intact and has the surface texture of pristine tooth enamel, it probably preserves the original carbon isotopic composition.

Applicability: Very good. Fossil teeth are common in fluvial sedimentary systems. The teeth need not be complete—small fragments will do.

Future directions: Despite the maturity of this method and its wide application, there is still much work to be done. Sampling is heavily biased towards the Neogene, for which it is now becoming possible to use an 'isoscares' approach (i.e., mapping out the spatial evolution of carbon isotopic compositions through time; Bowen, 2010). Much work needs to be done to fill out the Paleogene record, and to extend the method more fully to early mammals and Mesozoic reptiles. Rodents and other small mammals have received very little attention compared to large mammals despite the fact that they comprise the majority of mammalian species diversity. Advances in technology, including laser-ablation-based methods (Sharp and Cerling, 1995; Passey and Cerling, 2006), have made analysis of small mammal teeth a routine matter in properly equipped laboratories. Small mammal datasets are coming together, and much more will be learned about the paleoecology of these animals over the next few years.

Carbon isotopes in paleosol carbonates

Simplicity: Good. Compared to tooth enamel carbon isotopes, there are many more factors that control the carbon isotopic composition of pedogenic carbonate. If pedogenic carbonates form at depth (>50 cm) in soils that are highly productive and are leached of parent material carbonate, and atmospheric CO_2 levels are low, then their carbon isotopic compositions will mainly reflect those of prevailing vegetation. When using paleosol carbonates as a CO_2 barometer, assumptions have to be made about the production rate of respired CO_2 , the isotopic composition of atmospheric CO_2 , the isotopic composition of prevailing vege-

tation, and other parameters.

Value: Good (for purposes of paleoenvironmental reconstruction); Excellent (for reconstructing past levels of CO₂). For paleoenvironmental reconstruction, the value of the method is similar to that discussed above for carbon isotopes in teeth, but with the added advantage that soil carbonates may represent the prevailing vegetation more faithfully than tooth enamel. Constraining past levels of CO₂ is a key goal of paleoclimate research, so the method has high value despite its attendant uncertainties.

Preservation Potential: Excellent. Paleosol carbonates preserve carbon isotope signals that would be impossible to explain as artifacts of diagenesis, or that would not be observed if diagenesis were widespread. Examples include the PETM carbon isotope excursion recorded at many localities on different continents, and the expansion of C₄ vegetation in the late Neogene that is recorded in soil carbonates on many continents. The carbon isotopic compositions of Mesozoic and even Paleozoic paleosol carbonates appear to be reasonable in the context of the soil CO₂ diffusion model, and offsets between coexisting soil organic matter and paleosol carbonate are similar to values expected for C₃-dominated ecosystems (e.g., Ekart et al., 1999).

Applicability: Good. Paleosol carbonates are not uncommon, but many paleosols are devoid of pedogenic carbonate. Pedogenic carbonate tends to form in environments with less than about 1500 mm of precipitation per year, and especially in environments with seasonal dryness. So any method based on pedogenic carbonates is inherently biased to such conditions. While this may seem limiting, it should be noted that a wide range of climates and habitats can be found within the <1500 mm seasonal-dryness constraint, including Mediterranean climates, tropical savannas, temperate grasslands, and deserts.

Future Directions: The bias towards recent time is not as severe for paleosol carbonate carbon isotopes as it is for tooth enamel carbon isotopes, partly because of use of the method during Mesozoic and Paleozoic time as a CO₂ barometer, and of interest in the PETM event. Continued application of this method and an effort to assemble published data into a database could result in a terrestrial isotopic reference curve analogous to reference curves based on carbon and oxygen isotopes in marine carbonates (e.g., Veizer et al., 1999; Zachos et al., 2001).

Oxygen isotopes in fossil tooth enamel

Simplicity: Good (as a method of reconstructing meteoric water isotope compositions), Very Good (as an aridity index). There are many factors that influence the oxygen isotopic compositions of mammals relative to meteoric waters, including evaporation of water before it is consumed by the animal, dietary preference, water-use efficiency, and whether an animal pants or sweats. Despite this, the variety of taxon-specific equations do a reasonably good job at relating mammalian $\delta^{18}\text{O}$ to meteoric water $\delta^{18}\text{O}$, but it may be difficult to determine which equation to use for extinct animal species. As an aridity index, most of these variables are factored out. The method is based on the simple and well-understood process of enrichment in ^{18}O of waters that have experienced significant evaporation, which increases with decreasing relative humidity. A weakness of the method is that it relies on the existence of a dichotomy between animals that mainly consume evaporated water (most likely as leaf water) and animals that consume unevaporated surface waters, and coexistence of both kinds of animals in the same environment. How far into the past does this dichotomy in water use strategy extend?

Value: Fair/Good (as a method for reconstructing climate); Very Good (as an aridity index). Even if one can reconstruct meteoric water $\delta^{18}\text{O}$ values perfectly based on mammalian tooth enamel $\delta^{18}\text{O}$, what then do we do with this knowledge? Does an increase $\delta^{18}\text{O}$ values through time reflect increasing temperature, increasing aridity, a switch in predominant rainy season from winter to summer, or a change in prevailing storm trajectory and, therefore, moisture source? Much context is necessary for meaningful interpretation of mammalian $\delta^{18}\text{O}$ data. Aridity, on the other hand, is a straightforward aspect of climate. The aridity index has large error margins and is probably best used for gauging relative changes in aridity through time.

Preservation Potential: Very Good. Both the carbonate and phosphate components of tooth enamel are resistant to diagenesis. In many cases, there is clearly some diagenesis and alteration of isotopic compositions, as evidenced by changes in oxygen isotope spacing between the carbonate and phosphate components of tooth enamel (e.g., Tütken et al., 2006; Eagle et al., 2011). Despite this, patterns are often observed that suggest preservation of most of the original signal, including

taxonomic patterning, intra-tooth variability, and secular trends through time. For example, Secord et al. (2010, 2012) show that the carbonate and phosphate components of tooth enamel both show a similar transient increase during the PETM event in Wyoming.

Applicability: Very Good (for meteoric water reconstruction); Good (for the aridity index). As discussed above, teeth are fairly common in the geological record. Only very rich fossil localities yield sufficient numbers of species and individuals of each species for meaningful application of the aridity index approach.

Future Directions: The aridity index approach has not yet been extensively applied to the fossil record, but preliminary (mostly unpublished) results look promising, and a small dataset from the PETM interval in Wyoming (Secord et al., 2012), along with the unpublished data from the author's lab from the early Eocene of Wyoming, indicate that there are distinct taxonomic differences in $\delta^{18}\text{O}$ between coexisting taxa, suggesting the existence of differing water use strategies. The best modern calibration of the aridity index is from East Africa (Levin et al., 2006), and it will be important to evaluate the method in temperate-latitude settings. I suspect that most of the necessary data have already been published, and simply need to be compiled and interpreted in terms of an aridity index.

Clumped isotopes and oxygen isotopes in paleosol carbonates

Simplicity: Excellent (as a means of reconstructing soil temperature); Very Good (as a means of reconstructing soil water $\delta^{18}\text{O}$ as a proxy for meteoric water $\delta^{18}\text{O}$). The carbonate clumped isotope thermometer gives a direct measurement of soil temperature at the time of carbonate mineralization. If the system works as we currently understand, and is free of kinetic effects of the kind that appear to influence clumped isotopic compositions of speleothems (Affek et al., 2008), then the clumped isotope composition of a pedogenic carbonate should be determined strictly by temperature. The method also should provide a direct determination of the $\delta^{18}\text{O}$ value of soil water at the time of mineralization, but relating this value to the $\delta^{18}\text{O}$ of meteoric water requires an assumption about the extent of evaporation of soil water.

Value: Very Good (temperature aspect); Good (meteoric water $\delta^{18}\text{O}$ aspect). With this method, the long-sought goal of determining past tempera-

ture using a method firmly based in physics has been realized. But what do we do with this soil temperature, especially if it is seasonal maximum soil temperature? A challenge moving forward with this method is understanding how soil temperature relates to other climatic variables, and how it influences the ecosystem ecology. If this is to be one of the best available ways of reconstructing past temperature on land, we need to learn to think about terrestrial climate in terms of soil temperature. The value of the meteoric water aspect is essentially the same as that described above in the tooth-enamel oxygen-isotope section. The simplicity is better than for tooth enamel, and certainly much better than stand-alone measurements of $\delta^{18}\text{O}$ of carbonate (that is, $\delta^{18}\text{O}$ values without accompanying clumped isotope temperatures), but the relation of meteoric water $\delta^{18}\text{O}$ to climate is no more straightforward.

Preservation Potential: Fair/Good (?). Of all the methods discussed here, clumped isotopes are the most susceptible to alteration for the simple reason that any recrystallization will lead to breaking and reforming of C-O bonds, which leads to possible changes in relative ^{13}C - ^{18}O bond abundances. This contrasts with carbon and oxygen isotopes for which alteration occurs only when there is mass exchange of carbon and oxygen atoms between minerals and surrounding fluids. That said, clumped-isotope data from Neogene strata (Ghosh et al., 2006a; Passey et al., 2010) yield reasonable temperatures, and as-yet unpublished data from the Paleocene and Eocene of Wyoming and Utah also suggest good preservation, provided that secondary carbonates are avoided during sampling. In a few years, we should have a much better understanding of the preservation potential for paleosol carbonate clumped isotopes. Can the method be applied to Mesozoic and Paleozoic paleosol carbonates? Is it applicable only to the most shallowly buried samples? Time will tell.

Applicability: Good. The same considerations discussed under the "carbon isotopes in paleosol carbonates" section above apply here. Technically, the analysis is far more demanding than carbon for oxygen isotope analysis. There are only a handful of laboratories that are equipped to make the measurements, and even when properly equipped, it is challenging to produce quality data. Whereas most labs can analyze 30–50 carbonate samples per day for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, a good day in the author's clumped-isotope lab is only five or six analyses. It is unlikely that technical

improvements will increase sample throughput, since the precision is limited by shot-noise statistics, and acceptable levels of precision can only be achieved through long ion-beam counting/integration times or through analysis of very large samples, which has already been pushed to the limit using available mass spectrometers.

Future Directions: The pedogenic carbonate clumped-isotope method needs to see more characterizations of modern pedogenic carbonates. Do all soil carbonates record maximum warm season temperature, or are there instances where carbonates form during other times of the year? As discussed above, another important task is to define the temperature/burial-depth limits for good preservation. A productive strategy for addressing this question will be a combination of carefully controlled laboratory heating experiments and well-constrained natural experiments; for example, revealing how clumped isotope compositions vary as a function of maximum burial depth. A few such studies are under way or soon-to-be published. In general, more data from more contexts, both modern and fossil, are needed. Only with accumulated data will patterns emerge that might help distinguish primary and altered signals, and geological settings that are likely (or unlikely) to yield samples with good preservation. Provided sufficient well-preserved samples exist, an exciting goal is the construction of data-rich soil-temperature reference curves spanning large periods of time, such as a Cenozoic reference curve analogous to the benthic foraminifera $\delta^{18}\text{O}$ curve (e.g., Zachos et al., 2001). Given latitudinal variation in temperature, more than one curve could be constructed, such as a tropical/sub-tropical curve and a temperate curve. What would such curves look like? Will they be coherent and show clear changes through time, or scattered and inconclusive? Will patterns of biotic evolution mirror changes in temperature? There is only one way to find out!

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