ISOTOPIC RECONSTRUCTION OF PAST CONTINENTAL ENVIRONMENTS

Paul L. Koch

Department of Earth Sciences, University of California, Santa Cruz, California 95064;
email: pkoch@earthsci.ucsc.edu

ABSTRACT

Vertebrate fossils and continental sediments provide a rich record of variations in the isotopic composition of surface environments. To interpret these records, a greater understanding of isotopic sources, as well as fractionations associated with animal physiology, soil geochemistry, and diagenesis, has been essential. Tooth enamel and fish otoliths yield subannual records of surface environments, whereas soil minerals may integrate signals over many thousands of years. Carbon isotope variations in fossil vertebrates and soils record changes in the structure of vegetation and the isotope composition and concentration of atmospheric CO_2. Oxygen isotope variations may be indirectly related to climate, through reconstruction of the oxygen isotope composition of meteoric water, or directly related to temperature, through application of oxygen isotope paleothermometry to soil minerals or otoliths. In Africa, nitrogen isotope variations show promise as a proxy for rainfall abundance, though the generality of this association elsewhere has not been demonstrated.

INTRODUCTION

Natural variations in stable isotope ratios have become indispensable tools in fields as diverse as geochemistry, hydrology, ecology, and anthropology. The application of stable isotopes to paleoceanography and marine paleoclimatology has been spectacularly successful, revealing both long-term trends in marine climate and the response of the oceans to short-term orbital forcing and sudden

573

events (Imbrie et al 1984, Zachos et al 1993). Isotopic reconstruction of conditions on land is more difficult, however, because land ecosystems and climates exhibit greater spatial and temporal heterogeneity and the isotope systems applied in these settings are more complex. Even so, over the past decade, there has been a surge in studies of continental paleoclimates and paleoenvironments, spurred by the need to examine the response of land ecosystems to past climate change (Swart et al 1993).

I examine methods to reconstruct continental climates and environments that rely on the isotopic chemistry of fossil vertebrates and the authigenic minerals and organic matter associated with fossils in paleosols. There are three reasons for this focus. First, vertebrate localities are often well dated, placing isotopic records from these sites in a firm chronology. Second, biogenic materials integrate environmental isotope signals over a short period of time (months to decades), depending on the organism's life span and the rate of tissue turnover. Isotopic signals in pedogenic minerals and organic matter are integrated over greater intervals, though resolution of 10^2 to 10^4 years may be possible at sites with high depositional rates. Last, to understand the influence, or lack of influence, of changes in the physical environment on land biota, we need records of local environmental change. No records of environmental change are more closely tied to the biota than those extracted from the skeletons of dead animals or the soils that surround them.

Stable isotopes are useful as tracers because, as a result of mass differences, different isotopes of an element [^{1}H vs ^{2}H (or D), ^{12}C vs ^{13}C, ^{14}N vs ^{15}N, ^{16}O vs ^{18}O] have different thermodynamic and kinetic properties (Urey 1947). For elements with an atomic mass <40, these differences can lead to measurable isotopic partitioning between substances during physical and chemical processes (i.e. fractionation) that labels the substances with distinct isotope ratios. Natural fractionations are small, so isotopic abundances are reported as parts per thousand (‰) deviation in isotope ratio from a standard, using the δ notation, where $\delta X = [(R_{sample}/R_{standard}) - 1] \times 10^3$. R_{sample} and $R_{standard}$ are the high-mass to low-mass isotope ratios of the sample and the standard, respectively. Commonly used standards for ^{13}C/^{12}C, ^{15}N/^{14}N, and ^{18}O/^{16}O ratios are a marine carbonate, the Peedee belemnite (PDB), atmospheric nitrogen, and standard mean ocean water (SMOW), respectively (PDB is often used as an oxygen isotope standard for marine carbonate in paleoceanographic research; I report soil carbonate values relative to SMOW and PDB). Positive δ values indicate an enrichment in the high-mass isotope relative to the standard; negative values indicate depletion. Isotopic fractionations between two substances, a and b, are described using either a difference value (Δ), where $\Delta X_{a-b} = \delta X_a - \delta X_b$, or a fractionation factor (α), where $\alpha_{a-b} = (\delta X_a + 1000)/(\delta X_b + 1000)$.

The two measures of fractionation are related, as $1000 \ln\alpha_{a\text{-}b} \approx \Delta X_{a\text{-}b}$ (O'Neil 1986a, Hoefs 1997).

Two broad classes of phenomena produce isotopic fractionation: equilibrium exchange reactions and kinetic processes. Isotopic equilibrium may occur during the exchange of isotopes among substances by bidirectional chemical reactions. The partitioning of isotopes among substances is a function of differences in bond strength for the isotopic species in each substance, which are related to thermodynamic properties (O'Neil 1986b). The magnitude of equilibrium isotope fractionation is often sensitive to temperature, serving as the basis for isotope thermometry (O'Neil 1986b). Isotopic equilibrium may be attained in some of the simpler reactions discussed below, such as the precipitation of biological or pedogenic minerals from solution. At isotopic equilibrium near earth surface temperatures, most of these systems predict that minerals (a) will be enriched in the high-mass isotope relative to the solutions (b) from which they precipitate (i.e. $\alpha_{a\text{-}b} > 1$, $\Delta X_{a\text{-}b}$ is positive).

Kinetic isotope effects occur during transport processes and in either incomplete or branching unidirectional chemical reactions. Their magnitude is a function of differences in rates of diffusion or reaction for different isotopic species (O'Neil 1986b, Hoefs 1997). Kinetic isotope effects are important in the more complex biochemical processes discussed below, as well as in the diffusion of gases. In general, low-mass isotopic species react and diffuse more rapidly, leading to their enrichment in the products of processes (i.e. $\alpha_{a\text{-}b} < 1$, $\Delta X_{a\text{-}b}$ is negative).

Variations in carbon and oxygen isotope ratios form the core of this review. Carbon isotope variations in continental settings primarily reflect isotopic variations in land plants, but in recent years, carbon isotopes have been used to link events between land and sea, to reconstruct the partial pressure of CO_2 in the atmosphere (P_{CO_2}), and to study changes in floral composition and structure. Continental oxygen isotope records have been used to reconstruct surface temperature, as well as the $\delta^{18}O$ of meteoric water (rain and snow), which is itself sensitive to temperature and vapor transport. In evaluating these systems, materials with the potential to shed light on pre-Quaternary climates and environments are emphasized, though I discuss organic substrates, such as proteins, that are abundant only in the Quaternary. Finally, I briefly consider nitrogen isotopes ($^{15}N/^{14}N$) and the paleoenvironmental information they provide. Hydrogen isotope variations in cellulose and clay minerals have been used extensively in studies of the composition of ancient meteoric water (Yapp & Epstein 1977, Lawrence & Rashkes Meux 1993). As the oxygen and hydrogen isotope systems provide broadly similar information, I do not treat hydrogen isotopes here.

SOURCES OF THE RECORD

Fossil Vertebrates

Vertebrates have various calcified tissues with organic matrices that may survive in the fossil record, including endoskeletons of calcium phosphate (bones and teeth), calcium carbonate eggshells of birds and reptiles, and calcium deposits used in balance and hearing (otoliths). Isotopic records have been retrieved from biominerals from all these tissues. While proteins in bone, dentin, and eggshell have been the main substrates for organic isotope analysis, there is growing interest in individual amino acids and lipids (Stott & Evershed 1996, Fogel et al 1997).

The mineral in bone, tooth enamel, and tooth dentin is a form of hydroxylapatite ($Ca_{10}[PO_4,CO_3]_6[OH,CO_3]_2$). Bone is composed of tiny apatite crystals ($\sim100 \times 20 \times 4$ nm) intergrown with an organic matrix (chiefly composed of the protein collagen) that comprises $\sim30\%$ of its dry weight (Simkiss & Wilbur 1989). Enamel is much less porous than bone. It contains <5 wt% organic matter (chiefly non-collagenous proteins), and it has much larger crystals ($\sim1000 \times 130 \times 30$ nm) with fewer defects and substitutions (LeGeros 1981). The crystal size, organic content, and organic composition of tooth dentin resemble that of bone, whereas its porosity is intermediate between enamel and bone (Lowenstam & Weiner 1989).

Following initial deposition, bone is remodeled in the living organism by dissolution and reprecipitation (Lowenstam & Weiner 1989, Simkiss & Wilbur 1989). Remodeling is most active in mammals and birds, but it occurs to some extent in all vertebrates (Reid 1987). In contrast, enamel forms by accretion without remodeling, and mineralization is complete prior to tooth eruption. Like enamel, dentin grows by accretion with little remodeling (Lowenstam & Weiner 1989). Thus dentin and enamel in different teeth form at different times in an animal's life. Both tissues exhibit incremental laminations at a variety of temporal scales, from daily to annual (Carlson 1990), and sequential analysis of growth increments provide a time series of changes in body chemistry (Koch et al 1989). A caveat that must be recognized when studying teeth is that, except for groups with ever-growing teeth (e.g. elephants, rodents) or continuous tooth replacement (e.g. fish, amphibians, reptiles), mineralization takes place early in the animal's life.

Bird and crocodile eggshells are composed of tiny crystals secreted around a honeycomb of fibrous organic sheets. The crystalline portion of shells is almost entirely calcite. In bird eggs, mineral occurs in three distinct layers, covered externally by cuticle and anchored internally to a shell membrane (Simkiss & Wilbur 1989). The organic matrix comprises $\sim3\%$ of the mass of bird eggshell and is largely protein ($\sim70\%$) with lesser amounts of carbohydrate and lipid

(Burley & Vahedra 1989). Eggshell crystallization in the oviduct occurs rapidly, lasting only 20 h in chickens and perhaps 36 h in ostriches (Burley & Vahedra 1989, Johnson 1995).

Otoliths are mineralized bodies in the vertebrate inner ear (Panella 1980). In most vertebrates, the inner ear consists of a series of fluid-filled sacs and canals. Otolith mineralogy varies among vertebrates: Apatite occurs in agnathans, aragonite occurs in jawed fish and amphibians, and calcite occurs in amniotes (Simkiss & Wilbur 1989). In teleost fish, calcification occurs on a preformed organic matrix rich in non-collagenous proteins and mucopolysacchrides (Panella 1980). Teleost otoliths exhibit growth laminations formed at a variety of temporal scales (i.e. daily to lunar to annual) that are used in studies of age and growth rate (Panella 1980, Campana & Nielson 1985).

Controls on the Isotopic Composition of Vertebrates

Diet, behavior, and physiology act as filters between isotopic records in the environment and those retained in vertebrate tissues. Isotopic studies of physiology and diet are interesting in their own right, and they have been reviewed elsewhere (van der Merwe 1982, DeNiro 1987, Schwarcz & Schoeninger 1991, Koch et al 1994). Here, I present only the general background needed to interpret climatic and environmental isotope signals in organisms. Also, the discussion of isotopic controls on land vertebrates is limited to herbivores, who sample environmental signals in plants and surface waters most directly.

CARBON ISOTOPES IN VERTEBRATES   Carbon in fish otolith aragonite is derived from HCO_3^- dissolved in the inner ear fluid. This HCO_3^- is at least partly supplied by the water in which the fish lives. Otolith aragonite is often far from isotopic equilibrium with the environmental HCO_3^-, however (Kalish 1991a,b). A possible cause of disequilibrium is the presence of metabolic CO_2 in inner ear fluid (Kalish 1991b). As the $\delta^{13}C$ of otolith aragonite is a poor monitor of environmental $^{13}C/^{12}C$ ratios, I do not consider it further.

The source of carbon in the mineral and organic matrices of herbivore bones, teeth, and eggshells is food. Each tissue is offset in $\delta^{13}C$ from diet by a characteristic amount. In feeding experiments, $\Delta^{13}C$ between mammal apatite carbonate and bulk diet is $\sim+10‰$ (Table 1). The value estimated for wild mammals is greater, $+12–14‰$. The difference between bird eggshell carbonate and diet is larger still, $+14–+16‰$. The fractionations among dissolved CO_2 (derived from oxidation of food), blood HCO_3^-, and carbonate mineral at mammal and bird body temperatures are such that a $\Delta^{13}C$ of $\sim10‰$ is expected between apatite carbonate and food (von Schirnding et al 1982). Feeding studies show that the $\delta^{13}C$ of collagen is largely a function of the $\delta^{13}C$ of dietary protein, not bulk diet (Ambrose & Norr 1993, Tieszen & Fagre 1993). The $\delta^{13}C$ of herbivore

Table 1   Carbon and nitrogen isotope fractionations in vertebrates

Tissue	$\Delta_{\text{tissue-diet}}$ (‰)	Subjects	Site	Source[a]
Carbon isotopes				
Apatite CO_3	+9.0–10.3	Rodents, pig	Laboratory	1–5
Apatite CO_3	+12.0–14.0	Ungulates	Field	6–8
Collagen	+0.8–3.8	Rodents, pig, quail, chicken	Laboratory	2–4, 9, 10
Collagen	+5–6	Ungulates, ostrich	Field	2, 8, 11, 12
Eggshell CO_3	+15.0	Quail, duck	Laboratory	13
Eggshell CO_3	+16.1	Ostrich	Field	12, 14,
Eggshell protein	+3.5	Quail, duck	Laboratory	13
Eggshell protein	+1.5–2.1	Ostrich	Field	12, 14
Nitrogen isotopes				
Collagen	+0.7–2.4	Rodents, pig	Laboratory	4, 15, 16
Collagen	+3.5–5.0	Mammal	Field	17
Eggshell protein	+4.2	Quail, duck	Laboratory	13
Eggshell protein	+3.0	Ostrich	Field	14

[a]Sources: 1, DeNiro & Epstein (1978); 2, Ambrose & Norr (1993); 3, Tieszen & Fagre (1993); 4, Hare et al (1991); 5, this report[b]; 6, Lee-Thorp & van der Merwe (1987)[c]; 7, Bocherens et al (1996); 8, Bocherens & Mariotti (1992)[c]; 9, Tieszen et al (1983); 10, Hobson & Clark (1992)[d]; 11, Koch et al (1991); 12, von Schirnding et al (1982)[c]; 13, Hobson (1995)[e]; 14, Johnson (1995); 15, Gaebler et al (1966); 16, DeNiro & Epstein (1981); 17, Ambrose (1991).
[b]δ^{13}C bioapatite CO_3 for C3 pigs were −15.0 and −14.6‰; values for C4 pigs were −2.1 and −2.6‰.
[c]Estimated from 100% browsers or grazers, assuming C3 plants = −26.5‰ and C4 plants = −12.5‰.
[d]Did not use homogeneous diets.
[e]Measured on membrane, not matrix protein.

collagen tracks bulk diet because the δ^{13}C of plant protein covaries with that of bulk plant carbon (Abelson & Hoering 1961, Tieszen 1994). In laboratory animals raised on isotopically homogeneous diets, Δ^{13}C between collagen and bulk diet ranges from 1 to 4‰, whereas in wild mammals and birds, the estimated value is ~5‰. Δ^{13}C between eggshell matrix protein and bulk diet is ~2‰. The discrepancies between lab and field estimates of Δ^{13}C values are unresolved, but they may relate to differences in diet quality and the extent of fermentation during digestion (Metges et al 1990). In any case, the field estimates are remarkably consistent across a range of taxa and habitats (Table 1), which demonstrates that herbivore biominerals and organic matrices provide robust monitors of the Δ^{13}C of vegetation.

NITROGEN ISOTOPES IN VERTEBRATES   As with carbon, nitrogen in animal protein is supplied by the diet. Whole organism δ^{15}N values increase by ~3‰

from one trophic level to the next in natural food webs (Minagawa & Wada 1984, Schoeninger & DeNiro 1984). Feeding and field studies reveal similar $\Delta^{15}N$ values for collagen and eggshell protein versus diet (Table 1). The ^{15}N enrichment results from the excretion of urea and other nitrogenous wastes that are enriched in ^{14}N (Steele & Daniel 1978, Minagawa & Wada 1984). Higher $\Delta^{15}N$ values are observed in animals inhabiting arid regions, perhaps owing to differences in nitrogen cycling or urea loss associated with adaptations for drought tolerance (Heaton et al 1986, Sealy et al 1987, Ambrose 1991).

OXYGEN ISOTOPES IN VERTEBRATES   Otolith aragonite precipitates in oxygen isotope equilibrium with the water in which fish live (Kalish 1991a,b, Patterson et al 1993). The temperature-dependent fractionation for otolith aragonite, obtained by Patterson et al (1993) through analysis of benthic fish from large lakes and hatchery-reared fish, is

$$1000 \ln \alpha_{\text{aragonite-water}} = 18.56 \pm 0.32 \times 10^3 \, T^{-1} - 33.49 \pm 0.31 \; (r = 0.99), \quad (1)$$

where T is in kelvins. The slope of Equation 1 is identical to slopes obtained for other organisms by Grossman & Ku (1986), but the intercept differs by ~ 2.5‰.

The situation is more complex for land vertebrates. Biominerals are often assumed to form in oxygen isotope equilibrium with body fluids because of the rapid, enzyme-catalyzed exchange of oxygen among body water, blood phosphate, and blood carbonate (Nagy 1989). The few comparisons of body water and bird eggshell carbonate range from near equilibrium to an ^{18}O-enrichment of 3l greater than the equilibrium value (Folinsbee et al 1970, Schaffner & Swart 1991). Estimates of oxygen isotope fractionations between phosphate and water are similar across a phylogenetically diverse group of aquatic organisms, suggesting the fractionation is an equilibrium process and is not strongly influenced by biological/kinetic effects (Longinelli & Nuti 1973, Kolodny et al 1983, Lécuyer et al 1996). An example is the relationship obtained by Kolodny et al (1983) for benthic fish:

$$T = 113.3 - 4.38 \left(\delta^{18}O_{\text{PO}_4} - \delta^{18}O_{\text{H}_2\text{O}} \right) (r = 0.98), \quad (2)$$

where T is in degrees Celsius and $\Delta^{18}O$ values are relative to SMOW. At 37°C (mammal body temperature), Equation 2 yields a difference between the $\delta^{18}O$ of biogenic apatite and that of body water of 17.4‰. Observed differences for rats and cows range from 17.2 to 17.8‰, supporting the conclusion that the fractionation is one of equilibrium (Luz & Kolodny 1985, D'Angela & Longinelli 1990). Finally, because the $\delta^{18}O$ values of apatite phosphate and carbonate within individual mammals are strongly correlated, it is likely that carbonates are also in isotopic equilibrium with body water (Bryant et al 1996b,

Iacumin et al 1996, Cerling & Sharp 1996). Bryant et al (1996b) analyzed both phosphate and carbonate $\delta^{18}O$ from a suite of bones, then estimated the $\delta^{18}O$ of body water from phosphate $\delta^{18}O$ in order to calculate an α of 1.0263 between apatite carbonate and body water for mammals at 37°C.

The $\delta^{18}O$ values of biominerals that form in isotopic equilibrium with body water reflect both the temperature of mineral formation (chiefly of concern in studies of ectotherms) and the $\delta^{18}O$ of body water. While the $\delta^{18}O$ of body water in aquatic organisms is similar to that of external, environmental water, body water in land vertebrates differs from local water. Body water is a mixture of ingested water (both drinking water and water in plants) and metabolic water produced by oxidation of food (Luz et al 1984). Thus metabolic water includes oxygen from atmospheric O_2, which has a globally constant $\delta^{18}O$ value of $\sim+23‰$, significantly greater than that of surface waters (Hoefs 1997). Fortunately, there are taxon-specific relationships between the $\delta^{18}O$ of ingested water and body water that are predictable from body size and physiology (Bryant & Froelich 1995, Kohn 1996). Large animals ($>100\,kg$) track the $\delta^{18}O$ of ingested water most closely (Ayliffe et al 1992, Bryant & Froelich 1995). Studies of modern mammals and birds confirm that the $\delta^{18}O$ of biominerals and meteoric water covary, though tracking may be strongly affected by ^{18}O enrichment of ingested leaf water (Folinsbee et al 1970, Land et al 1980, Longinelli 1984, Luz & Kolodny 1985, Ayliffe & Chivas 1990) (Figure 1).

DIAGENETIC ALTERATION OF VERTEBRATE FOSSILS   Many studies have shown that apatite from bone and dentin undergoes pervasive isotopic alteration. Removal of altered material by pretreatment is difficult, as is independent diagnosis of the extent of alteration (Nelson et al 1986, Lee-Thorp & van der Merwe 1991, Ayliffe et al 1994, Wang & Cerling 1994, Kolodny et al 1996, Koch et al 1997). A likely mechanism for alteration is recrystallization of tiny bone and dentin crystals to a more stable form of apatite (Sillen 1989). Barrick et al (1996) present intriguing evidence that suggests that dinosaur bones may retain original phosphate $\delta^{18}O$ values, but the general consensus is that, with the exception of unusually well-preserved Holocene/Pleistocene materials, bone and dentin are poor substrates for analysis. In contrast, there is mounting evidence that the large apatite crystals in enamel retain isotopic values acquired during life. The strongest evidence for isotopic preservation is the occurrence, within a single deposit, of expected differences among ecologically distinct taxa (Lee-Thorp & van der Merwe 1987, Morgan et al 1994, Bocherens et al 1996). While enamel apatite carbonate appears isotopically robust, small shifts ($\sim2‰$) in $\delta^{13}C$ value towards the value for co-occurring sedimentary carbonate have been detected that may reflect early alteration and stabilization (Lee-Thorp & van der Merwe 1987, Quade et al 1992).
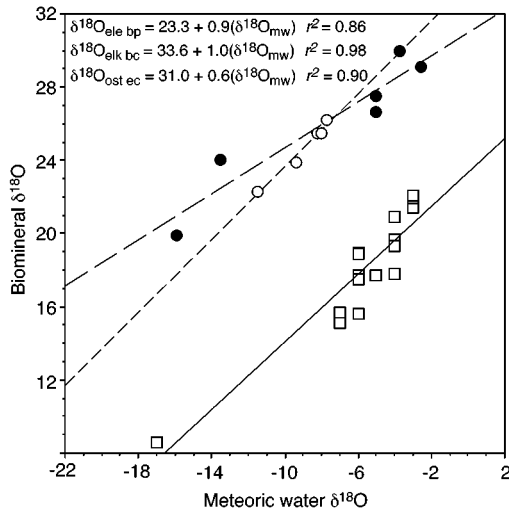
Figure 1   Relationships between $\delta^{18}O$ of biominerals and meteoric water (mw) for elephant bone phosphate (ele bp) (*open square* and *solid line*, *Loxodonta africana* and *Elephas maximus*), elk bone carbonate (elk bc) (*open circle* and *short-dash line*, *Cervus elaphus*), and ostrich eggshell carbonate (ost ec) (*filled circle* and *long-dash line*, *Struthio camelus*). Data from Ayliffe et al (1992), Johnson (1995), and Iacumin et al (1996). All values reported relative to standard mean ocean water (SMOW).

Aragonitic skeletons undergo transformation to calcite with time. It has commonly been assumed that if a fossil is composed entirely of aragonite, then it will yield original isotopic values (Dettman & Lohmann 1993, Patterson 1998). Because eggshells are composed of calcite, their state of preservation is harder to assess. Trace element composition and shell microstructure have been used to diagnose preservational state (Erben et al 1979), but neither of these criteria are sufficient to guarantee isotopic preservation (Banner & Kaufman 1994). Eggshells of Holocene/Pleistocene age are unlikely to be strongly altered, but results from older materials must be viewed with caution.

As with aragonite, it is usually assumed that if a complex biomolecule survives in a fossil, then its isotopic composition is unaltered. Contamination by exogenous organics is a problem, but methods are available to extract proteins from biominerals (Koch et al 1994, Johnson 1995). Isotopic effects induced by decay are poorly understood, but they may alter the isotopic composition of organic residues relative to that of the living organism (Tuross et al 1988, Silfer et al 1992, Johnson 1995). Useful guides to protein preservation are the presence of an organic replica of the fossil after demineralization, protein

yield, and the C:N ratio and amino acid composition of the residue (DeNiro & Weiner 1988, Tuross et al 1988, Ambrose 1990). When organic matrices have been badly degraded or contaminated, isotopic records can be retrieved from individual amino acids (Tuross et al 1988, Johnson et al 1993,Ostrom et al 1994).

Pedogenic Minerals and Organic Residues

Isotopic records have been obtained from many substrates in paleosols and continental sediments. In this review, I focus on soil carbonates, iron oxides, and organic residues. Soil mineral formation has been treated largely as a problem in inorganic chemistry, but an appreciation of the role of plants and soil microbes on mineral dissolution and formation, which has always been acknowledged, is growing (Fischer 1988, Sposito 1989, Monger et al 1991). Plants are the ultimate source of organic carbon in soils, of course, but decay processes also affect the isotopic composition of soil organics.

Modern soils in arid to sub-humid climates, as well as many paleosols, contain horizons rich in authigenic calcium carbonate (Birkeland 1984), which I refer to as soil carbonate. (There are other carbonate-containing phases in soils, but of these, only goethite is mentioned below.) Soil carbonate formation is largely controlled by carbonate-bicarbonate equilibria:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca^{2+} + 2HCO_3^- \tag{3}$$

(Birkeland 1984). Soil CO_2, which is the ultimate source of carbon in soil carbonates, is derived from soil respiration and atmospheric CO_2; dissolution of parent-rock carbonates contributes little carbon to soil CO_2 (Cerling & Quade 1993). High soil CO_2 production and organic decay generate acidic solutions that leach the upper part of a soil. As fluids percolate downward into the soil, an increase in $[Ca^{2+}]$ or pH may lead to calcite precipitation (Equation 3). Leaching of parent-rock carbonate and incipient precipitation of soil carbonate may occur in hundreds to thousands of years, but the formation of thick layers of carbonate takes tens to hundreds of thousands of years (Birkeland 1984). Carbonate may also form at the top of the water table (Wright & Vanstone 1991), but pedogenic carbonates can be recognized by their relationships to other soil features (Koch et al 1995, Quade & Cerling 1995).

Iron oxides occur in modern soils and surface deposits as dispersed microcrystalline particles, cements, and nodules. There are two common crystalline iron oxide phases in surface deposits—goethite ($\alpha FeOOH$) and hematite (αFe_2O_3). The chemistry of iron oxide formation in surface deposits is complex and poorly constrained at present. Hematite probably forms by dehydration and internal rearrangement of ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$), a structurally similar but highly disordered and poorly crystalline precursor. Goethite probably forms by

nucleation and crystal growth directly from solution, with dissolved iron supplied by a variety of sources (Schwertmann & Taylor 1989). Goethite formation is favored in organic-rich sediments in cool, wet regions, whereas hematite formation occurs in organic-poor sediments in warm, dry regions (Schwertmann 1988). Microbial activity is involved in the precipitation of some iron oxides, usually with ferrihydrite as a precursor (Crerar et al 1979, Gehring et al 1994). Goethite also occurs as a product of the weathering of oolitic limestone (Kimberley 1979).

Carbon isotope ratios have been measured in many different types of organic matter, including humic and fulvic acids, kerogen, bulk organic matter, organic matter in soil minerals, coal, and fossilized leaves. Humic and fulvic acids are dissolved organic fractions produced by decay of soil organic matter, and as such, they contain a complex mixture of organic compounds derived from the range of organisms present on and in soils (Sposito 1989). Bulk soil and mineral-occluded organic matter are rarely characterized geochemically prior to isotopic analysis but are extracted in a manner similar to kerogen (i.e. highly insoluble, resistant sedimentary organic matter). Classically, kerogen was thought to form by polymerization and condensation of organic molecules released by decay (e.g. humic substances, traces of resistant macromolecules) (de Leeuw & Largeau 1993). However, because most sedimentary organic carbon is remineralized by microbial communities, it has recently been argued that kerogen is dominated by resistant biomacromolecules. For example, Tegelaar et al (1991) have demonstrated that fossil leaf cuticles are largely composed of the resistant biopolymer cutan.

Controls on the Isotopic Composition of Pedogenic Minerals and Organic Residues

CARBON ISOTOPES IN PALEOSOLS   Organic residues in modern soils reflect the $\delta^{13}C$ of the overlying flora in areas that have not experienced recent floral change (Balesdent et al 1993, Tieszen et al 1997). At advanced stages of decomposition, insoluble soil organic matter is enriched in ^{13}C by $\sim$1–2‰ relative to the overlying flora, though the dynamics of carbon isotopes during decomposition are complex (Melillo et al 1989, Balesdent et al 1993, Wedin et al 1995). Different plant macromolecules (e.g. proteins, lipids, lignins, cellulose) have distinct $\delta^{13}C$ values; therefore, differential loss of components during decomposition may lead to isotopic shifts (Benner et al 1987, Wedin et al 1995). Mineral-occluded organic matter has been favored in paleoenvironmental studies, as it is less susceptible to contamination. However, Bird et al (1994) demonstrated that even insoluble, mineral-occluded, organic carbon can be contaminated by "young" organic matter. To circumvent diagenetic and contaminant effects, and to characterize discrete members of ancient ecosystems,
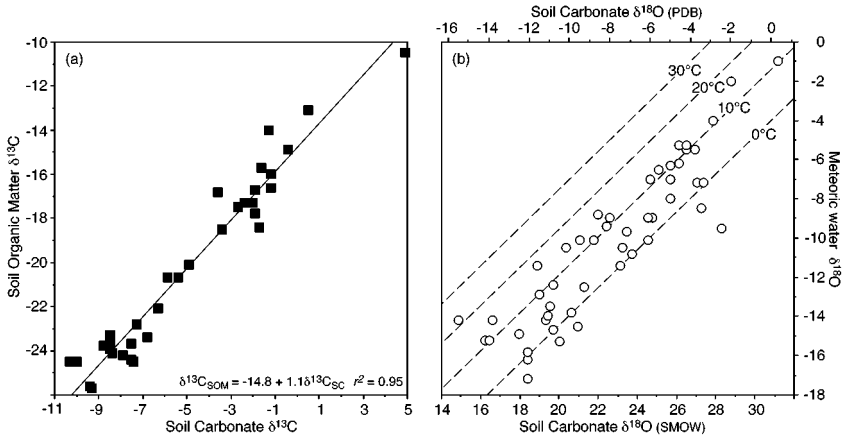
Figure 2 Relationships between (*a*) the $\delta^{13}C$ of soil organic matter and soil carbonates (PDB) and (*b*) the $\delta^{18}O$ of soil carbonate and meteoric water (SMOW) for modern soils. *Lines* represent calcite in equilibrium with meteoric water at 0° through 30°C, calculated using Equation 4. Data from Cerling & Quade (1993).

many marine isotope studies now examine molecular biomarkers rather than bulk organic carbon (Hayes et al 1990). This approach would improve continental isotope studies as well (Macko et al 1993).

Because its carbon is derived from soil CO_2, the $\delta^{13}C$ of soil carbonate is strongly correlated to that of soil organic matter and the overlying flora (Figure 2*a*). Atmospheric CO_2, which has a $\delta^{13}C$ value less negative than that of plants, contributes to soil CO_2 near the surface, but the CO_2 deep (>30 cm) in a soil with a moderate to high respiration rate is largely supplied by plant decay and root respiration. These processes generate CO_2 that is isotopically similar to organic matter (Figure 3). Diffusion of CO_2 from the soil to the atmosphere leads to a ^{13}C enrichment of ~4.4‰ for CO_2 at depth in a soil relative to soil organic matter (Amundson 1989, Cerling & Quade 1993). Finally, temperature-dependent fractionations associated with precipitation of calcite sum to ~10.5‰ (Figure 3). As a consequence of these processes, modern carbonates forming below ~30-cm depth have $\delta^{13}C$ values 15.1 ± 1.1‰ higher than those of organic matter. Cerling (1984) developed a diffusion-reaction model that explains much of the spatial and depth-related variation in the $\delta^{13}C$ of soil carbonate. An implication of the model is that, under higher P_{CO_2}, more of the CO_2 at depth in soils would be derived from the atmosphere, increasing the $\Delta^{13}C$ between soil carbonate and organic matter (Cerling 1992b). This
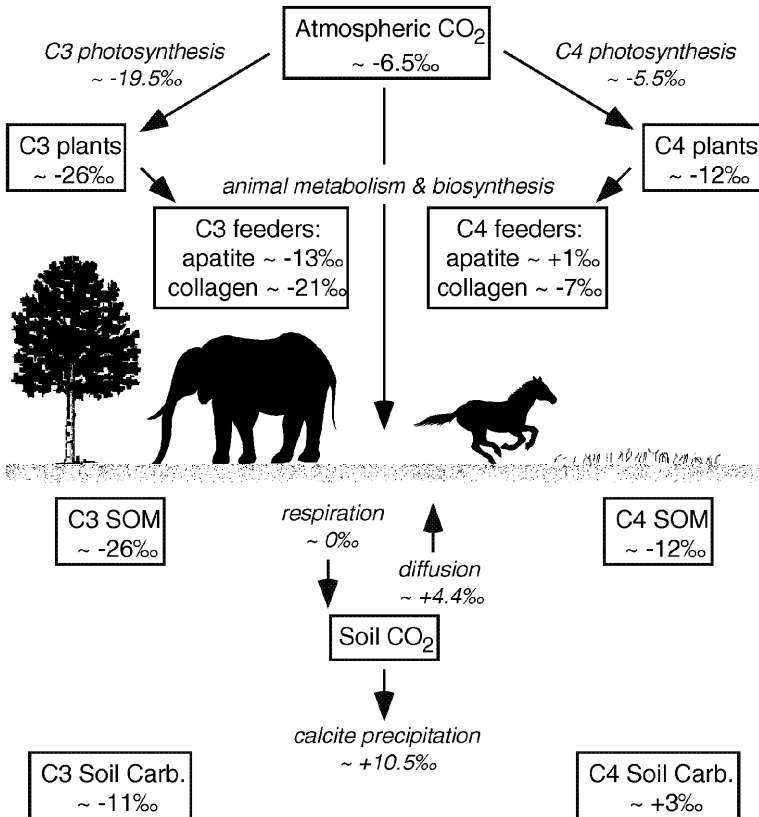
Figure 3   Carbon isotope values and fractionations among carbon-bearing materials in continental ecosystems. Fractionating processes are indicated in italics. The figure uses the pre-industrial value for atmospheric CO_2. Values for all materials, and some fractionations, will change with differences in the isotope composition and concentration of atmospheric CO_2.

feature of the system (and the somewhat analogous behavior for carbonate in goethite) has been used to generate estimates of past atmospheric P_{CO_2} that are in accord with the results of geochemical modeling (Cerling 1992b, Mora et al 1996, Yapp & Poths 1996, Berner 1997).

OXYGEN ISOTOPES IN PALEOSOLS   Assuming isotopic equilibrium, the $\delta^{18}O$ of soil carbonate is controlled by the $\delta^{18}O$ of soil water and temperature-dependent fractionation of oxygen isotopes during precipitation, which follows

the relationship

$$1000 \ln\alpha_{\text{calcite-water}} = 2.78 \times 10^6 \, T^{-2} - 2.89, \tag{4}$$

where T is in kelvins (Friedman & O'Neil 1977). At depths of ∼1 m, monthly averages for soil and air temperature are similar, and the $\delta^{18}O$ of soil water is relatively invariant and closest in value to meteoric water (Allison et al 1984, Amundson 1989, Brady 1990). As expected, the $\delta^{18}O$ of modern, deeply formed soil carbonates is correlated to the $\delta^{18}O$ of meteoric water (Figure 2b). Yet soil carbonate is typically ^{18}O-enriched by 2–10‰ relative to calcite in equilibrium with meteoric water, most likely owing to evaporative enrichment of soil water (Cerling & Quade 1993). Thus, paleosol carbonates do not yield quantitative estimates of temperature or the $\delta^{18}O$ of meteoric water. Rather, they serve as general indicators of environmental differences through time or among sites.

The fractionation of oxygen isotopes between goethite and water, determined by Yapp (1990) through laboratory synthesis experiments, is

$$1000 \ln\alpha_{\text{goethite-water}} = 1.63 \times 10^6 \, T^{-2} - 12.3, \tag{5}$$

where T is in kelvins. At two thoroughly characterized modern sites, goethite forms in equilibrium with meteoric water, even when bacteria are involved in mineral formation (Yapp 1997). Goethites with less well-known environments of formation show greater deviations from equilibrium (Yapp 1987). Oxygen isotope fractionation between hematite and water is less well understood. Yapp (1990) suggested that the hematite-water and goethite-water fractionations are similar. Yet the hematite-water fractionation calculated theoretically (Zheng 1991, Zheng & Simon 1991), using a method that produces good matches to experimentally determined oxygen isotope fractionations for other minerals, is very different from Yapp's (1990) fractionation. The source of this discrepancy is unclear and requires further testing. As iron oxides "mature" from poorly crystalline precursors to more crystalline phases, they probably equilibrate with deeper soil water and shallow groundwater. This process may integrate isotopic signals over a longer time span than in soil carbonates, but it should reduce the impact of evaporation of soil waters on iron oxides.

DIAGENETIC ALTERATION OF PALEOSOL MINERALS   Micritic soil carbonates may undergo recrystallization during burial, and fractures filled with later spar are common. While the $\delta^{13}C$ of recrystallized micrite is similar to that of unaltered micrite, the impact on $\delta^{18}O$ values is much greater (Koch et al 1995). Through microsampling, ideally from thin sections, fracture-filling spars can be avoided. The $\delta^{18}O$ of iron oxides are thought to be extremely resistant to diagenetic alteration (Becker & Clayton 1976, Yapp 1991).

CARBON ISOTOPES: ATMOSPHERIC CHEMISTRY AND LAND VEGETATION

Land plants are the ultimate source of carbon in land vertebrates, soil organic matter, and soil carbonates. The $\delta^{13}C$ of land plants is a function of the photosynthetic pathway used to fix CO_2 (Smith & Epstein 1971). The C3 pathway is most common, occurring in all trees, most shrubs and herbs, and many grasses. In C3 photosynthesis, CO_2 is fixed as a three-carbon sugar solely by the enzyme RUBP (Ribulose-1,5-bisphosphate) carboxylase. Because the large kinetic isotope effect associated with this enzyme is strongly expressed, C3 plants have $\delta^{13}C$ values (mean $\sim-27‰$, range -22 to $-35‰$) that are much lower than those of atmospheric CO_2 ($\sim-7.7‰$) (O'Leary 1988, Fogel & Cifuentes 1993). C4 photosynthesis occurs in dry/warm climate grasses and some sedges and herbs. It involves initial fixation by PEP (phosphoenolpyruvate) carboxylase to a four-carbon acid. As a result of extremely efficient CO_2 fixation, C4 plants have $\delta^{13}C$ values (mean $\sim-13‰$, range -19 to $-9‰$) that are more similar to those of the atmosphere (O'Leary 1988). The crassulacean acid metabolism (CAM) pathway is least common, occurring in succulent plants adapted to arid climates. CAM plants may fix CO_2 by either pathway and exhibit a range of values (Ehleringer & Monson 1993).

There are strong abiotic influences on the distribution and isotopic composition of plants using different pathways. Among grasses, the incidence of C4 photosynthesis is correlated with growing season temperature, with higher C4 species abundance and biomass in regions with warm growing seasons (Ehleringer & Monson 1993, Tieszen et al 1997). CAM plants and C4 dicots are most abundant in arid regions. Among C3 plants, a number of factors (light level, water and osmotic stress, nutrient levels, temperature, P_{CO_2}) produce predictable variations in plant $\delta^{13}C$ values (Ehleringer & Monson 1993). For example, in dense, closed-canopy forests, the $\delta^{13}C$ of forest floor leaves may be ^{13}C depleted by up to 8l relative to leaves from the top of the canopy, owing to recycling of ^{13}C-depleted CO_2 and the effects of low irradiance (van der Merwe & Medina 1991). Because of their efficient method of carbon fixation, C4 plants show little environmental variability in $\delta^{13}C$ values (Marino & McElroy 1991). CAM plants in arid regions have $\delta^{13}C$ values similar to those of C4 plants, whereas in wetter regions, CAM plants have values intermediate between those of C3 and C4 plants (Ehleringer & Monson 1993).

Detecting Changes in the Isotope Composition of the Atmosphere

Atmospheric CO_2 is the source of carbon in land plants. Thus materials that contain carbon derived from plants monitor the $\delta^{13}C$ of the atmosphere (Figure 3).

On short time scales ($<10^6$ years), shifts in the $\delta^{13}C$ of atmospheric CO_2 may result from changes in aspects of the surface carbon cycle, such as the rate of export of carbon from surface to deep water, the relative proportions of CO_2 uptake by land biota vs the ocean, or the rate of methane release from sediments (Marino et al 1992, Dickens et al 1997). On longer time scales, the $\delta^{13}C$ of all surface carbon reservoirs is controlled by geologic factors, such as the relative rates of burial of organic carbon vs carbonate carbon and the rate of volcanic degassing (Berner 1989, Derry et al 1992). Also, many marine $\delta^{13}C$ excursions are associated with marine biotic events (Holser & Magaritz 1992). Because continental and marine surface carbon reservoirs are linked via rapid exchange with the atmosphere, $\delta^{13}C$ variations provide a tool for correlating between land and sea at times of biotic turnover (Thackeray et al 1990, Koch et al 1992).

To study recent changes in the carbon cycle using the $\delta^{13}C$ of atmospheric CO_2, proxies are needed to supplement the short instrumental time series. Marino & McElroy (1991), noting the low $\delta^{13}C$ variability in C4 plants, analyzed kernels of corn, a C4 plant, and determined that the $\delta^{13}C$ of atmospheric CO_2 has dropped $\sim 1.5‰$ since 1950 because of fossil fuel burning. Their estimates matched the direct measurements of the $\delta^{13}C$ of atmospheric CO_2, including a few measurements made in the mid-1950s and the continuous record collected since 1978, extremely well. Estimates based on C3 plants have been plagued by high within- and between-plant $\delta^{13}C$ variability, yet similar estimates for the change in the atmosphere were obtained from tree ring $\delta^{13}C$ chronologies compiled from pinyon pines and from tooth dentin in C3-feeding moose (Leavitt & Long 1989, Bada et al 1990, Leavitt 1993). Using ^{14}C-dated C4 plants, Marino et al (1992) estimated that the $\delta^{13}C$ of the atmosphere was $\sim -7.5‰$ at the full glacial maximum, in contrast to a pre-industrial Holocene average of $\sim -6.5‰$.

Prior to the origin of C4 plants, large temporal variations in the $\delta^{13}C$ of land plants should have been related to changes in the atmosphere driven by changes in the $\delta^{13}C$ of marine surface waters. Koch et al (1992) examined the modern carbon cycle and proposed a model to predict relationships in $\delta^{13}C$ among surface marine carbonate, paleosol organic matter and carbonate, and apatite, then examined isotopic coupling among marine and continental carbon reservoirs across the Paleocene-Eocene (P-E) boundary. The P-E transition is marked by a gradual increase in marine temperatures from ~ 58 to 50 million years ago, punctuated by a brief pulse ($<150,000$ years long) of extreme warming ~ 55 million years ago (Kennett & Stott 1991, Zachos et al 1993). Marine $\delta^{13}C$ records show a similar pattern, with a gradual drop of $\sim 3‰$ across the P-E boundary, and a brief drop of $\sim 4‰$ during the short-term warming.

Paleosol carbonates and apatite carbonates from the Bighorn Basin, Wyoming, matched the expected long- and short-term shifts in the marine record in timing, magnitude, and duration (Koch et al 1992, 1995) (Figure 4a). The
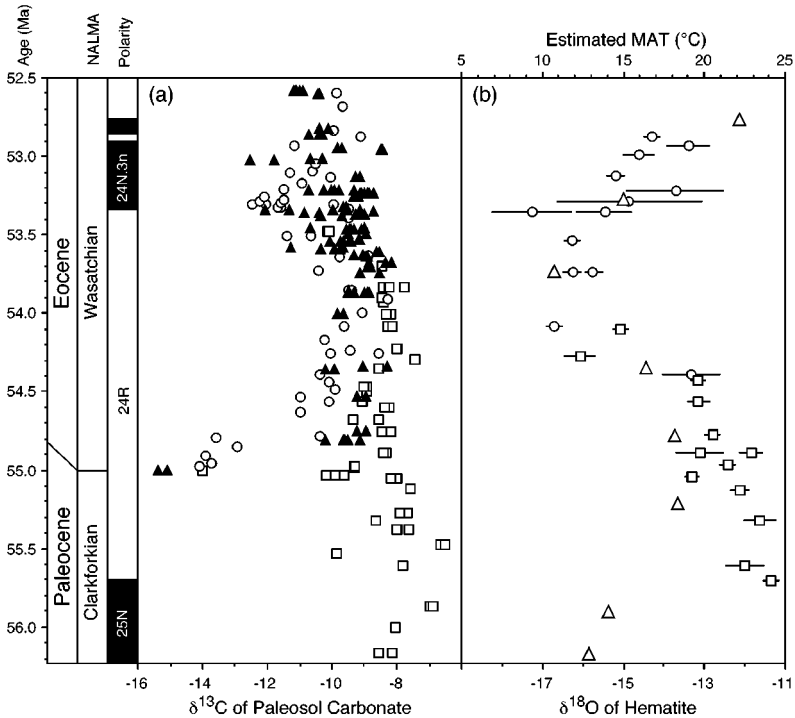
Figure 4   Change in (*a*) the $\delta^{13}C$ of soil carbonate and (*b*) the $\delta^{18}O$ of pedogenic hematite across the Paleocene-Eocene boundary in the Bighorn Basin, Wyoming. Soil carbonates were collected from three different areas (*open square*, Clarks Fork Basin; *filled triangle*, McCulloughs Peak; *open circle*, Central Basin) and correlated using bio- and magnetostratigraphy. In all three sections, a short-term negative excursion coincides with the transition from the Clarkforkian to the Wasatchian North American Land Mammal "Ages," and low values occur again in magnetic polarity zone C24N. Pedogenic hematite was recovered from the Clarks Fork and Central Basin sections. In both sections, a drop in $\delta^{18}O$ occurs ∼1.5 million years after the short-term $\delta^{13}C$ excursion. Mean annual temperature (MAT) estimated from leaf margin analysis (*open triangle*) (Wing 1998) drops and then rises in synchrony with changes in hematite $\delta^{18}O$ values. Ages are assigned using the magnetic polarity time scale of Cande & Kent (1995). Carbonate data for the Clarks Fork Basin are from Koch et al (1995); data for the other sections are new. Hematite data are from H Bao, PL Koch, and D Rumble (manuscript in preparation).

spacing between apatite and soil carbonate was in the expected range, though at most stratigraphic levels, both phases were slightly ^{13}C-enriched relative to expectations from the model. This offset may indicate diagenetic alteration of both phases or a real difference in the carbon cycle between the Paleogene and the Recent.

Isotopic correlation revealed that a major turnover in North American mammal faunas near the P-E boundary coincided with the short-term pulse of marine warming and low marine δ^{13}C values. Several modern mammal orders first appeared in North America during this event (Primates, Artiodactyla, Perissodactyla). These groups appeared near the P-E boundary on other Holarctic continents, but the timing of first appearances is debated (Dashzeveg 1988, Gunnell et al 1993). Recent studies of organic carbon from discontinuous P-E outcrops in Europe suggest that mammalian first appearances were coeval with the short-term warming there as well (Stott et al 1996). The timing of mammalian arrivals in Asia and the Arctic relative to the short-term warming and δ^{13}C excursion has not been evaluated. While the correlations to the marine record supplied by carbon isotopes provide no direct information about continental climate, it is tempting to speculate that the wave of arrivals in North America (and perhaps elsewhere in the Holarctic) are related to sudden warming, which may have promoted mammalian originations or allowed migration among Holarctic continents via high-latitude land connections. The causes of short-term warming and unusually low δ^{13}C values are unclear. A hypothesis linking these events to the sudden release of methane clathrates from ocean floor sediments appears promising and deserves further testing (Dickens et al 1997).

A dramatic (>6‰) drop and rise in the δ^{13}C of marine carbonate and organic matter occurred across the Permian-Triassic (P-T) boundary, the time of the greatest extinction in earth history (Holser & Magaritz 1992). The precise relationships among the δ^{13}C shift, the P-T boundary, and marine extinction remain unclear. It has been even more difficult to relate marine events to the profound floral and faunal changes on land. In a pioneering study, Thackeray et al (1990) examined the δ^{13}C of apatite from late Permian dicynodonts in South Africa. They noted a drop of ~7‰ across four assemblage zones approaching the P-T boundary, but they did not sample Triassic specimens and so could not detect a later rise in values. Adult dicynodonts lack tooth enamel (Hotton 1986), so Thackeray et al (1990) must have analyzed diagenetically suspect tooth dentin. The correlation of South African continental deposits to the marine record is being re-examined through carbon isotope analysis of soil carbonates and dicynodont tusks from continuous stratigraphic sections (MacLeod et al 1997). Faure et al (1995) found a small shift in the δ^{13}C of South African coals across the P-T boundary, and Retallack et al (1996) reported a drop of

~4‰ in organic matter at the boundary in Australia, but again, neither study documented a Triassic rise. Further study of tooth enamel, soil carbonates, and organic matter from other sections across the P-T boundary would be useful.

Detecting Changes in Vegetation

Carbon isotope analysis has been used with great success to explore changes in vegetation on a range of time scales. For example, by comparing organic carbon in surface vs deep layers of modern soils, Steuter et al (1990) showed that C3 woodlands in Nebraska have expanded onto adjacent C4 prairie since European settlement. A similar analysis revealed that the forest-savanna ecotone occurred higher along the Kenya Rift Valley in the mid-Holocene than at present (Ambrose & Sikes 1991). Soil carbonate and organic matter from paleosols in the Great Plains have been used to document shifts in C3 vs C4 grass abundance associated with changing temperature and aridity since the Pleistocene (Humphrey & Ferring 1994, Nordt et al 1994, Fredlund & Tieszen 1997).

Inferences about floral change using carbon isotope ratios of paleosols have low temporal resolution. Soil carbonates may form over thousands of years. Translocation of organic carbon may modify isotopic signatures in soils. Time averaging occurs over a shorter interval in isotopic records from fossils. Individual fossil organisms contain carbon ingested over a short life span, and each specimen, at least in principle, may be analyzed to deconvolute the effects of stratigraphic mixing. Furthermore, dietary specializations of animals can be exploited to probe more subtle aspects of floral cover. The $\delta^{13}C$ values of grazers[1] reflect the proportion of C3 to C4 grasses, whereas mixed-feeding herbivores monitor the proportions of C3 to C4 plants in the flora as a whole.

Bison are non-selective grazers, and the $\delta^{13}C$ of fossil bison collagen from the northern Great Plains supports the finding that C4 grasses increased in abundance from late Pleistocene to Holocene (Tieszen 1994). Figure 5 presents enamel $\delta^{13}C$ values for late Pleistocene herbivores from Texas. Grazers (bison and mammoth) have high $\delta^{13}C$ values, demonstrating the dominance of C4 grasses in the region in the late Pleistocene. The diets of presumed browsers on trees and shrubs (mastodon, tapir, deer) consisted almost entirely of C3 plants. Surprisingly, horses, presumed grazers, ate a large amount of C3 vegetation, either by selectively grazing on C3 grasses and sedges or by browsing on trees and shrubs (Koch et al 1998). These data reveal that a vegetational mosaic existed in the region, with woodland patches interspersed with open areas dominated by C4 grass. Of course, faunal isotope records could give a biased impression of

[1]Grazers are animals that feed primarily or exclusively on grasses or low herbs. Browsers consume mostly leaves and twigs of trees, shrubs, and taller herbs. Mixed-feeding herbivores consume both types of vegetation.
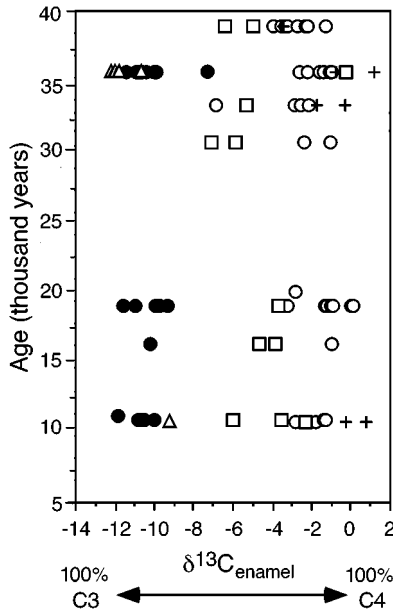
Figure 5 Carbon isotope values for Pleistocene tooth enamel from herbivores in southern and central Texas. Browsers include mastodon (*filled circle*, *Mammut*), deer (*filled triangle*, *Odocoileus*), and camelids (*open triangle*, *Paleolama* and *Camelops*). Grazers include mammoths (*open circle*, *Mammuthus*) and bison (*cross*, *Bison*). Horses (*open square*, *Equus*) are presumed grazers, but they consumed a significant amount of C3 vegetation. Data from 10 to 20 thousand years ago are associated with radiocarbon dates. Data from 30 to 40 thousand years ago are from terraces of the Trinity River near Dallas and the Ingleside site on the Texas coast. The Trinity River sites were deposited prior to the last glacial maximum, probably between 40 and 70 thousand years ago (Ferring 1990). The age for the Ingleside site, which formed during an interglacial or interstadial, is uncertain. Previously unpublished data were obtained following methods of Koch et al (1998).

local floral heterogeneity if the animals were migratory. Such a bias is unlikely to be significant when inferences about vegetation are based on isotopic records from small herbivores, but records from large herbivores must be viewed with caution until methods for identifying migratory behavior are developed.

Although fossil grasses are rare, there is evidence from mammalian morphology and paleosols that grasslands have existed for the last 20 million years (Retallack 1990, Janis 1993, MacFadden 1997). Today, C4 grasses are important in temperate prairies, tropical savannas, and arid grasslands (Ehleringer & Monson 1993). The rise of C4 plants has been revealed through isotopic analyses of tooth enamel from grazing mammals, which reflect changes within the grass component of the flora, and soil carbonates, which record changes in
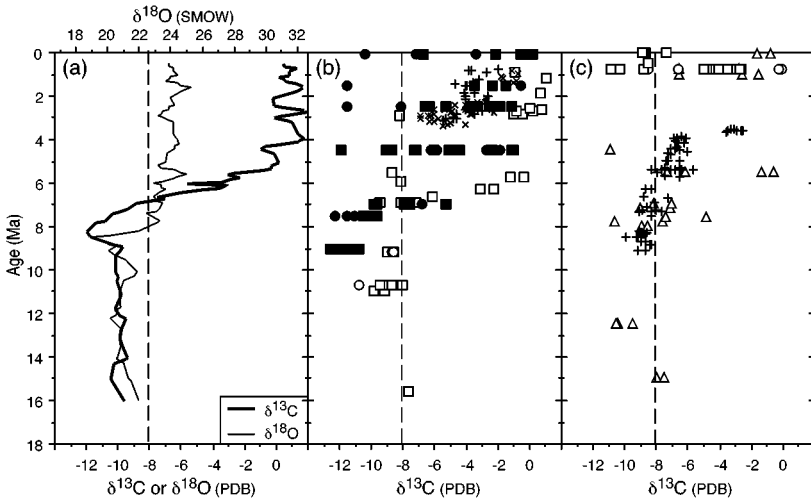
Figure 6 (*a*) δ^{13}C and δ^{18}O values of soil carbonate from Pakistan (three-point running average of data from Quade & Cerling 1995). (*b*) δ^{13}C of tooth enamel and soil carbonate in North America, including enamel from equids (*squares*) and proboscideans (*circles*) from the southwestern United States (*open symbols*) and Florida (*closed symbols*) (Wang et al 1994, MacFadden & Cerling 1996, Latorre et al 1997) and soil carbonates from Arizona (x) and New Mexico (*cross*) (Wang et al 1993, Mack et al 1994). (*c*) δ^{13}C values of tooth enamel and soil carbonate in South America, including equids (*open squares*), proboscideans (*open circles*), and toxodontids (*open triangle*) from northern Argentina and low altitude sites in Bolivia (MacFadden et al 1994, 1996, MacFadden & Shockey 1996, Latorre et al 1997) and soil carbonates in northern Argentina (*cross*) (Latorre et al 1997). δ^{13}C values greater than the *dashed lines* suggest the presence of C4 plants.

the flora as a whole. By summing possible environmental effects on the δ^{13}C of C3 plants, Latorre et al (1997) argued that enamel or soil carbonate values above -8‰ are strong evidence for the presence of C4 plants.

In south Asia, isotopic records from soil carbonates and tooth enamel (as well as eggshell carbonate and soil organics) reveal a dramatic increase in the abundance of C4 plants at 7 ± 1 million years ago (Quade et al 1992, 1995, Morgan et al 1994, Stern et al 1994, Quade & Cerling 1995) (Figure 6*a*). The observation that organic matter in marine-deposited sediments on the Bengal Fan increased by 10‰ during this interval is evidence that the biomass of the entire region was affected by this change (France-Lanord & Derry 1994). The records from other continents are more complicated. The δ^{13}C values of tooth enamel from grazing mammals in East Africa and low-latitude North and South America significantly transgressed the -8‰ limit ~7 million years ago (Figure 6*b*,*c*), whereas values from grazers at higher latitudes in North America only

rose later (~3 million years ago), and those from western Europe never deviated from the C3 range (Morgan et al 1994, Cerling et al 1997b). Paleosol carbonates in southwestern North America, northern Argentina, and East Africa reveal a different pattern than those from Asia. Dominance of local ecosystems by C4 plants in these regions occurred later, between 3.5 and 2 million years ago (Figure 6b,c) (Cerling 1992a, Kingston et al 1994). Thus the general pattern is one of a sudden increase in the proportion of plants using C4 photosynthesis within low-latitude grasses ~7 million years ago, followed by the dominance of some ecosystems by C4 grasses at later times.

The cause of the sudden expansion of C4 grasses 7 million years ago is debated. Based on differences in the efficiency of CO_2 fixation between C3 and C4 plants, Cerling et al (1997b) suggested that a drop in atmospheric P_{CO_2} below a critical threshold in the late Miocene may have favored C4 plants. On the other hand, C4 plants also have a competitive edge under hotter/drier conditions, thus their rise could be linked to climate change (Latorre et al 1997). Cerling et al (1997b) argued that the global synchrony of the rise in C4 grass abundance is evidence for a global forcing mechanism. Since climates are likely to show regional variation, they argued for changes in P_{CO_2} as the cause. It may be that changes in atmospheric P_{CO_2} drove the shift from C3 to C4 grasses within ecosystems, whereas regional climate determined when (or whether) grasses dominated local floras.

The impact of the expansion of C4 plants on mammalian faunas has not been evaluated critically. There are marked turnover events among herbivores in southern Asia, North America, and East Africa that appear to be associated with the rise in abundance of C4 plants (MacFadden 1997, Cerling et al 1997b). What is driving these events? C3 plants contain significantly more nitrogen than C4 plants (Barbehenn & Bernays 1992, Ehleringer & Monson 1993). C4 grasses may contain a higher content of difficult to digest cell wall constiuents, and a lower content of easily digested soluble carbohydrates, than C3 plants (Demment & Van Soest 1985). Furthermore, because the most nutrient-rich tissues in C4 plants are shielded by thick-walled bundle sheath cells, these tissues may be less digestible than the nutrient-rich tissues in C3 plants (Caswell et al 1973). Thus the shift to C4 grass dominance very likely resulted in a decrease in the quality of forage for grazers.

The effects of this decrease on herbivores may have varied, depending on their body size and digestive physiology (Demment & Van Soest 1985, Illius & Gordon 1992). Given their ability to recycle urea nitrogen back to their microbial gut faunas (Van Soest 1982), ruminant artiodactyls might be expected to tolerate the drop in protein content of grasses better than nonruminant artiodactyls and hindgut fermenters. Furthermore, large-bodied herbivores are capable of subsisting on more fibrous forage than smaller-bodied herbivores, owing

to their greater gut capacities relative to metabolic requirements (Demment & Van Soest 1985). Consequently the greater fiber content, and potentially lower digestibility, of C4 grasses may have favored large-bodied grazers. These trends in herbivores (increased abundance of ruminants, increased body size) seem to be borne out by the North American record (Janis et al 1994, Webb et al 1995), but the question of the herbivore response to the rise of C4 plants is an exciting one that requires careful study.

Attempts to reconstruct the habitats of extinct apes and hominids have been made in a number of studies. For example, interpretations of the paleoenvironment at the 14-million-year-old Fort Ternan site in Kenya, which yields fossil apes, have varied from a savanna to a woodland-bushland to a closed tropical forest (Cerling et al 1997a). Carbon isotope analysis of tooth enamel and soil carbonates provide no conclusive evidence for C4 vegetation (Cerling et al 1991, 1997a). However, this site predates the Neogene expansion of C4 plants by millions of years, so this result is not especially surprising. The isotopic evidence does preclude reconstruction of Fort Ternan as a modern tropical savanna, as the grasses in these ecosystems are almost exclusively C4. Because none of the herbivores exhibited extreme ^{13}C-depletions, a closed-canopy tropical forest seems unlikely as well (Cerling et al 1997a). While many taxa have morphologic attributes common to browsers, microwear analysis of tooth enamel indicates that several taxa may have been mixed-feeders or grazers (Cerling et al 1997a). A more open woodland with patches of C3 grass seems most consistent with all the data.

Study of tooth enamel from mammals at Swartkrans Cave, South Africa ($\sim$1.8 to 1.0 million years old), has been enlightening (Lee-Thorp et al 1994). Browsing bovids at the site consumed nearly 100% C3 plants, whereas grazing bovids had 100% C4 diets. Thus, as in Texas, the areas around the cave in the Pleistocene included both C3 trees and shrubs and C4 grasses. Among baboons, two species of *Papio* related to modern savanna baboons consumed C3-rich diets, whereas *Theropithecus* spp. (related to the modern gelada) ate mostly C4 grass. The hominid *Australopithecus robustus* also occurs in these deposits. *A. robustus* had large molars with thick enamel and powerful jaw musculature and has been viewed as a specialized vegetarian, perhaps consuming seeds, pods, or hard fruits. Enamel microwear analysis provides no evidence of grass consumption (Grine & Kay 1988). In contrast, δ^{13}C values from *A. robustus* are higher than those of co-occurring browsers, indicating a contribution of carbon from C4 grass to the diet. As direct grass consumption is precluded, Lee-Thorp et al (1994) concluded that *A. robustus* must have obtained C4 carbon indirectly, from the meat of grazers. Study of *Australopithecus africanus*, which occurs in older cave deposits nearby, as well as early *Homo spp.*, could address questions about the role of competition in the history of hominids.

OXYGEN ISOTOPES AND PALEOCLIMATOLOGY

Climatic influences on the δ^{18}O of meteoric water have been recognized since global precipitation monitoring began in the 1950s (Dansgaard 1964). In temperate and boreal regions, mean annual temperature (MAT) and mean annual meteoric water δ^{18}O values show a strong, positive correlation. The slope for the relationship between MAT and δ^{18}O at sites with a MAT between $0°$ and $20°$C is $\sim$6.0‰ per degree Centigrade (r > 0.8); higher slopes are observed in polar regions (Rozanski et al 1993). Individual mid- to high-latitude sites also exhibit a seasonal relationship between the δ^{18}O of meteoric water and temperature, with lower values in cold months. These average and seasonal relationships result from ^{16}O enrichment during evaporation from warm oceans, loss of ^{18}O-enriched water via rainout during vapor transport to cooler regions, and equilibration of falling droplets with local water vapor (Gat 1996). In tropical and subtropical regions, seasonal variations are smaller, and the average δ^{18}O value is more strongly related to the amount of precipitation, with lower values in areas with greater rainfall. The slope for the relationship between mean annual rainfall and mean annual meteoric water δ^{18}O values at tropical island sites is -0.013‰ per millimeter (r > 0.8) (Rozanski et al 1993). The phenomenon of ^{16}O enrichment via rainout has been modeled as a Rayleigh process (Gat 1996), and the modern annual and seasonal distributions of meteoric water δ^{18}O values have been simulated with general circulation models (Jouzel et al 1991). Spatially derived modern relationships have been used to reconstruct climatic changes from temporal changes in δ^{18}O values, though the assumptions underlying the approach are debated (Lawrence & White 1991, Boyle 1997).

Land animals that drink from rivers and lakes that have not experienced significant evaporation may ingest a representative sample of local meteoric water. The extent to which local surface waters express the seasonal variations in the δ^{18}O of meteoric water is highly variable, depending on the hydrologic characteristics of the catchment basin and groundwater system (Gat & Gonfiantini 1981). The water in plants supplies a large fraction of the water ingested by some land animals. The δ^{18}O value of plant water is similar to that of surface water, except for water in leaves, which is ^{18}O-enriched by evapotranspiration. The enrichment is greatest under hot, dry conditions (Dongmann et al 1974, Yakir et al 1990). The δ^{18}O values of fish otoliths and soil minerals are influenced by the δ^{18}O of meteoric water (or soil water) and by temperature-dependent changes in fractionation.

Reconstructing the Average δ^{18}O of Meteoric Water

The δ^{18}O of meteoric water is a key proxy in many approaches to paleoclimatic reconstruction, including studies of plants, speleothems, ice cores, vertebrates,

and soil minerals. Much of this work has focused on the Holocene and Pleistocene. For example, climate change during the Little Ice Age has been implicated in the decline of Norse colonies in coastal Greenland. To investigate local climate change, Fricke et al (1995) measured the $\delta^{18}O$ of apatite phosphate from enamel of Norse and Inuit inhabitants. They detected a 4‰ drop during the Little Ice Age, which they tentatively interpreted as a cooling of $\sim6°C$. These reconstructed changes in $\delta^{18}O$ and MAT are much larger than those in coeval ice core records from central Greenland, however, perhaps because of conflation of signals from changing cultural practices, hydrology, and climate (Bryant & Froelich 1996). Whatever the cause, the study provides clear evidence for a major environmental perturbation in coastal Greenland.

Models of oxygen mass balance suggest that large carnivores and obligate-drinking herbivores should track changes in the $\delta^{18}O$ of meteoric water most faithfully (Bryant & Froelich 1995, Kohn 1996). Proboscideans (elephants and their kin) fit the latter description nicely, and unlike carnivores, they are abundant in Neogene deposits. Ayliffe et al (1992) used a calibration between the $\delta^{18}O$ of meteoric water and modern elephant phosphate (Figure 1) to estimate glacial-interglacial changes from fossil proboscidean enamel from England. As expected, the $\delta^{18}O$ estimate from full glacial mammoths was lower than the estimate from interglacial animals. Analysis of apatite carbonate from proboscideans in southeast Florida revealed that full glacial animals ($\sim21,000$ years old) ingested water that was ~1.8‰ more negative than that ingested by late glacial animals ($\sim12,000$ years old) (Koch et al 1998). Assuming proboscideans ingested representative meteoric water, and correcting for the drop in $\delta^{18}O$ of the ocean resulting from glacial melting, the shift in $\delta^{18}O$ between full glacial and late glacial times in Florida was ~2.3‰. Applying the modern $\delta^{18}O$/MAT slope, this difference suggests that the full glacial climate in south Florida was at least $4°C$ cooler than today. This is consistent with estimates for temperature change from corals in Barbados (Guilderson et al 1994). These results demonstrate that mammals retain records of meteoric water $\delta^{18}O$ values that can be used in paleoclimatic studies for at least the Pleistocene and perhaps for the entire Cenozoic (Sánchez Chillón et al 1994, Bryant et al 1996a, Reinhard et al 1996).

The $\delta^{18}O$ values of drought-tolerant mammals, and those that ingest a large amount of leaf water, are also affected by relative humidity (Ayliffe & Chivas 1990, Luz et al 1990). Cormie et al (1994) presented a method for estimating relative humidity using collagen hydrogen isotope ratios (δD) and phosphate $\delta^{18}O$ values from deer. In essence, the δD of ingested plant hydrogen is not affected by evapotranspiration and thus is used to estimate the $\delta^{18}O$ of meteoric water, whereas the $\delta^{18}O$ of ingested leaf water is strongly sensitive to humidity. The method provides reasonable estimates of modern relative humidity, but it has never been applied to fossils. Kohn (1996) suggested that comparisons

of $\delta^{18}O$ values of drought-tolerant mammals with those of obligate-drinkers or carnivores might supply an index of relative humidity, but this idea is untested.

Soil minerals are valuable independent proxies for the $\delta^{18}O$ of meteoric water. For example, the $\delta^{18}O$ of soil carbonates from Asia (Figure 6a), South America, and East Africa all increased by ~3‰ in phase with the Neogene C4-grass expansion (Latorre et al 1997). Possible climatic causes are increased summer rainfall, increased MAT, or decreased humidity. Alternatively, the increase may be an effect of grassland expansion, as higher rates of evaporation (and concomitant ^{18}O enrichment of soil water) might be expected in grasslands relative to woodlands. Study of browsing mammals might discriminate between these hypotheses. If climatic factors are shifting the $\delta^{18}O$ of meteoric water, the $\delta^{18}O$ values of browsers should increase along with those of soil carbonates and grazers; if higher evaporation from grasslands is the cause, browsers may not show the increase.

The $\delta^{18}O$ of hematite is being used to evaluate climatic change at the P-E boundary in Wyoming (H Bao, PL Koch, D Rumble III, in preparation). Hematite encrusts fossil vertebrates from paleosols and is intergrown with soil carbonate, which demonstrates its pedogenic origin. The hematite-water fractionations of Zheng & Simon (1991) and Yapp (1990) are both relatively insensitive to temperature changes from $0°$ to $100°C$; thus, variations in the $\delta^{18}O$ of hematite can be taken as a relatively direct proxy for changes in the $\delta^{18}O$ of water. Hematite $\delta^{18}O$ values are high from the latest Paleocene to early Eocene, before and after the interval of short-term marine warming (no samples are available from the event itself) (Figure 4d). Hematite $\delta^{18}O$ values drop in the early Eocene and remain low until their rapid rise ~53 million years ago. These trends mirror changes in MAT estimated from leaf margin analysis, which suggests warm temperatures from late Paleocene to early Eocene, followed by a cool interval ~54 million years ago and then rapid warming to the Eocene thermal maximum (Wing 1998). If the modern $\delta^{18}O$/MAT slope is applied, the changes in MAT inferred from meteoric water $\delta^{18}O$ estimates and leaf margin analysis are similar. This close match between independent proxies demonstrates the great potential of authigenic minerals for quantitative paleoclimatic reconstruction.

Reconstructing Seasonal Changes in Temperature and the $\delta^{18}O$ of Meteoric Water

While multi-year averages of temperature or the amount of precipitation capture many features of the climate system, intra-annual variability of these characteristics have a powerful impact on ecosystem structure, geomorphology, and geochemical processes. Climatic simulations now reproduce broad trends in MAT for distant time periods quite well, but they do not match the sparse paleoclimatic record for seasonality of temperature, particularly for midcontinents

in warm climate intervals (Sloan 1994). Proxies for seasonality are a priority in paleoclimatic research.

Isotopic analysis of growth laminations in teeth has been explored as a proxy for seasonal cycles in the δ^{18}O of meteoric water and temperature. Koch et al (1989) detected cyclic variations in the δ^{18}O of carbonate from proboscidean tusks, with the lowest values in slow growth zones, which is expected if slow growth occurred in winter. These tusks are composed entirely of dentin, however, so diagenetic dampening of seasonal cycles is a concern. Subsequent studies using tooth enamel have detected subannual δ^{18}O cycles in fossil beaver (Stuart-Williams & Schwarcz 1997), proboscideans (Fox & Fisher 1996, Koch et al 1998), and bison (Fricke & O'Neil 1996), and Cerling & Sharp (1996) made a major advance in high-resolution microsampling by in situ laser fluorination. To date, however, no study of modern enamel has successfully reconstructed the full amplitude of seasonal cycles in the δ^{18}O of meteoric water, including a study of samples collected at very high temporal resolution from ever-growing beaver incisors (Stuart-Williams & Schwarcz 1997). The amplitudes for fossils are suspiciously low as well. Unpredictable hydrologic mixing may make quantitative reconstruction of seasonal cycles in meteoric water δ^{18}O values impossible. However, the fact that different growth bands in teeth have season-specific δ^{18}O values remains an important tool in paleoecological studies of seasonal changes in diet, habitat, and mortality (Koch et al 1989, 1998, Fisher 1996).

Isotopic analysis of otoliths shows greater promise as a proxy for seasonality. In otolith analysis, the δ^{18}O of water inhabited by the fish is evaluated independently, then shifts in aragonite δ^{18}O across the otolith are used to estimate seasonal changes in water temperature (Smith & Patterson 1994, Patterson 1998). When otoliths from large lakes are examined, it is assumed that the δ^{18}O of lake water does not change seasonally. Lake water δ^{18}O values are estimated using taxa from clades with well-known temperature limits on growth. In these animals, the highest δ^{18}O values for each year of growth correspond to aragonite formed in isotopic equilibrium with lake water at the lowest growth temperature. Thus the method supplies an estimate of δ^{18}O, as well as seasonal changes in lake temperature. Computer-aided micro-milling permits collection of aragonite formed over intervals as short as three days.

The method was used on drum (a kind of fish) collected at archaeological sites in western Lake Erie (Patterson 1998). Drum do not grow at temperatures <10°C; thus otolith aragonite only records fluctuations between 10°C and the summer maximum. Patterson (1998) modeled the full range of seasonal temperature variation by fitting the measured portion of the seasonal cycle with a sine curve. He concluded that the δ^{18}O of lake water dropped from −6.3‰ at 930 AD to −8.2‰ at 1570 AD (the Little Ice Age) (Figure 7). Mean lake temperature
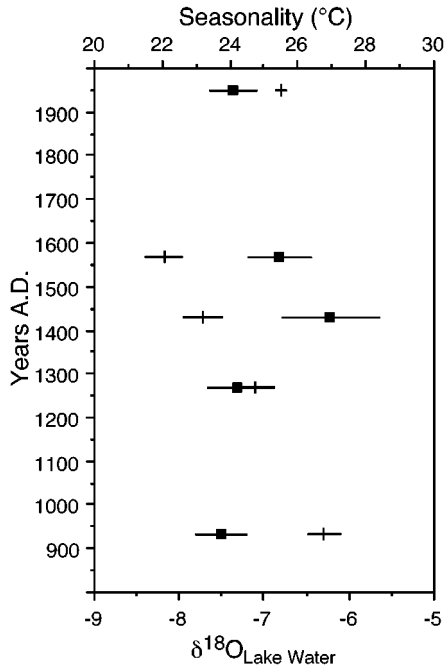
Figure 7 Changes in lake water $\delta^{18}O$ values (*cross*) and seasonal range of temperatures (*filled square*) reconstructed through isotopic analysis of drum otolith aragonite from western Lake Erie (Patterson 1998). *Symbols* are the mean, and *error bars* represent one standard deviation for measurements over several years of otolith growth. Lake water $\delta^{18}O$ for 1950 is the modern value.

dropped $\sim 4.5°C$ across this interval, and seasonality and year-to-year differences in mean temperature increased. Patterson (1998) attributed these changes to shifts in the position of the circumpolar vortex. Smith & Patterson (1994) estimated the $\delta^{18}O$ and summer temperature of Lake Idaho, a mid-Pliocene lake on the Snake River plain. The $\delta^{18}O$ of lake water was estimated from deep water sculpin that today prefer water of $\sim 4°C$, whereas temperature variations were determined using an otolith from a surface-dwelling sunfish. Maximum summer temperature did not change, though faunal evidence suggests longer growing seasons and warmer winters in the Pliocene.

NITROGEN ISOTOPES AND RAINFALL ABUNDANCE

The nitrogen isotope composition of land herbivores reflects that of ingested plants. Several trends have been recognized in the $\delta^{15}N$ of plants. First, the

processes by which nitrogen is lost from soils (ammonia volatilization, denitrification, loss of dissolved species) lead to ^{15}N enrichment of soil nitrogen relative to atmospheric N_2. As a result, N_2-fixing plants have slightly lower δ^{15}N values than non-fixing plants, though there is broad overlap in values (Nadelhoffer & Fry 1994). Second, a negative correlation between rainfall abundance and plant δ^{15}N values has been observed in Africa (Heaton 1987), as have negative correlations between soil moisture and plant δ^{15}N values on a local scale (Evans & Ehleringer 1994). These correlations may reflect greater ^{15}N enrichment of soil nitrogen in dry soils (Shearer et al 1978) due to higher rates of nitrogen loss. Third, the δ^{15}N of non-fixing plants is higher in coastal regions, perhaps owing to deposition of marine nitrate (Virginia & Delwiche 1982, Heaton 1987).

Herbivore collagen δ^{15}N values shows the expected negative correlation with rainfall abundance in southern Africa, though as mentioned above, the Δ^{15}N between collagen and diet is larger in arid regions (Heaton et al 1986, Sealy et al 1987, Ambrose 1991). Shifts in the δ^{15}N of herbivores were interpreted as evidence for decreasing rainfall abundance from early to late Holocene in the Kenya Rift Valley (Ambrose & DeNiro 1989). The relationship between rainfall abundance and herbivore δ^{15}N values is more difficult to evaluate in North America because the use of nitrogen fertilizers masks natural variability. Cormie & Schwarcz (1996) attempted to account for this effect in a study of North American deer, and they only found a negative correlation between rainfall abundance and δ^{15}N in deer consuming a large amount of C4 grass. Tieszen (1994) detected no significant δ^{15}N variations in Great Plains bison during the Holocene.

Johnson (1995) reported a relationship between the δ^{15}N of ostrich eggshell protein and rainfall abundance in southern Africa and then applied the relationship in a multi-isotope study of climate change using fossil eggshells from Equus Cave, South Africa (Johnson et al 1997). Individual eggshell fragments were dated using a ^{14}C-calibrated amino acid racemization curve. Organic δ^{13}C and δ^{15}N and carbonate δ^{13}C and δ^{18}O values of all dated fragments were measured. Today the vegetation around the cave is a savanna, where C4 grass coexists with C3 trees and shrubs. Ostriches are mixed feeders, but they prefer trees and shrubs over grass. Eggshell protein δ^{13}C values were invariant from 17,000 years ago to present; thus C3 browse was available throughout this time. The δ^{13}C of enamel from grazing mammal fossils at the cave indicates dominance by C4 grasses, with sporadic periods of higher C3 grass cover, perhaps due to changes in the seasonality of rainfall (Lee-Thorp & Beaumont 1995). Today rainfall near the cave is low ($\sim$450 mm/year), and it arrives chiefly in the summer. MAT is $\sim$16°C. Eggshell protein δ^{15}N values suggest that annual precipitation was $\sim$190 mm/year from 17,000 and 14,000 years ago, then increased to $\sim$600 mm/year by 6,000 years ago, after which it remained relatively

constant. Eggshell $\delta^{18}O$ values were low from 17,000 to 4,000 years ago, then rose to a maximum ~1,000 years ago. Ostriches obtain most of their water from plant tissues, so eggshell $\delta^{18}O$ values dominantly reflect the effect of evapotranspiration on leaf water. To explain low ^{18}O enrichment between 17,000 and 14,000 years ago, when eggshell $\delta^{15}N$ values provides strong evidence for a dry climate, Johnson et al (1997) concluded that MAT must have been low as well, which would reduce both evapotranspiration and the $\delta^{18}O$ of meteoric water.

CONCLUSION

A large amount of information about ancient environments is locked in vertebrate fossils and the soils and sediments that surround them. Carbon isotopes record changes in the structure of vegetation and the concentration and isotopic composition of atmospheric CO_2, though the former subject is only touched on briefly above. Oxygen isotope variations may be indirectly related to climate, through the $\delta^{18}O$ of meteoric water, or directly related to temperature, as, for example, in the analysis of fish otoliths from large lake systems. Nitrogen isotope variations show promise as a proxy for rainfall abundance. I conclude by examining the current limitations on these methods and the directions that might be explored profitably in the future.

A key goal of paleoclimatic and paleoenvironmental research is the generation of quantitative estimates of ancient conditions. At present, our ability to put hard numbers on percentages of C3 vs C4 cover, the $\delta^{18}O$ of meteoric water, or the amount of rainfall through analysis of vertebrate fossils is limited by uncertainties about biological fractionations. These uncertainties may be resolved only through experimental work on isotopic physiology and more careful monitoring of wild animals (Gannes et al 1997). The situation for inorganic mineral-water fractionations is better, except for lingering uncertainties about the hematite-water fractionation.

Carbon isotope analysis of ancient ecosystems is a relatively mature discipline. A large body of research over the past 10 years has fleshed out the pattern of Neogene C4 plant expansion, and the C3/C4 difference is the basis for most Neogene paleodietary research. The antiquity and abundance of plants following the CAM photosynthetic pathway, which has the potential to serve as an isotopic label in pre-Miocene ecosystems, has not been extensively investigated using stable isotopes (Bocherens et al 1993). Also, the environmental and biological controls on $\delta^{13}C$ variation within 100% C3 ecosystems are rarely exploited in paleoenvironmental research. For example, C3 plants in water-limited microhabitats have higher $\delta^{13}C$ values than do plants in wetter microhabitats (Ehleringer & Cooper 1988). Among boreal plants, different life forms (e.g. evergreen tree vs deciduous herbs) consistently differ by up to

6‰ (Brooks et al 1997). Landscape-scale differences in soil moisture or local plant cover may be detectable through isotopic analyses of soil carbonate or micromammal teeth collected along individual paleosols. The ^{13}C depletion of forest-floor plants in closed canopy ecosystems is strong, and it is easily detected in modern ecosystems through comparison of $^{13}C/^{12}C$ ratios of forest-floor vs arboreal herbivores (Ambrose & DeNiro 1986, van der Merwe & Medina 1991). This approach can provide information about forest density in the past. For example, Koch et al (1998) discovered that deer and tapir at Pleistocene localities in Florida have unusually low $\delta^{13}C$ values, which suggests that the forest patches inhabited by these species were relatively dense, despite the fact that both of these species are recovered in association with open country herbivores.

Oxygen isotope analysis of paleoclimates using vertebrate fossils and paleosol minerals has great scope for growth. Isotopic microanalysis of fish otoliths has just become technically feasible and should be a rich source of data on Neogene, and perhaps older, climates. The key limitations to otolith work are the quality of the biological assumptions needed to estimate lake water $\delta^{18}O$ values and the assumption that lake surface water $\delta^{18}O$ values do not vary seasonally. However, both these assumptions may be evaluated using data from independent sources. The controls on oxygen isotope variation in land vertebrates are coming into clearer focus, owing to both a growing number of analyses of samples from natural ecosystems (Bocherens et al 1996, Kohn et al 1996) and to increasing success in modeling of $^{18}O/^{16}O$ ratios of vertebrates (Bryant & Froelich 1995, Kohn 1996). It remains to be seen whether we will be able to develop robust models for reconstructing ingested water $\delta^{18}O$ values from the apatite of extinct species. For ancient systems, analysis of authigenic minerals in paleosols will be extremely important.

A number of applications of oxygen isotopes to paleoclimate reconstruction have not yet been explored thoroughly. Methods for assessing relative humidity are in development, but they have not been applied to ancient settings. A derivative application of ancient meteoric water $\delta^{18}O$ values that, so far, has gone unexplored, is estimation of paleoaltitude. Rainout processes lead to ^{18}O depletion from low to high altitudes along storm tracks (Dansgaard 1964). It should be possible to monitor ocean-mountain $\delta^{18}O$ gradients to determine tectonic uplift history. If so, it would be important not only to tectonic studies but also to recent controversies over the impact of mountain uplift on global climates and biogeochemical cycles (Molnar & England 1990, Raymo & Ruddiman 1992).

Finally, in both paleoenvironmental and paleoclimatic analysis, more explicit integration with climate modeling is essential. For example, Tieszen et al (1997) determined the relationship between the $\delta^{13}C$ of soil organic matter and the proportions of C3 vs C4 biomass at a large number of sites in the Great Plains. These data, if coupled with local climate data, could be used to generate transfer functions that relate change in key climatic parameters, such as growing

season temperature or rainfall abundance, to C3 vs C4 abundance and soil δ^{13}C values. Ultimately, local records of change in relative proportions of C3 and C4 cover could be compared with reconstructions of change from climatic simulations. This is analogous to the approach taken in palynofloral/climate simulation comparisons (Webb 1995).

The need for greater links to atmospheric and oceanic modeling is even more pressing for studies attempting to interpret paleoclimatic change from the record of meteoric water δ^{18}O values. The δ^{18}O/MAT relationship is a valuable global approximation, but it has always been recognized that the relationship has a large amount of scatter that may be interpretable in view of factors such as local temperature at sites of evaporation and precipitation, the direction of storm tracks, orographic effects, and the type of precipitation (rain vs snow). Ideally, information on the δ^{18}O of meteoric water for an ancient time interval should be gathered at a network of continental sites, so that these data could be used to constrain climatic simulations for that interval that include isotopes as a hydrologic tracer. Models capable of forging these links exist, and they have been applied to the Quaternary ice core record (Charles et al 1994). At present, the history of variations in MAT or the δ^{18}O of meteoric water on land is far from complete, but the tools needed to reconstruct these records, including the isotope chemistry of vertebrate, invertebrate, and plant fossils, as well as authigenic minerals, are now in hand.

Visit the *Annual Reviews home page* at
http://www.AnnualReviews.org.

Literature Cited

Abelson PH, Hoering TC. 1961. Carbon isotope fractionation in formation of amino acids by photosynthetic organisms. *Proc. Natl. Acad. Sci. USA* 47:623–32

Allison GB, Barnes CJ, Hughes MW, Leany FWJ. 1984. The effect of climate and vegetation on the oxygen-18 and deuterium pro-files in soils. In *Isotope Hydrology 1983*, pp. 105–23. Vienna: Int. At. Energy Agency

Ambrose SH. 1990. Preparation and characterization of bone and tooth collagen for isotopic analysis. *J. Archaeol. Sci.* 17:431–51

Ambrose SH. 1991. Effects of diet, climate and physiology on nitrogen isotope abun-

dance in terrestrial foodwebs. *J. Archaeol. Sci.* 18:293–317

Ambrose SH, DeNiro MJ. 1986. The isotopic ecology of East African mammals. *Oecologia* 69:395–406

Ambrose SH, DeNiro MJ. 1989. Climate and habitat reconstruction using stable carbon and nitrogen isotope ratios of collagen in prehistoric herbivore teeth from Kenya. *Quat. Res.* 31:407–22

Ambrose SH, Norr L. 1993. Experimental evidence for the relationship of the carbon isotope ratios of whole diet and dietary protein to those of bone collagen and carbonate. See Lambert & Grupe 1993, pp. 1–37

Ambrose SH, Sikes NE. 1991. Soil carbon isotope evidence for Holocene habitat change in the Kenya Rift Valley. *Science* 253:1402–5

Amundson R. 1989. The use of stable isotopes in assessing the effect of agriculture on arid and semi-arid soils. See Rundel et al 1989, pp. 318–41

Ayliffe LK, Chivas AR. 1990. Oxygen isotope composition of the bone phosphate of Australian kangaroos: potential as a palaeoenvironmental recorder. *Geochim. Cosmochim. Acta* 54:2603–9

Ayliffe LK, Chivas AR, Leakey MG. 1994. The retention of primary oxygen isotope composition of fossil elephant skeletal phosphate. *Geochim. Cosmochim. Acta* 58:5291–98

Ayliffe LK, Lister AM, Chivas AR. 1992. The preservation of glacial-interglacial climatic signatures in the oxygen isotopes of elephant skeletal phosphate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 99:179–91

Bada JL, Peterson RO, Schimmelmann A, Hedges REM. 1990. Moose teeth as environmental isotopic monitors. *Oecologia* 82:102–4

Balesdent JC, Girardin C, Mariotti A. 1993. Site-related δ^{13}C of tree leaves and soil organic matter in a temperate forest. *Ecology* 74:1713–21

Banner JL, Kaufman J. 1994. The isotopic record of ocean chemistry and diagenesis preserved in non-luminescent brachiopods from Mississippian carbonate rocks, Illinois and Missouri. *Geol. Soc. Am. Bull.* 106:1074–83

Barbehenn RV, Bernays EA. 1992. Relative nutritional quality of C3 and C4 grasses for a gramnivorous lepidopteran, *Paratrytone melane* (Hesperiidae). *Oecologia* 92:97–103

Barrick RE, Showers WJ, Fischer AG. 1996. Comparison of thermoregulation of four ornithischian dinosaurs and a varanid lizard from the Cretaceous Two Medicine Formation: evidence from oxygen isotopes. *Palaios* 11:295–305

Becker RH, Clayton RN. 1976. Oxygen isotope study of a Precambrian banded iron-formation, Hamersley Range, Western Australia. *Geochim. Cosmochim. Acta* 40:1153–65

Benner R, Fogel ML, Sprague EK, Hodson RE. 1987. Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies. *Nature* 329:708–10

Berner RA. 1989. A model for atmospheric CO_2 over Phanerozoic time. *Am. J. Sci.* 291:339–76

Berner RA. 1997. The rise of plants and their effect on weathering and atmospheric CO_2. *Science* 276:544–46

Bird MI, Quade J, Chivas AR, Fifield LK, Allan GL, et al. 1994. The carbon isotope composition of organic matter occluded in iron nodules. *Chem. Geol.* 114:269–79

Birkeland PW. 1984. *Soils and Geomorphology.* New York: Oxford Univ. Press. 372 pp.

Bocherens H, Friis EM, Mariotti A, Pedersen KR. 1993. Carbon isotopic abundances in Mesozoic and Cenozoic fossil plants: palaeoecological implications. *Lethaia* 26:347–58

Bocherens H, Koch PL, Mariotti A, Geraads D, Jaeger J-J. 1996. Isotopic biogeochemistry (^{13}C, ^{18}O) of mammal enamel from African Pleistocene hominid sites: implications for the preservation of paleoclimatic signals. *Palaios* 11:306–18

Bocherens H, Mariotti A. 1992. Biogéochimie isotopique du carbone dans les os de mammifères actuels et fossiles de zones froides et tempérées. *CR Acad. Sci. Sér. II* 315:1147–53

Boyle EA. 1997. Cool tropical temperatures shift the global δ^{18}O-T relationship: an explanation for the ice core δ^{18}O-borehole thermometry conflict? *Geophys. Res. Lett.* 24:273–76

Brady NC. 1990. *The Nature and Properties of Soils.* New York: Macmillan. 621 pp.

Brooks JR, Flanagan LB, Buchmann N, Ehleringer JR. 1997. Carbon isotope composition of boreal plants: functional grouping of life forms. *Oecologia* 110:301–11

Bryant JD, Froelich PN. 1995. A model of oxygen isotope fractionation in body water of large mammals. *Geochim. Cosmochim. Acta* 59:4523–37

Bryant JD, Froelich PN. 1996. Oxygen isotope composition of human tooth enamel from medieval Greenland: linking climate and society: comment. *Geology* 24:477–78

Bryant JD, Froelich PN, Showers WJ, Genna BJ. 1996a. Biologic and climatic signals in the oxygen isotopic composition of Eocene-Oligocene equid enamel phosphate. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126:75–89

Bryant JD, Koch PL, Froelich PN, Showers

WJ, Genna BJ. 1996b. Oxygen isotope partitioning between phosphate and carbonate in mammalian apatite. *Geochim. Cosmochim. Acta* 60:5145–48

Burley RW, Vadehra DV. 1989. *The Avian Egg: Chemistry and Biology.* New York: Wiley & Sons. 472 pp.

Campana SE, Nielson JD. 1985. Microstructure of fish otoliths. *Can. J. Fish. Aquat. Sci.* 42:1014–32

Cande SC, Kent DV. 1995. Revised calibration of the geomagnetic polarity timescale for the Late Cretaceous and Cenozoic. *J. Geophys. Res. B* 100:6093–95

Carlson SJ. 1990. Vertebrate dental structures. In *Skeletal Biomineralization: Patterns, Processes and Evolutionary Trends*, ed. JG Carter, 1:531–56. New York: Van Nostrand Reinhold

Caswell H, Reed F, Stephenson SN, Werner PA. 1973. Photosynthetic pathways and selective herbivory: a hypothesis. *Am. Nat.* 107:465–80

Cerling TE. 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.* 71:229–40

Cerling TE. 1992a. Development of grasslands and savannas in East Africa during the Neogene. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 97:241–47

Cerling TE. 1992b. Use of carbon isotopes in paleosols as an indicator of the $P(CO_2)$ of the paleoatmosphere. *Glob. Planet. Change* 6:307–14

Cerling TE, Harris JM, Ambrose SH, Leakey MG, Solounias N. 1997a. Dietary and environmental reconstruction with stable isotope analyses of herbivore tooth enamel from the Miocene locality of Fort Ternan, Kenya. *J. Hum. Evol.* 30:In press

Cerling TE, Harris JM, MacFadden BJ, Leakey MG, Quade J, et al. 1997b. Global vegetation change through the Miocene/Pliocene boundary. *Nature* 389:153–58

Cerling TE, Quade J. 1993. Stable carbon and oxygen isotopes in soil carbonates. See Swart et al 1993, pp. 217–31

Cerling TE, Quade J, Ambrose SH, Sikes NE. 1991. Fossil soils, grasses, and carbon isotopes from Fort Ternan, Kenya: grassland or woodland? *J. Hum. Evol.* 21:295–306

Cerling TE, Sharp ZD. 1996. Stable carbon and oxygen isotope analysis of fossil tooth enamel using laser ablation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126:173–86

Charles CD, Rind D, Jouzel J, Koster RD, Fairbanks RG. 1994. Glacial-interglacial changes in moisture sources for Greenland: influences on the ice core record of climate. *Science* 263:508–11

Cormie AB, Luz B, Schwarcz HP. 1994. Relationship between the hydrogen and oxygen isotopes of deer bone and their use in the estimation of relative humidity. *Geochim. Cosmochim. Acta* 58:3439–49

Cormie AB, Schwarcz HP. 1996. Effects of climate on deer bone $\delta^{15}N$ and $\delta^{13}C$: lack of precipitation effects on $\delta^{15}N$ for animals consuming low amounts of C4 plants. *Geochim. Cosmochim. Acta* 60:4161–66

Crerar DA, Knox GW, Means JL. 1979. Biogeochemistry of bog iron in the New Jersey Pine Barrens. *Chem. Geol.* 24:111–35

D'Angela D, Longinelli A. 1990. Oxygen isotopes in living mammals' bone phosphate: further results. *Chem. Geol.* 86:75–82

Dansgaard W. 1964. Stable isotopes in precipitation. *Tellus* 16:436–68

Dashzeveg D. 1988. Holarctic correlation of non-marine Paleocene-Eocene boundary strata using mammals. *J. Geol. Soc. London* 145:473–78

de Leeuw JW, Largeau C. 1993. A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal, and petroleum formation. See Engel & Macko 1993, pp. 23–72

Demment MW, Van Soest PJ. 1985. A nutritional explanation for body-size patterns of ruminant and nonruminant herbivores. *Am. Nat.* 125:641–72

DeNiro MJ. 1987. Stable isotopes and archaeology. *Am. Sci.* 75:182–91

DeNiro MJ, Epstein S. 1978. Influence of diet on the distribution of carbon isotopes in animals. *Geochim. Cosmochim. Acta* 42:495–506

DeNiro MJ, Epstein S. 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochim. Cosmochim. Acta* 45:341–51

DeNiro MJ, Weiner S. 1988. Chemical, enzymatic and spectroscopic characterization of "collagen" and other organic fractions from prehistoric bones. *Geochim. Cosmochim. Acta* 52:2197–206

Derry LA, Kaufman AJ, Jacobsen SB. 1992. Sedimentary cycling and environmental change in the Late Proterozoic: evidence from stable and radiogenic isotopes. *Geochim. Cosmochim. Acta* 56:1317–29

Dettman DL, Lohmann KC. 1993. Seasonal changes in Paleogene surface water $\delta^{18}O$: fresh-water bivalves of western North America. See Swart et al 1993, pp. 153–63

Dickens GR, Castillo MM, Walker JCG. 1997. A blast of gas in the latest Paleocene; simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology* 25:259–62

Dongmann G, Nurnberg HW, Förstel H, Wagener K. 1974. On the enrichment of $H_2^{18}O$

in the leaves of transpiring plants. *Radiat. Environ. Biophys.* 11:41–52

Ehleringer JR, Cooper TA. 1988. Correlations between carbon isotope ratio and microhabitat in desert plants. *Oecologia* 76:562–66

Ehleringer JR, Monson RK. 1993. Evolutionary and ecological aspects of photosynthetic pathway variation. *Annu. Rev. Ecol. Syst.* 24:411–39

Engel MH, Macko SA, eds. 1993. *Organic Geochemistry.* New York: Plenum. 861 pp.

Erben HK, Hoefs J, Wedepohl KH. 1979. Paleobiological and isotopic studies of eggshells from a declining dinosaur species. *Paleobiology* 5:380–414

Evans RD, Ehleringer JR. 1994. Water and nitrogen dynamics in an arid woodland. *Oecologia* 99:233–42

Faure K, de Wit MJ, Willis JP. 1995. Late Permian global coal hiatus linked to ^{13}C-depleted CO_2 flux into the atmosphere during the final consolidation of Pangea. *Geology* 23:507–10

Ferring CR. 1990. Late Quaternary Geology and Geoarchaeology of the Upper Trinity River Drainage Basin, Texas. *Geol. Soc. Am. Field Trip Guidebook #11.* Dallas, TX: Dallas Geol. Soc.

Fischer WR. 1988. Microbiological reactions of iron in soils. In *Iron in Soils and Clay Minerals,* ed. JW Stucki, BA Goodman, U Schwertmann, *NATO ASI Ser. C* 217:715–48. Boston: Reidel

Fisher DC. 1996. Extinction of proboscideans in North America. In *The Proboscidea: Evolution and Palaeoecology of Elephants and Their Relatives,* ed. J Shoshani, P Tassy, pp. 296–315. New York: Oxford Univ. Press

Fogel ML, Cifuentes LA. 1993. Isotope fractionation during primary production. See Engel & Macko 1993, pp. 73–98

Fogel ML, Tuross N, Johnson BJ, Miller GH. 1997. Biogeochemical record of ancient humans. *Org. Geochem.* 26:In press

Folinsbee RE, Fritz P, Krouse HR, Robblee AR. 1970. Carbon-13 and oxygen-18 in dinosaur, crocodile, and bird eggshells indicate environmental conditions. *Science* 168:1353–56

Fox DL, Fisher DC. 1996. Oxygen isotope variation in proboscidean tusks; comparison of Miocene and Pleistocene material. *J. Vertebr. Paleontol. Suppl.* 16:34 (Abstr.)

France-Lanord C, Derry LA. 1994. δ^{13}C of organic carbon in the Bengal Fan: source evolution and transport of C3 and C4 plant carbon to marine sediments. *Geochim. Cosmochim. Acta* 21:4809–14

Fredlund GG, Tieszen LL. 1997. Phytolith and carbon isotope evidence for late Quaternary vegetation and climate change in the southern Black Hills, South Dakota. *Quat. Res.* 47:206–17

Fricke H, O'Neil JR. 1996. Inter- and intra-tooth variation in the oxygen isotope composition of mammalian tooth enamel phosphate: implications for palaeoclimatological and palaeobiological research. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126:91–100

Fricke H, O'Neil JR, Lynnerup N. 1995. Oxygen isotope composition of human tooth enamel from medieval Greenland: linking climate and society. *Geology* 23:869–72

Friedman I, O'Neil JR. 1977. Compilation of stable isotope fractionation factors of geochemical interest. In *Data of Geochemistry,* ed. M Fleischer, *US Geol. Surv. Prof. Pap. 440-KK.* 12 pp.

Gaebler OH, Vitti TG, Vukmirovich R. 1966. Isotope effects in metabolism of ^{14}N and ^{15}N from unlabeled dietary proteins. *Can. J. Biochem.* 44:1249–57

Gannes LZ, O'Brien DM, Martínes del Rio C. 1997. Stable isotopes in animal ecology: assumptions, caveats, and a call for more laboratory experiments. *Ecology* 78:1271–76

Gat JR. 1996. Oxygen and hydrogen isotopes in the hydrological cycle. *Annu. Rev. Earth Planet. Sci.* 24:225–62

Gat JR, Gonfiantini R, eds. 1981. *Stable Isotope Hydrology, Deuterium and Oxygen-18 in the Water Cycle. IAEA Tech. Rep. Ser.* 210:177–201

Gehring AU, Langer MR, Gehring CA. 1994. Ferriferous bacterial encrustations in lateritic duricrusts from southern Mali (West Africa). *Geoderma* 61:213–22

Grine FE, Kay RF. 1988. Early hominid diets from quantitative image analysis of dental microwear. *Nature* 333:765–68

Grossman EL, Ku TL. 1986. Oxygen and carbon isotopic fractionation in biogenic aragonite; temperature effects. *Chem. Geol.* 59:59–74

Guilderson TP, Fairbanks RG, Rubenstone JL. 1994. Tropical temperature variations since 20,000 years ago: modulating interhemispheric climate change. *Science* 263:663–65

Gunnell GF, Bartels W, Gingerich PD. 1993. Paleocene-Eocene boundary in continental North America: biostratigraphy and geochronology, northern Bighorn Basin, Wyoming. *N. Mex. Mus. Nat. Hist. Sci. Bull.* 2:137–44

Hare PE, Fogel ML, Stafford TW, Mitchell AD, Hoering TC. 1991. The isotopic composition of carbon and nitrogen in individual amino acids isolated from modern and fossil proteins. *J. Archaeol. Sci.* 18:277–92

Hayes JM, Freeman KH, Popp BN, Hoham CH. 1990. Compound-specific isotopic analyses: a novel tool for reconstruction of ancient

biogeochemical processes. *Org. Geochem.* 16:1115–28

Heaton THE. 1987. The ^{15}N/^{14}N ratios of plants in South Africa and Namibia: relationship to climate and coastal/saline environments. *Oecologia* 74:236–46

Heaton THE, Vogel JC, von la Chevallerie G, Gollett G. 1986. Climatic influence on the isotopic composition of bone nitrogen. *Nature* 322:822–23

Hobson KA. 1995. Reconstructing avian diets using stable-carbon and nitrogen isotope analysis of egg components: patterns of isotopic fractionation and turnover. *Condor* 97:752–62

Hobson KA, Clark RG. 1992. Assessing avian diets using stable isotopes II: factors influencing the diet-tissue fractionation. *Condor* 94:189–97

Hoefs J. 1997. *Stable Isotope Geochemistry.* New York: Springer-Verlag. 201 pp.

Holser WT, Magaritz M. 1992. Cretaceous/Tertiary and Permian/Triassic boundary events compared. *Geochim. Cosmochim. Acta* 56:3297–309

Hotton N III. 1986. Dicynodonts and their role as primary consumers. In *The Ecology and Biology of Mammal-Like Reptiles*, ed. N Hotton III, PD MacLean, JJ Roth, EC Roth, pp. 71–82. Washington: Smithson. Inst.

Humphrey JD, Ferring CR. 1994. Stable isotopic evidence for latest Pleistocene and Holocene climatic change in north-central Texas. *Quat. Res.* 41:200–13

Iacumin P, Bocherens H, Mariotti A, Longinelli A. 1996. Oxygen isotope analysis of coexisting carbonate and phosphate in biogenic apatite: a way to monitor diagenetic alteration of bone phosphate? *Earth Planet. Sci. Lett.* 142:1–6

Illius AW, Gordon IJ. 1992. Modelling the nutritional ecology of ungulate herbivores: evolution of body size and competitive interactions. *Oecologia* 89:428–34

Imbrie J, Hays J, Martinson D, McIntyre A, Mix A, et al. 1984. The orbital theory of Pleistocene climate: support from a revised chronology of the marine δ^{18}O record. In *Milankovitch and Climate*, ed. A Berger, J Imbrie, J Hays, G Kukla, B Saltzman, pp. 269–306. Dordrecht: Reidel

Janis CM. 1993. Tertiary mammal evolution in the context of changing climates, vegetation, and tectonic events. *Annu. Rev. Earth Planet. Sci.* 24:467–500

Janis CM, Gordon IJ, Illius AW. 1994. Modelling equid/ruminant competition in the fossil record. *Hist. Biol.* 8:15–29

Johnson BJ. 1995. *The stable isotope biogeochemistry of ostrich eggshell and its application to late Quaternary paleoenvironmental reconstructions in South Africa.* PhD thesis. Univ. Colo. Boulder. 229 pp.

Johnson BJ, Fogel ML, Miller GH. 1993. Paleoecological reconstruction in southern Egypt based on the stable carbon and nitrogen isotopes in the organic fraction and stable carbon isotopes in individual amino acids of fossil ostrich eggshell. *Chem. Geol.* 107:493–97

Johnson BJ, Miller GH, Fogel ML, Beaumont PB. 1997. The determination of late Quaternary paleoenvironments at Equus Cave, South Africa, using stable isotopes and amino acid racemization in ostrich eggshell. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 136:121–37

Jouzel J, Koster RD, Suozzo RJ, Russell GL, White JWC, et al. 1991. Simulations of the HDO and H_2^{18}O atmospheric cycles using the NASA GISS general circulation model: sensitivity experiments for present-day conditions. *J. Geophys. Res.* 96:7495–507

Kalish JM. 1991a. Oxygen and carbon stable isotopes in otoliths of wild and laboratory-reared Australian salmon (*Arripis trutta*). *Mar. Biol.* 110:37–47

Kalish JM. 1991b. [13]C and [18]O isotopic disequilibria in fish otoliths: metabolic and kinetic effects. *Mar. Ecol. Prog. Ser.* 75:191–203

Kennett JP, Stott LD. 1991. Abrupt deep-sea warming, paleoceanographic changes and benthic extinctions at the end of the Paleocene. *Nature* 353:225–29

Kimberley MM. 1979. Origin of oolitic iron formation. *J. Sediment. Petrol.* 40:1216–25

Kingston JD, Marino BD, Hill A. 1994. Isotopic evidence for Neogene hominid paleoenvironments in the Kenya Rift Valley. *Science* 264:955–59

Koch PL, Behrensmeyer AK, Fogel ML. 1991. *The isotopic ecology of plants and animals in Amboseli National Park, Kenya. Annu. Rep. Dir. Geophys. Lab., Carnegie Inst. Wash. 1990–1991*, pp. 163–71

Koch PL, Fisher DC, Dettman DL. 1989. Oxygen isotopes in the dentition of extinct proboscideans: a measure of season-of-death and seasonality. *Geology* 17:515–19

Koch PL, Fogel ML, Tuross N. 1994. Tracing the diets of fossil animals using stable isotopes. See Lajtha & Michener 1994, pp. 63–92

Koch PL, Hoppe KA, Webb SD. 1998. The isotopic ecology of late Pleistocene mammals in North America, Part 1: Florida. *Chem. Geol.* In press

Koch PL, Tuross N, Fogel ML. 1997. The effects of sample treatment and diagenesis on the isotopic integrity of carbonate in biogenic hydroxylapatite. *J. Archaeol. Sci.* 24:417–29

Koch PL, Zachos JC, Dettman DL. 1995. Stable isotope stratigraphy and paleocli-

matology of the Paleogene Bighorn Basin (Wyoming, U.S.A.). *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 115:61–89

Koch PL, Zachos JC, Gingerich PD. 1992. Correlation between isotope records in marine and continental carbon reservoirs near the Palaeocene/Eocene boundary. *Nature* 358:319–22

Kohn MJ. 1996. Predicting animal δ^{18}O; accounting for diet and physiological adaptation. *Geochim. Cosmochim. Acta* 60:4811–29

Kohn MJ, Schoeninger MJ, Valley JW. 1996. Herbivore tooth oxygen isotope compositions; effects of diet and physiology. *Geochim. Cosmochim. Acta* 60:3889–96

Kolodny Y, Luz B, Navon O. 1983. Oxygen isotope variation in phosphate of biogenic apatites, I. Fish bone apatite—rechecking the rules of the game. *Earth Planet. Sci. Lett.* 64:398–404

Kolodny Y, Luz B, Sander M, Clemens WA. 1996. Dinosaur bones: fossils or pseudomorphs? The pitfalls of physiology reconstruction from apatitic fossils. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126:161–72

Lajtha K, Michener B, eds. 1994. *Stable Isotopes in Ecology and Environmental Science.* Oxford: Blackwell Sci. 316 pp.

Lambert J, Grupe G, eds. 1993. *Prehistoric Human Bone, Archaeology at the Molecular Level.* Berlin: Springer-Verlag

Land LS, Lundelius EL Jr, Valastro S Jr. 1980. Isotopic ecology of deer bones. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 32:143–51

Latorre C, Quade J, McIntosh WC. 1997. The expansion of C4 grasses and global climate change in the late Miocene: stable isotope evidence from the Americas. *Earth Planet. Sci. Lett.* 146:83–96

Lawrence JR, Rashkes Meux J. 1993. The stable isotopic composition of ancient kaolinites of North America. See Swart et al, 1993, pp. 249–61

Lawrence JR, White JWC. 1991. The elusive climate signal in the isotopic composition of precipitation. In *Stable Isotope Geochemistry: A Tribute to Sam Epstein*, ed. HP Taylor Jr, JR O'Neil, IR Kaplan, *Geochem. Soc. Spec. Publ.* 3:169–85

Leavitt SW. 1993. Environmental information from ^{13}C/^{12}O ratios of wood. See Swart et al 1993, pp. 325–31

Lécuyer C, Grandjean P, Emig CC. 1996. Determination of oxygen isotope fractionation between water and phosphate from living lingulids: potential applications to palaeoenvironmental studies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126:101–8

Lee-Thorp JA, Beaumont PB. 1995. Vegetation and seasonality shifts during the Late Quaternary deduced from ^{13}C/^{12}C ratios of grazers at Equus Cave, South Africa. *Quat. Res.* 43:426–32

Lee-Thorp JA, van der Merwe NJ. 1987. Carbon isotope analysis of fossil bone apatite. *S. Afr. J. Sci.* 83:712–15

Lee-Thorp JA, van der Merwe NJ. 1991. Aspects of the chemistry of modern and fossil biological apatites. *J. Archaeol. Sci.* 18:43–54

Lee-Thorp JA, van der Merwe NJ, Brain CK. 1994. Diet of *Australopithecus robustus* at Swartkrans from stable carbon isotopic analysis. *J. Hum. Evol.* 27:361–72

LeGeros RZ. 1981. Apatites in biological systems. In *Inorganic Biological Crystal Growth*, ed. B Pamplin, pp. 1–45. New York: Pergamon

Longinelli A. 1984. Oxygen isotopes in mammal bone phosphate: A new tool for paleohydrological and paleoclimatological research? *Geochim. Cosmochim. Acta* 48:385–90

Longinelli A, Nuti S. 1973. Revised phosphate-water isotopic temperature scale. *Earth Planet. Sci. Lett.* 19:373–76

Lowenstam H, Weiner S. 1989. *On Biomineralization.* New York: Oxford Univ. Press. 324 pp.

Luz B, Cormie AB, Schwarcz HP. 1990. Oxygen isotope variations in phosphate of deer bones. *Geochim. Cosmochim. Acta* 54:1723–28

Luz B, Kolodny Y. 1985. Oxygen isotope variations in phosphate of biogenic apatites, IV. Mammal teeth and bones. *Earth Planet. Sci. Lett.* 75:29–36

Luz B, Kolodny Y, Horowitz M. 1984. Fractionation of oxygen isotopes between mammalian bone-phosphate and environmental water. *Geochim. Cosmochim. Acta* 48:1689–93

MacFadden BJ. 1997. Origin and evolution of the grazing guild in New World terrestrial mammals. *Trends Ecol. Evol.* 12:182–87

MacFadden BJ, Cerling TE. 1996. Mammalian herbivore communities, ancient feeding ecology, and carbon isotopes: a 10 million-year sequence from the Neogene of Florida. *J. Vertebr. Paleontol.* 16:103–15

MacFadden BJ, Cerling TE, Prado J. 1996. Cenozoic terrestrial ecosystem evolution in Argentina: evidence from carbon isotopes of fossil mammal teeth. *Palaios* 11:319–27

MacFadden BJ, Shockey BJ. 1996. Ancient feeding ecology and niche differentiation of Pleistocene mammalian herbivores from Tarija, Bolivia: morphological and isotopic evidence. *Paleobiology* 23:77–100

MacFadden BJ, Wang Y, Cerling TE, Anaya F. 1994. South American fossil mammals and carbon isotopes: a 25 million-year sequence from the Bolivian Andes. *Palaeo-*

geogr. Palaeoclimatol. Palaeoecol. 107:257–68

Mack GH, Cole DR, James WC, Giordana TH, Salyards SL. 1994. Stable carbon and oxygen isotopes of pedogenic carbonates as indicators of Plio-Pleistocene climate in the southern Río Grande Rift, south-central New Mexico. *Am. J. Sci.* 294:621–40

Macko SA, Engel MH, Parker PL. 1993. Early diagenesis of organic matter in sediments: assessment of mechanisms and preservation by the use of isotopic molecular approaches. See Engel & Macko 1993, pp. 211–24

MacLeod KG, Smith RMH, Koch PL, Ward PD. 1997. Multiple carbon isotope excursions in the Permo-Triassic boundary interval of South Africa. *Geol. Soc. Am. Abstr. Prog.* 29:462 (Abstr.)

Marino BD, McElroy MB. 1991. Isotopic composition of atmospheric CO_2 inferred from carbon in C4 plant cellulose. *Nature* 349:127–31

Marino BD, McElroy MB, Salawitch RJ, Spaulding WG. 1992. Glacial-to-interglacial variations in the carbon isotopic composition of atmospheric CO_2. *Nature* 357:461–66

Melillo JM, Aber JD, Linkings AE, Ricca A, Fry B, et al. 1989. Carbon and nitrogen dynamics along the decay continuum: plant litter to soil organic matter. *Plant Soil* 115:189–98

Metges C, Kempe K, Schmidt H-L. 1990. Dependence of the carbon-isotope contents of breath carbon dioxide, milk, serum and rumen fermentation products on the $\delta^{13}C$ value of food in dairy cows. *Br. J. Nutr.* 63:187–96

Minagawa M, Wada E. 1984. Stepwise enrichment of ^{15}N along food chains: further evidence and the relation between $\delta^{15}N$ and animal age. *Geochim. Cosmochim. Acta* 48:1135–40

Molnar P, England P. 1990. Late Cenozoic uplift of mountain ranges and global climate change: chicken or egg? *Nature* 346:29–34

Monger HC, Daugherty LA, Lindemann WC, Liddell CM. 1991. Microbial precipitation of pedogenic calcite. *Geology* 19:997–1000

Mora CI, Driese SG, Colarusso LA. 1996. Middle to Late Paleozoic atmospheric CO_2 levels from soil carbonate and organic matter. *Science* 271:1105–7

Morgan ME, Kingston JD, Marino BD. 1994. Carbon isotopic evidence for the emergence of C4 plants in the Neogene from Pakistan and Kenya. *Nature* 387:162–65

Nadelhoffer KJ, Fry B. 1994. Nitrogen isotope studies in forest ecosystems. See Lajtha & Michener 1994, pp. 22–44

Nagy KA. 1989. Doubly-labeled water studies of vertebrate physiological ecology. See Rundel et al 1989, pp. 270–87

Nelson BK, DeNiro MJ, Schoeninger MJ, De-Paolo DJ, Hare PE. 1986. Effects of diagenesis on strontium, carbon, nitrogen and oxygen concentration and isotopic composition of bone. *Geochim. Cosmochim. Acta* 50:1941–49

Nordt LC, Boutton TW, Hallmark CT, Water MR. 1994. Late Quaternary vegetation and climate change in central Texas based on the isotopic composition of organic carbon. *Quat. Res.* 41:109–20

O'Leary MH. 1988. Carbon isotopes in photosynthesis. *BioScience* 38:328–36

O'Neil JR. 1986a. Appendix: terminology and standards. In *Stable Isotopes in High Temperature Geological Processes*, ed. JW Valley, HP Taylor Jr, JR O'Neil, *Rev. Mineral* 16:561–70. Chelsea, MI: Mineral. Soc. Am.

O'Neil JR. 1986b. Theoretical and experimental aspects of isotopic fractionation. In *Stable Isotopes in High Temperature Geological Processes*, ed. JW Valley, HP Taylor Jr, JR O'Neil, Rev. *Mineral* 16:1–40. Chelsea, MI: Mineral. Soc. Am.

Ostrom PH, Zonneveld J-P, Robbins LL. 1994. Organic geochemistry of hard parts: assessment of isotopic variability and indigeneity. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 107:201–12

Panella G. 1980. Growth patterns in fish sagittae. In *Skeletal Growth of Aquatic Organisms*, ed. DC Rhoads, RA Lutz, pp. 519–60. New York: Plenum

Patterson WP. 1998. North American continental seasonality during the last millennium: high-resolution analysis of sagittae. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* In press

Patterson WP, Smith GR, Lohmann KC. 1993. Continental paleothermometry and seasonality using the isotopic composition of aragonitic otoliths of freshwater fishes. See Swart et al 1993, pp. 191–202

Quade J, Cater JML, Ojha TP, Adam J, Harrison TM. 1995. Late Miocene environmental change in Nepal and the northern Indian subcontinent: stable isotopic evidence from paleosols. *Geol. Soc. Am. Bull.* 107:1381–97

Quade J, Cerling TE. 1995. Expansion of C4 grasses in the late Miocene of northern Pakistan: evidence from stable isotopes in paleosols. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 115:91–116

Quade J, Cerling TE, Barry J, Morgan MM, Pilbeam DR, et al. 1992. A 16-Ma record of paleodiet using carbon and oxygen isotopes in fossil teeth from Pakistan. *Chem. Geol.* 94:183–92

Raymo ME, Ruddiman WF. 1992. Tectonic forcing of late Cenozoic climate. *Nature* 359:117–22

Reid REH. 1987. Bone and dinosaurian "endothermy." *Mod. Geol.* 11:133–54

Reinhard E, de Torres T, O'Neil J. 1996. $^{18}O/^{16}O$ ratios of cave bear tooth enamel: a record of climate variability during the Pleistocene. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 126:45–59

Retallack GJ. 1990. *Soils of the Past.* London: Unwin-Hyman. 520 pp.

Retallack GJ, Veevers JJ, Morante R. 1996. Global coal gap between Permian-Triassic extinction and Middle Triassic recovery of peat-forming plants. *Geol. Soc. Am. Bull.* 108:195–207

Rozanski K, Araguás-Araguás L, Gonfiantini R. 1993. Isotopic patterns in modern global precipitation. See Swart et al 1993, pp. 1–35

Rundel PW, Ehleringer JR, Nagy KA, eds. 1989. *Stable Isotopes in Ecological Research.* New York: Springer-Verlag. 525 pp.

Sánchez Chillón B, Alberdi MT, Leone G, Bonadonna FP, Stenni B, et al. 1994. Oxygen isotopic composition of fossil equid tooth and bone phosphate: an archive of difficult interpretation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 107:317–28

Schaffner FC, Swart PK. 1991. Influence of diet and environmental water on the carbon and oxygen isotopic signatures of seabird eggshell carbonate. *Bull. Mar. Sci.* 48:23–38

Schoeninger MJ, DeNiro MJ. 1984. Nitrogen and carbon isotopic composition of bone collagen from marine and terrestrial animals. *Geochim. Cosmochim. Acta* 48:625–39

Schwarcz HP, Schoeninger MJ. 1991. Stable isotope analyses in human nutritional ecology. *Yearb. Phys. Anthropol.* 34:283–321

Schwertmann U. 1988. Occurrence and formation of iron oxides in various pedoenvironments. In *Iron in Soils and Clay Minerals*, ed. JW Stucki, BA Goodman, U Schwertmann, *NATO ASI Ser. C* 217:267–308. Boston: Reidel

Schwertmann U, Taylor RM. 1989. Iron oxides. In *Minerals in Soil Environments*, ed. JB Dixon, SB Weed, pp. 379–438. Madison: Soil Sci. Soc. Am.

Sealy JC, van der Merwe NJ, Lee-Thorp JA, Lanham JL. 1987. Nitrogen isotopic ecology in southern Africa: implications for environmental and dietary tracing. *Geochim. Cosmochim. Acta* 51:2707–17

Shearer G, Kohl DH, Chien S-H. 1978. The nitrogen-15 abundance in a wide variety of soils. *Soil Sci. Soc. Am. J.* 42:899–902

Silfer JA, Engel MH, Macko SA. 1992. Kinetic fractionation of stable carbon and nitrogen isotopes during peptide bond hydrolysis: experimental evidence and geochemical implications. *Chem. Geol.* 101:211–21

Sillen A. 1989. Diagenesis of the inorganic phase of cortical bone. In *The Chemistry of Prehistoric Human Bone*, ed. TD Price, pp. 211–29. New York: Cambridge Univ. Press

Simkiss K, Wilbur KM. 1989. *Biomineralization: Cell Biology and Mineral Deposition.* San Diego: Academic. 337 pp.

Sloan LC. 1994. Equable climates during the early Eocene: significance of regional paleogeography for North American climate. *Geology* 22:881–84

Smith BN, Epstein S. 1971. Two categories of $^{13}C/^{12}C$ ratios of higher plants. *Plant Physiol.* 47:380–84

Smith GR, Patterson WP. 1994. Mio-Pliocene seasonality on the Snake River plain: comparison of faunal and oxygen isotopic evidence. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 107:291–302

Sposito G. 1989. *The Chemistry of Soils.* New York: Oxford Univ. Press. 277 pp.

Steele KW, Daniel RM. 1978. Fractionation of nitrogen isotopes by animals: a further complication to the use of variations in the natural abundance of ^{15}N for tracer studies. *J. Agric. Sci.* 90:7–9

Stern LA, Johnson GD, Chamberlain CP. 1994. Carbon isotope signature of environmental change found in fossil ratite eggshells from a South Asian Neogene sequence. *Geology* 22:419–22

Steuter AA, Jasch B, Ihnen J, Tieszen LL. 1990. Woodland/grassland boundary changes in the middle Niobrara valley of Nebraska identified by $\delta^{13}C$ values of soil organic matter. *Am. Midl. Nat.* 124:301–8

Stott AW, Evershed RP. 1996. $\delta^{13}C$ analysis of cholesterol preserved in archaeological bones and teeth. *Anal. Chem.* 68:4402–8

Stott LD, Sinha A, Thiry M, Aubry M-P, Berggren WA. 1996. Global $\delta^{13}C$ changes across the Paleocene-Eocene boundary; criteria for terrestrial-marine correlations. In *Correlation of the early Paleogene in Northwest Europe*, ed. RWO'B Knox, RM Corfield, RE Dunay, *Geol. Soc. Spec. Publ.* 101:381–99. London: Geol. Soc. London

Stuart-Williams HLQ, Schwarcz HP. 1997. Oxygen isotopic determination of climatic variation using phosphate from beaver bone, tooth enamel, and dentine. *Geochim. Cosmochim. Acta* 61:2539–50

Swart PK, Lohmann KC, McKenzie J, Savin S, eds. 1993. *Climate Change in Continental Isotope Records, Geophys. Monogr. 78.* Washington, DC: Am. Geophys. Union. 374 pp.

Tegelaar EW, Kerp JHF, Visscher H, Schenck PA, de Leeuw JW. 1991. Bias of the paleobotanical records as a consequence of variations in the biochemical composition of vascular plant cuticles. *Paleobiology* 17:133–44

Thackeray JF, van der Merwe NJ, Lee-Thorp JA, Sillen A, Lanham JL, et al. 1990. Changes in carbon isotope ratios in late Permian recorded in therapsids tooth apatite. *Nature* 347:751–53

Tieszen LL. 1994. Stable isotopes on the Plains: vegetation analyses and diet determinations. In *Skeletal Biology in the Great Plains*, ed. DW Owsley, RL Jantz, pp. 261–82. Washington, DC: Smithson. Inst.

Tieszen LL, Boutton TW, Tesdahl KG, Slade NA. 1983. Fractionation and turnover of stable carbon isotopes in animals tissues: implications for $\delta^{13}C$ analysis of diet. *Oecologia* 57:32–37

Tieszen LL, Fagre T. 1993. Effect of diet quality and composition on the isotopic composition of respiratory CO_2, bone collagen, bioapatite and soft tissue. See Lambert & Grupe 1993, pp. 121–55

Tieszen LL, Reed BC, Bliss NB, Wylie BK, Dejong DD. 1997. NDVI, C-3 and C-4 production and distributions in Great Plains grassland land cover classes. *Ecol. Appl.* 7:59–78

Tuross N, Fogel ML, Hare PE. 1988. Variability in the preservation of the isotopic composition of collagen from fossil bone. *Geochim. Cosmochim. Acta* 52:929–35

Urey HC. 1947. The thermodynamic properties of isotopic substances. *J. Chem. Soc. London,* pp. 562–81

van der Merwe NJ. 1982. Carbon isotopes, photosynthesis, and archaeology. *Am. Sci.* 70:596–606

van der Merwe NJ, Medina E. 1991. The canopy effect, carbon isotope ratios and foodwebs in Amazonia. *J. Archaeol. Sci.* 18:249–59

Van Soest PJ. 1982. *Nutritional Ecology of the Ruminant.* Corvallis, OR: O & B Books

Virginia RA, Delwiche CC. 1982. Natural ^{15}N abundance of presumed N_2-fixing and non-N_2-fixing plants from selected ecosystems. *Oecologia* 54:317–25

von Schirnding Y, van der Merwe NJ, Vogel JC. 1982. Influence of diet and age on carbon isotope ratios in ostrich eggshell. *Archaeometry* 24:3–20

Wang Y, Cerling TE. 1994. A model of fossil tooth and bone diagenesis: implications for paleodiet reconstructions from stable isotopes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 107:281–89

Wang Y, Cerling TE, MacFadden BJ. 1994. Fossil horses and carbon isotopes: new evidence for Cenozoic dietary, habitat, and ecosystem changes in North America. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 107:269–79

Wang Y, Cerling TE, Quade J, Bowman JR, Smith GA, et al. 1993. Stable isotopes of paleosols and fossil teeth as paleoecology and paleoclimate indicators: an example from the St. David Formation, Arizona. See Swart et al 1993, pp. 241–48

Webb SD, Hulbert RC Jr, Lambert WD. 1995. Climatic implications of large-herbivore distributions in the Miocene of North America. In *Paleoclimate and Evolution with Emphasis on Human Origins*, ed. ES Vrba, GH Denton, TC Partridge, LH Burckle. New Haven: Yale Univ. Press

Webb T III. 1995. Postglacial magnitudes and rates of vegetation change in eastern North America: implications for the future. In *Preparing for Global Change: A Midwestern Perspective*, ed. GR Carmichael, GE Folk, JL Schnoor, pp. 155–69. Amsterdam: SPB Acad.

Wedin DA, Tieszen LL, Dewey B, Pastor J. 1995. Carbon isotope dynamics during grass decomposition and soil organic matter formation. *Ecology* 76:1383–92

Wing SL. 1998. Late Paleocene–early Eocene floral and climatic change in the Bighorn Basin, Wyoming. In *Late Paleocene-Early Eocene Biotic and Climatic Events*, ed. W Berggren, MP Aubry, S Lucas. New York: Columbia Univ. Press. In press

Wright VP, Vanstone SD. 1991. Assessing the carbon dioxide content of ancient atmospheres using palaeocalcretes: theoretical and empirical constraints. *J. Geol. Soc. London* 148:945–47

Yakir D, DeNiro MJ, Gat JR. 1990. Natural deuterium and oxygen-18 enrichment in leaf water of cotton plants grown under wet and dry conditions: evidence for water compartmentation and its dynamics. *Plant Cell Environ.* 13:49–56

Yapp CJ. 1987. Oxygen and hydrogen isotope variations among goethites (α-FeOOH) and the determination of paleotemperatures. *Geochim. Cosmochim. Acta* 51:355–64

Yapp CJ. 1990. Oxygen isotopes in iron (III) oxides: 1, mineral-water fractionation factors. *Chem. Geol.* 85:329–35

Yapp CJ. 1991. Oxygen isotopes in an oolitic ironstone and the determination of goethite $\delta^{18}O$ values by selective dissolution of impurities: the 5M NaOH method. *Geochim. Cosmochim. Acta* 55:2627–34

Yapp CJ. 1997. An assessment of isotopic equilibrium in goethites from a bog iron and a lateritic regolith. *Chem. Geol.* 135:159–71

Yapp CJ, Epstein S. 1977. Climatic implications of meteoric water over North America (9,500 to 22,000 B.P.) as inferred from ancient wood cellulose C-H hydrogen. *Earth Planet. Sci. Lett.* 34:333–50

Yapp CJ, Poths H. 1996. Carbon isotopes in continental weathering environments and variations in ancient atmospheric CO_2 pressure. *Earth Planet. Sci. Lett.* 137:71–82

Zachos JC, Lohmann KC, Walker JCG, Wise SW. 1993. Abrupt climate change and transient climates during the Paleogene: a marine perspective. *J. Geol.* 101:191–213

Zheng Y-F. 1991. Calculation of oxygen isotope fractionation in metal oxides. *Geochim. Cosmochim. Acta* 55:2299–307

Zheng Y-F, Simon K. 1991. Oxygen isotope fractionation in hematite and magnetite: a theoretical calculation and application to geothermometry of metamorphic iron-formations. *Eur. J. Mineral.* 3:877–86