CHAPTER 4

CONTINENTAL CARBONATES AS INDICATORS OF PALEOCLIMATE

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Contents

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Developments in Sedimentology, Volume 62
ISSN 0070-4571, DOI 10.1016/S0070-4571(09)06204-9

1. INTRODUCTION

The various processes by which carbonates accumulate in continental environments reflect the complex interplay between sediment availability, chemical activity, hydrologic conditions, and biotic productivity, with particular processes, such as abiotic precipitation or pedogenic reworking, dominating in specific environments. Influencing these processes are major overarching controls such as climate and tectonics. Hence, studies of calcareous paleosols, lacustrine and palustrine carbonates have proven immensely useful in research that integrates paleoclimatic and tectonic controls on sedimentation. The utility and temporal resolution of paleoclimate modeling in particular has improved dramatically in recent decades, in part through the increasing reliance on isotopic analyses of lacustrine, palustrine, tufa, speleothem and pedogenic carbonates as paleoclimate archives. The resulting studies have added greatly to our knowledge of climate change through deep time, and have also significantly improved the resolution of more recent (i.e., Quaternary) history, particularly when combined with additional paleoclimate proxies.

Calcrete, the accumulation of $CaCO_3$ in the subsurface environment as nodules or cemented horizons, has proven valuable in paleoenvironmental studies because of its high preservation potential and common association with soil-forming processes in semiarid climates. In addition to climate, however, the morphology and maturity of all paleosols, including those that are calcareous, are controlled by a variety of factors, such as the sediment accumulation rate, which controls the residence time of sediment in the soil-forming environment, vegetative cover, subsurface biotic activity, and host-sediment composition. The controls on the rate of sediment accumulation, which in general is inversely related to paleosol maturity, are particularly complex. Although climate exerts some control over the delivery of sediment to the receiving basin, tectonic activity greatly influences sediment deposition, both through enhancement of sediment production by source-area uplift, and through control of basin configuration and accommodation space.

Lacustrine and palustrine carbonate facies are also recognized as important archives of information on the conditions of subsidence, climate, base level, and clastic sediment supply during deposition. Indeed, the interpretation of the complex interplay of these factors often is no easy task, as changes in one factor, such as tectonics, can mask the variations of others, for example, climate. The true potential for speleothem carbonates and tufas to answer important questions on the timing and duration of climatic events, primarily in regard to the Quaternary, has been recognized only since the 1990s.

The specifics of the depositional controls for the various types of terrestrial carbonates are described in detail in other chapters of this volume (see Alonso-Zarza and Wright, 2009a,b; Arenas-Abad et al., 2009; Frisia and Borsato, 2009; Gierlowski-Kordesch, 2009; Jones and Renaut, 2009). Thus, the purpose of this chapter is not to reiterate mechanisms for the genesis or identification of these deposits, but rather to summarize some of the important methods of interpreting paleoclimatic information from them, and to present the limitations inherent in their use.

2. PEDOGENIC CARBONATES

2.1. Introduction

Historically, a variety of terms have been used to refer to the soluble salts, most commonly $CaCO_3$, that accumulate in the subsurface in soil profiles. The term "caliche" derives from Blake (1902), and has been used widely in the United States, but it has evolved to become largely synonymous with the term "calcrete," defined by Goudie (1983) as indurated masses of carbonate in the sediment subsurface. Because this latter term is nongenetic, that is, calcrete may form by the action of groundwater flow or capillary draw, most authors now prefer the more precise descriptor "pedogenic calcrete" or "pedogenic carbonate" to refer to accumulations of $CaCO_3$ that form by illuviation in the Bk or K horizons of soils. The discussion of the paleoclimatic interpretation of pedogenic carbonates that follows refers to this usage.

2.2. Climatic significance

Precipitation of calcium carbonate in soils involves the same carbonate/bicarbonate equilibria as in aqueous environments,

$$CaCO_3 + H_2CO_3 \approx Ca^{2+} + 2HCO_3^-$$

where an increase in either H_2O, as soil moisture, or CO_2 from root respiration or aerobic microbial decay drives the reaction to the right (dissolution of $CaCO_3$). Conversely, less water or reduced biotic activity favors precipitation. Hence, the formation of soil carbonate horizons is heavily dependent on the availability of soil moisture. Pedogenic carbonate accumulations are common in Holocene soils in regions where the climate is warm and seasonally to mostly dry (i.e., torric, ustic and xeric soil-moisture regimes). Seasonally dry climates with 100–500 mm mean annual precipitation are thought most conducive to the formation of calcareous soil horizons (Reeves, 1976; Goudie, 1983; Birkeland, 1999). Retallack (2000) points out that the isohyet boundary between calcareous and non-calcareous soils may vary regionally from 350 mm or less to 750 mm or more, depending on temperature and seasonality. The vegetative cover in these regions is quite varied and ranges from desert to grassland prairie to piñon pine-juniper forest, although an important consideration in the study of older relict soils is that the present vegetation and climate regime are not necessarily the same as those that prevailed during the accumulation of the carbonate (Machette, 1985). Moreover, Machette (1985) demonstrated quite clearly that pedogenic carbonate accumulates over time scales that range from 10^3 to over 10^5 years. Hence, paleoclimatic interpretations based on measurements derived from pedogenic carbonate must take the duration of paleosol formation into consideration. Furthermore, as indicated by the equilibrium reaction above, $CaCO_3$ precipitation is controlled also by the availability of $CaCO_3$. Thus, Machette (1985) cautioned that pedogenic carbonate may accumulate in almost any moisture regime if the parent material is sufficiently calcareous.

All too often, geologists relate the presence of pedogenic carbonate in paleosols with the climatic conditions associated with the modern soil order Aridisol, particularly in truncated paleosols (i.e., missing an epipedon). Nevertheless, it is quite clear that calcic B horizons (Bk or K horizons) in modern soils are not limited to this soil order, but may in fact occur also in Alfisols, Mollisols, Vertisols, and Entisols (Figure 1) (Soil Survey Staff, 1998). In part, the inability to accurately relate many paleosols to modern soil classification at the order level prompted Mack et al. (1993) to devise a classification scheme specific for paleosols, one in which those with a Bk or K horizon are classified as Calcisols.

Figure 1 Calcrete nodules are prominent locally in the Upper Triassic Blue Mesa Formation (Chinle Group) in the Four Corners Region of the American Southwest, although the formation commonly displays gley and vertic features. View from Arches National Park, eastern Utah. The scale is 20 cm long.

Commonly, the simple presence or absence of calcareous horizons in paleosols is presented as evidence for aridity. Hubert (1978), for example, cited the presence of well-developed calcrete in the Upper Triassic fluvial deposits of the Hartford Basin as evidence that climate during deposition in this rift basin was semiarid, with 100–500 mm mean annual precipitation, rather than tropical humid, as had been interpreted earlier by Krynine (1950). The successive presence and absence of calcrete-bearing paleosols in sedimentary successions has been utilized to interpret changes in climatic regime between less arid and more arid states. Driese and Mora (2002), for example, documented the change from non-calcareous to calcareous paleosols in the Durham subbasin of North Carolina and cited this as evidence of a shift from wetter-to-drier climate conditions during the Carnian–Norian (Late Triassic). As an additional case in point, Miller et al. (1996) interpreted the cyclical alternation between vertic and calcic paleosols in stacked sequences from the Lower Permian (Wolfcampian) of the North American Midcontinent as indicating cyclical climate variations that correlate with the well-known glacial/interglacial cycles of this time interval. Similarly, Tandon and Gibling (1997) described nodular calcretes in the coal-bearing cyclothems of the Upper Carboniferous in the Canadian Maritimes and interpreted this interesting juxtaposition as evidence that arid climate conditions prevailed during glacio-eustatic lowstands, contrasting with the humid climate of the highstands, during which peat accumulated that eventually became coal.

An important caveat to the direct interpretation of general paleoclimatic conditions from pedogenic features is the importance of landscape controls. It has been established clearly that soil morphology is influenced in part by such landscape factors as local topography and drainage (Jenny, 1941; Buol et al., 1997; Soil Survey Staff, 1998; Birkeland, 1999). Soil catenas are suites of laterally equivalent soil profiles that formed contemporaneously on a landscape, and thus record the spatial variations in environmental conditions through their morphological differences. Therefore, the recognition of paleosol catenas can be essential to an accurate interpretation of paleoclimate. Due to differences in hydrologic conditions, different positions on the landscape could yield substantially different interpretations of paleoprecipitation. Tabor et al. (2006) illustrated this well with their study of a catena from the Upper Triassic of the Ischigualasto-Villa Union Basin, Argentina. These authors found well-developed calcic paleosols on the basin margin, where accommodation space and sediment accumulation rates were low, and less-developed, redoximorphic paleosols in the thickest part of the basin fill where sediment accumulation was much more rapid. However, recognition of such paleocatenas is both difficult, due to the degree of outcrop control required, and unusual, for the infrequent preservation of a continuous topographic surface (cf. Ruskin and Jordan, 2007). Nonetheless, the understanding and recognition that paleosols formed on floodplain surfaces closer to the channel axes are more likely to be redoximorphic than distally formed paleosols could prove invaluable to the correct interpretation of paleoclimate (cf. Mack, 1992).

2.3. Calcrete morphology

Many workers have observed that the ongoing accumulation of carbonate in relict soils allows for a continuous increase in the "maturity" of the calcic horizon, that is, a progressive change in morphology through a regular and predictable series of stages. For example, Gile et al. (1966) described four morphological stages of progressive development with time, a conceptual framework that was subsequently augmented by Machette (1985). As Allen (1986) observed, however, it is climate and carbonate flux in conjunction with time that control subsurface carbonate accumulation. Machette (1985) made a study of relict calcic soils and found that soils of similar age from several locations in eastern New Mexico, and forming under similar climatic conditions, varied in morphology by more than one full stage of maturity. He attributed the differences as primarily due to variations in the carbonate flux rate. Hence, morphology alone cannot be used to determine either the age of a soil, or the climate conditions under which the carbonate accumulated; two of these variables must be known to correctly interpret the third.

The criteria for identifying hydromorphic calcareous paleosols, or groundwater calcretes, and distinguishing them from true pedogenic calcretes have received considerable attention, in large part due to the importance of recognizing the paleoclimatic implications of each (Pimentel et al., 1996; Alonso-Zarza, 2003; Alonso-Zarza and Wright, 2009b). Pedogenic carbonate, which is precipitated in the vadose zone, is best distinguished from groundwater calcrete, which is formed by phreatic precipitation, on the basis of the vertical distribution of the carbonate; pedogenic calcretes commonly display an asymmetric profile in which the carbonate horizon has a sharp top and the carbonate content decreases downward. Conversely, groundwater calcrete profiles may be symmetrical or display a carbonate horizon with a sharp base and the carbonate content increases upward. As groundwater calcretes form under conditions of a high water table, their occurrence in stratigraphic sections may signal climate-related changes in base level. For example, Smith (1994) reconstructed a broad paleoclimatic history for late-stage filling of a Neogene extensional basin in south-eastern Arizona by combining data on calcrete morphology with sedimentologic and isotopic data. He found that the occurrence of groundwater calcretes to the exclusion of pedogenic calcretes in the sedimentary section was consistent with other evidence for an increasingly moist climate and higher water tables.

Wright and Tucker (1991) stated that the volume of literature published on the topic of calcrete micromorphology was "enormous," and this volume has grown considerably since. Of particular significance to the present chapter is the topic of alpha and beta fabrics of pedogenic calcrete. The former form ostensibly by abiotic processes involving displacive growth and grain replacement by calcite cement, whereas the latter consist of a variety of features (e.g., *Microcodium*, alveolar septal fabrics) associated with biogenic processes (Wright and Tucker, 1991; Tandon and Kumar, 1999). Hence, alpha fabrics are typically associated with soils forming under more arid conditions and lacking extensive vegetative influence, this despite studies which show that alpha fabrics form in modern soils with up to 50% vegetative cover (Wright and Tucker, 1991). Conversely, beta fabrics, with their extensive evidence of biotic processes, have been associated with semiarid to subhumid climates. Wright and Tucker (1991) suggested, however, that the differences in these fabrics may reflect mainly taphonomic factors; that is, climate does not control which processes occur so much as it governs the preservation of the evidence of this activity. Thus, similar types of biotic activity occur in calcareous soils in a wide range of environments, but the evidence for this activity is not preserved in drier climates.

2.4. Depth to carbonate

McFadden and Tinsley (1985) examined the rate and depth of carbonate accumulation in soils using a compartmental model that considered the rate of carbonate dust accumulation at the surface, the volume of water flowing through the soil, soil porosity and soil temperature. Their model predicted that in a semiarid thermic (15–22°C) climate, the maximum depth of accumulation would be reached after a remarkably short period. In only a few thousand years, the maximum $CaCO_3$ concentration is established at a depth of 25–30 cm in sandy alluvium, and at depths of 40–50 cm in gravelly alluvium. They also noted that their model predicted that a non-calcareous B-horizon could not form in an arid, hyperthermic (>22°C) climate regime. These modeling results accorded well with their observations of the depth and age of carbonate accumulation in Holocene soils.

The precipitation of calcium carbonate at depth in a soil profile occurs as carbonate solubility is lost in meteoric waters, which are naturally acidic due to dissolution of atmospheric and soil-respired CO_2. In part, the depth at which conditions of calcium-carbonate solubility change to insolubility is controlled by the flow of water through the vadose zone, that is, meteoric precipitation. Jenny and Leonard (1934), in the first study of its kind, were able to demonstrate a correlation between mean annual precipitation and depth to the carbonate horizon for 104 soils ($r^2 = 0.64$). Numerous authors have applied this general relationship to paleosols as a proxy for paleoprecipitation (e.g., Blodgett, 1988; Retallack, 1994; Quade and Cerling, 1995; Caudill et al., 1996). Blodgett (1988), for example, in his study of the calcareous paleosols of the Upper Triassic Dolores Formation, Colorado, found that the relationship of Jenny and Leonard (1934) predicted

Figure 2 Calcretes of the Upper Triassic Dolores Formation, in southwestern Colorado, commonly exhibit vertically stacked nodules, or rhizocretions, and other features of biotic activity. Photo from roadcut north of Dolores, Colorado.

that these soils formed under conditions of 400 mm annual precipitation. Blodgett (1988) noted, however, the abundance of biotic features (beta fabrics) in the Dolores Formation (Figure 2). Additionally, Blodgett remarked that sedimentary evidence and paleolatitudinal reconstructions for North America in the Late Triassic supported an interpretation of a strongly seasonal climate. Noting further that the relationship of Jenny and Leonard (1934) is not necessarily valid under these conditions, Blodgett (1988) concluded that the mean paleoprecipitation during formation of the Dolores paleosols was likely greater than 400 mm. Retallack (1994) refined this relationship with his own compilation of depth to the carbonate-bearing horizons in Quaternary soils and derived the following relation between mean annual precipitation (*P*) and depth (*D*),

$$P = 139.6 - 6.388D - 0.01303D^2$$

for which the correlation coefficient $r^2 = 0.79$. In describing this relationship, Retallack (1994) noted the importance of identifying potential confounding factors. These include: (1) the erosional truncation of paleosols, as a complete profile is required for the depth measurement (Figure 3); (2) quantifying the consequence of compaction of the sediments, which reduces the soil thickness; and (3) the effect of varying atmospheric $p\mathrm{CO}_2$, which can cause variations in the depth of carbonate accumulation. Mack (1997) added that paleosols with a K horizon are not well suited for this measurement as the impermeable, plugged horizon causes subsequent carbonate accumulation to occur progressively higher within the soil profile.

Royer (1999) critiqued the depth to carbonate/mean annual precipitation relationship with a test of measurements to the top of the carbonate horizon in 1,168 modern soil profiles and found no correlation ($r^2 = 0.03$). Royer did find that including data of previous studies (Jenny and Leonard, 1934; Retallack, 1994) with the new data improved the correlation ($r^2 = 0.31$), but still advised against use of depth to carbonate measurements as a close indicator of paleoprecipitation, and suggested that these measurements be combined with other observations (e.g., floral assemblages, leaf physiognomy, soil clay mineralogy). Nonetheless, the data showed a robust correlation between the presence of soil carbonate at any depth and mean annual precipitation of <760 mm.

Retallack (2000, 2005) countered that Royer's (1999) data set included soils of greatly varying ages (i.e., young to relict) that compromised the study, and also that it included thin soils formed on steep slopes and bedrock. Royer (2000) replied that even though the relationship of Retallack (1994) is most commonly applied to paleosols in which the depth to carbonate $D < 100$ cm, the correlation is particularly weak ($r^2 = 0.38$) if all soils with $D > 100$ cm are eliminated from the compilation. Lastly, Retallack (2005) presented a new compilation of 807 measurements from soils formed exclusively on sedimentary parent materials. The soils represented a range of

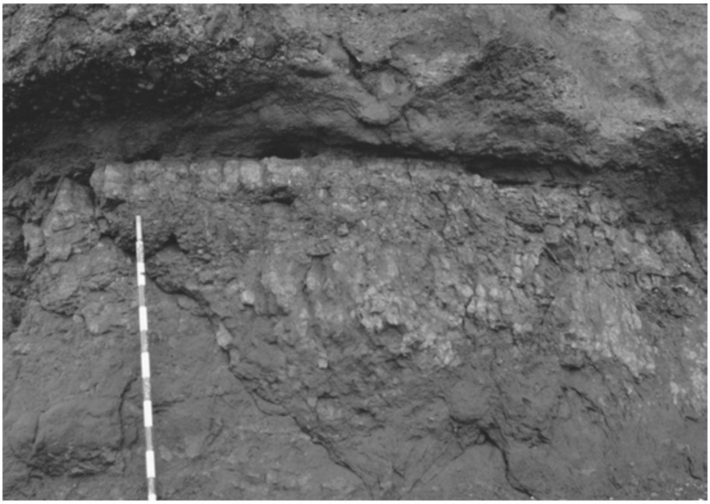

Figure 3 Calcrete in the Lower Jurassic McCoy Brook Formation, near Parrsboro, Nova Scotia, featuring a plugged upper layer, or K horizon. The profile is sharply truncated by overlying stream channel sandstones, and so is unsuitable for a depth to calcareous horizon measurement. The similarity in isotopic composition of calcrete from this formation to calcretes from various Upper Triassic formations was cited by Tanner et al. (2001) as evidence for relative stability of atmospheric $p\mathrm{CO}_2$ across the Triassic/Jurassic boundary. The divisions on the staff are 10 cm.

climatic conditions spanning hyperarid to subhumid. In this study, Retallack found that depth (*D*) to the carbonate horizon correlated well ($r^2 = 0.52$) with mean annual precipitation (*P*) through the nonlinear function:

$$P = 137.24 + 6.45D - 0.013D^2$$

This study also found that the mean annual range of precipitation (the difference between the wettest and driest months) correlated well ($r^2 = 0.58$) with the thickness of the carbonate nodule-bearing zone; greater seasonal differences resulted in thicker zones, presumably because carbonate precipitated at shallower depths during the dry season is remobilized to greater depths during the wet season. Additionally, Retallack (2005) noted that higher levels of atmospheric $p\mathrm{CO}_2$ resulted in carbonate horizons that are thinner and deeper in the soil profile.

2.5. Isotopic composition

Perhaps no single development has had a greater effect on the utility of pedogenic carbonates in paleoclimatic studies than the routine use of stable-isotope analysis. The analysis of carbon and oxygen isotopes, which can be measured relative to the standards PDB or SMOW (Peedee Belemnite or Standard Mean Ocean Water, respectively), has now become standard practice, in large part for the information it may provide about the paleoenvironment. This topic is given more detailed treatment elsewhere in this volume (Deocampo, 2009), and so will be dealt with here only briefly.

The $\delta^{13}\mathrm{C}$ of pedogenic carbonate is useful for estimating atmospheric paleo-$p\mathrm{CO}_2$, which provides the broader context of paleoclimate within greenhouse and icehouse states (see Royer et al., 2004, for discussion on Phanerozoic climate). Paleo-$p\mathrm{CO}_2$ can be estimated via the diffusion-reaction model (Cerling, 1991, 1999; Ekart et al., 1999),

$$\mathrm{C_a} = \mathrm{S(Z)}\frac{\delta^{13}\mathrm{C_s} - 1.0044^{13}\mathrm{C}_{\Phi} - 4.4}{\delta^{13}\mathrm{C_a} - \delta^{13}\mathrm{C_s}}$$

where $\mathrm{C_a}$ is atmospheric $p\mathrm{CO}_2$, S(Z) is $p\mathrm{CO}_2$ (ppmV) contributed by soil respiration, $\delta^{13}\mathrm{C_s}$ is the isotopic composition of soil CO_2, $\delta^{13}\mathrm{C}_{\Phi}$ is the isotopic composition of soil-respired CO_2, and $\delta^{13}\mathrm{C_a}$ is the isotopic composition of atmospheric CO_2. Obviously, numerous factors control the carbon-isotope composition of soil carbonate: the $\mathrm{C}_3/\mathrm{C}_4$ vegetation ratio; the depth of carbonate accumulation; the temperature of carbonate precipitation; the isotopic composition of atmospheric carbon (a value well constrained by studies of marine carbonates); and soil productivity ($\mathrm{S(Z)} = p\mathrm{CO}_{2\mathrm{soil}} - p\mathrm{CO}_{2\mathrm{atm}}$), which is largely dependent on the climatic regime. Hence, some knowledge of the likely mean soil temperature and soil moisture during carbonate accumulation is required to find $p\mathrm{CO}_2$, as is knowledge of the vegetation type. There is no evidence for C_4 vegetation prior to the Neogene (see review in Cerling, 1999), so this factor is ignored in studies of older paleosols. One caveat to the use of this technique is that the depth of the carbonate within the soil profile is important, as the isotopic composition of carbonate precipitated less than 25 cm below the surface may be influenced by isotopically heavy (compared to the soil-respired CO_2) atmospheric CO_2, particularly in vertic soils. Another is that the paleosol must be free of carbonate inherited from the parent material, because isotopically heavy marine carbonate that is incorporated in pedogenic carbonate introduces an unwanted bias.

Values of paleo-$p\mathrm{CO}_2$ derived from the diffusion-reaction model are similar to values from other sources, such as geochemical modeling (Figure 4; see Berner and Kothavala, 2001, for a review). For example, numerous studies of paleosols have yielded consistent results indicating $p\mathrm{CO}_2$ levels that were 6–12 times higher than modern levels during the early Mesozoic (Cerling, 1991, 1999; Ekart et al., 1999; Tanner et al., 2001), falling in the Late Cretaceous (Ghosh et al., 1995), and falling further through the

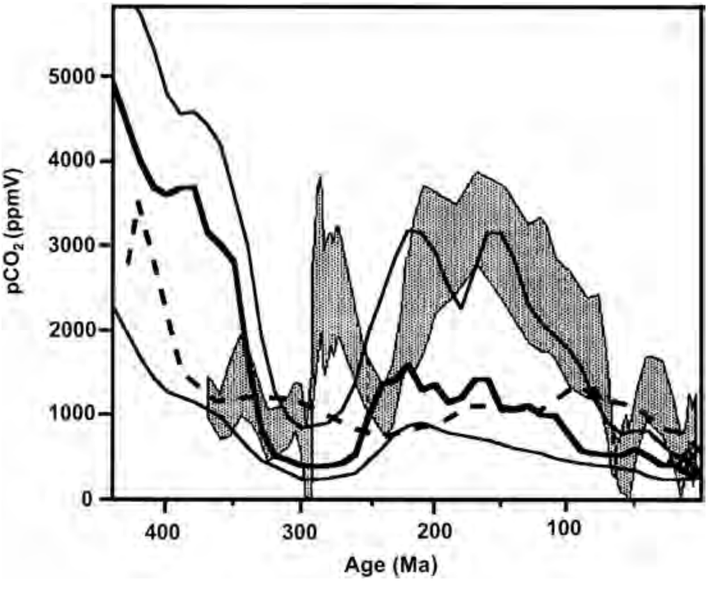

Figure 4 Comparison of $p\mathrm{CO}_2$ calculated from $\delta^{13}\mathrm{C}$ measurements of pedogenic carbonate by the method of Cerling (1991) with geochemical models (adapted from Ekart et al., 1999). The stippled area represents the range of uncertainty of the carbonate-based values. The solid lines are the mean and upper and lower uncertainty limits of the GEOCARB II model of Berner (1994), with the mean value indicated by the heavy line. The dashed line is the model of Worsley et al. (1994).

Cenozoic (Cerling, 1991). Tanner et al. (2001) cited the consistency of the isotopic composition of pedogenic calcretes in paleosols spanning the Triassic–Jurassic boundary (Figure 3) as evidence against an abrupt and sustained increase in paleo-$p\text{CO}_2$ during the Early Jurassic, contrary to earlier assertions based on the isotopic composition of pedogenic goethite and counts of fossil plant stomata (Yapp and Poths, 1996; McElwain et al., 1999).

Plants that use the C_4 photosynthetic pathway produce organic carbon that is isotopically much heavier ($\delta^{13}C = -11$ to -13‰) than that produced by C_3 vegetation ($\delta^{13}C = -24$ to -30‰). Hence, for paleosols formed since the advent of C_4 vegetation, $\delta^{13}C$ may be useful as an indicator of the proportion of C_3/C_4 biomass, and/or record shifts in this proportion over time. This knowledge is useful because the grasses and sedges that use the C_4 photosynthetic pathway typically live in regions with very warm growing seasons, that is, temperate-to-tropical biomes, while C_3 vegetation, which includes trees, shrubs and cool-season grasses, inhabit a wider range of biomes (Deines, 1980). Exemplary studies employing $\delta^{13}C$ of soil carbonate to determine the relative contributions of C_3 and C_4 vegetation include those by Quade et al. (1989), Koch et al. (1995), Quade and Cerling (1995), Slate et al. (1996), Fox and Koch (2003), Levin et al. (2004), and Behrensmeyer et al. (2007). Some studies have examined lateral variations in carbonate $\delta^{13}C$ at individual stratigraphic levels that can be explained as due to variations in the distribution of C_3 and C_4 vegetation (Levin et al., 2004; Behrensmeyer et al., 2007).

Kraus (1999) reviewed the techniques of analyzing paleosols and pointed out the limitations of isotopic analysis. In particular, a pedogenic origin of the carbonate must be verifiable. Pedogenic carbonate may be subject to post-depositional modification/contamination by carbonate precipitated from groundwater and by burial diagenesis. Both processes have the potential to yield carbonate with isotopic compositions that differ substantially from that of pedogenic carbonate. As noted by Cerling (1991), however, diagenesis seems to affect the isotopic composition of carbon substantially less severely than it does oxygen. Additionally, Driese and Mora (1993) noted (as described above) in a study of Devonian paleosols that the vertic fractures that characterize Vertisols allow isotopically heavy atmospheric CO_2 to penetrate deeper into the soil and influence the isotopic composition of the carbonate. Driese and Mora (1993) found that rhizoliths that formed deeper in the soil profile yielded much more reliable isotopic results than nodules that formed at a shallower level. Conversely, Tanner (1996) found the opposite effect in examining Upper Triassic and Lower Jurassic calcareous paleosols in the Fundy Basin, Nova Scotia; rhizoliths yielded consistently higher $\delta^{13}C$ values than nodules.

Measurements of $\delta^{18}O$ of pedogenic carbonate also have proven useful in paleoclimate studies because $\delta^{18}O_{cc}$ of pedogenic calcite is controlled by both $\delta^{18}O$ of the water from which carbonate crystallizes (meteoric water

$\delta^{18}O_p$), and the mean annual temperature (MAT; T°) of the soil, related through the empirical function of Friedman and O'Neil (1977):

$$\delta^{18}O_{cc(SMOW)} - \delta^{18}O_{p(SMOW)} = 2.78(10^6T^{-2}) - 2.89$$

Thus, pedogenic carbonate becomes increasingly enriched with ^{18}O at higher MATs and evaporation rates (O'Neil et al., 1969; Cerling, 1984; Cerling and Quade, 1993; Yapp, 1993, 2000; Mack, 1997). Mack et al. (1994) applied this principle when they cited the increase in both $\delta^{18}O$ and $\delta^{13}C$ in the Plio-Pleistocene fill of the southern part of the Rio Grande rift (the Camp Rice Formation) in interpreting a trend of increasing temperature and decreasing precipitation, with consequent increase in C_4 vegetative cover. Similarly, Behrensmeyer et al. (2007) interpreted the up-section increase in both $\delta^{18}O$ and $\delta^{13}C$ in paleosols of the Miocene–Pliocene Siwalik Group, northern Pakistan, as recording a decrease in precipitation coeval with the spread of C_4 vegetation.

Use of the function above to obtain quantitative information on paleotemperatures might seem problematic at first, due to the presence of the two unknowns (T° and $\delta^{18}O_p$). Dworkin et al. (2005) noted, however, that these two variables are parametrically correlated through the relation based on the fractionation constant for calcite in water (O'Neil et al., 1969), and that when the regression-line equation for the empirical relationship between T° and $\delta^{18}O_p$ for rainfall in mid-latitudes is combined with the initial function, the following third-order polynomial results:

$$-0.50\,T^3 + (\delta^{18}O_{cc(SMOW)} + 152.04)T^2 - 2.78 \times 10^6 = 0$$

Dworkin et al. (2005) also noted that the data of Cerling and Quade (1993) defines an empirical relationship between T° and $\delta^{18}O_{cc}$ ($r^2 = 0.59$; Dworkin et al., 2005):

$$\delta^{18}O_{cc}‰_{PDB} = 0.49\,T^\circ - 12.65$$

These authors tested the accuracy of the solutions by analyzing at high resolution a sequence of paleosols in West Texas that spans the K/T boundary. Their results indicated that both of the equations above indicate warming events in the Middle and Late Maastrichtian, in addition to a climate event at the boundary, but that the third-order equation above provided a closer correlation to paleotemperature reconstructions from the marine record and from paleobotanical studies.

Tabor and Montañez (2002) investigated latitudinal gradients in paleosol $\delta^{18}O$ for the Late Paleozoic, noting depletion by 6‰ with 10° of latitude from the paleoequator. Mack and Cole (2005), investigating this relationship further, modeled the variation in $\delta^{18}O$ of pedogenic calcite (modern and ancient) versus latitude, and found that $\delta^{18}O$ is a function of the isotopic composition of the meteoric waters, the soil temperature, the percentage of soil–water evaporation, and the depth of precipitation. Tabor et al. (2006) pointed out that due to the significant difference in $\delta^{18}O$ for precipitation in continental interiors, where precipitation is depleted in ^{18}O, versus marine coastal regions where it is enriched (Ferguson et al., 1999), the above equations must be modified for carbonate precipitated in soils in marine coastal environments.

Kraus (1999) issued important caveats for the use of the isotopic composition of pedogenic carbonate for paleoclimatic interpretations. First, paleosols that spend extremely long residence times in the soil-forming environment may be imprinted by more than one climatic regime; that is, the final isotopic composition may reflect an averaging of MATs (Cerling, 1984). Second, the isotopic composition of pedogenic carbonate may not always result from precipitation in equilibrium with meteoric waters; that is, the carbonate composition may be affected by evaporative enrichment of pore waters (Ferguson et al., 1999; Tabor et al., 2006). Third, burial diagenesis may modify the isotopic composition of the pedogenic carbonate. While the carbon-isotope composition appears relatively immune to diagenetic recrystallization, burial diagenesis generally leads to lower $\delta^{18}O$ values (Driese and Mora, 1993). Due in part to the wide compositional range of the pedogenic carbonate in the Ischigualasto Basin, potentially resulting from deviations from equilibrium precipitation conditions and/or post-depositional alteration, Tabor et al. (2006) declared that calculating a specific paleotemperature for this basin was unrealistic. They stated, however, that broader conclusions were reasonable, for example, that soil formation occurred under cool-to-cold conditions.

Prochnow et al. (2006) utilized a multi-proxy approach in their reconstruction of the Middle to Late Triassic paleoclimate from the study of Moenkopi and Chinle paleosols in eastern Utah. They combined paleoprecipitation estimates from geochemical weathering indices and depth-to-carbonate measurements with paleotemperature calculations from $\delta^{18}O$ of pedogenic carbonate to infer changing environmental conditions that varied from semiarid and mesic-to-thermic conditions during the Anisian, to a subhumid to humid early Carnian and a semiarid to subhumid, thermic to hyperthermic Norian.

3. LACUSTRINE CARBONATES

3.1. Introduction

The presence of a lake on the surface of the Earth reflects the unique convergence of climatic, tectonic, and eustatic factors that cause the impoundment of a water body (Carroll and Bohacs, 1999; Bohacs et al., 2000). Hence, lake sediments are among the most highly prized archives of environmental data. If the influence of the confounding factors of tectonics and eustasy can be controlled, for instance, then variations in organic content, isotopic composition of carbonate, or amount and composition of siliciclastics or evaporites can reveal a history of climate change during deposition. The East African rift lakes, for example, have provided extensive records of the Pleistocene climate that inform our understanding of human evolution (e.g., Scholz et al., 2007). Establishing and qualifying these controlling factors is by no means a simple task, however. As described by Bohacs et al. (2000), the size, chemistry, sedimentology, and biota of lakes vary enormously on temporal and spatial scales both large and small.

3.2. Climatic significance

The deposition of carbonate sediments in lacustrine environments is often associated with semiarid settings. The rationale is that in more humid climates, the aqueous carbonate concentration is likely to be too dilute to facilitate precipitation, and a high siliciclastic influx through surface run-off will overwhelm carbonate sediments; conversely, overly dry climates are not conducive to maintaining perennial water bodies (Dean, 1981; Cecil, 1990; Platt and Wright, 1991; Sanz et al., 1995; De Wet et al., 1998; Gierlowski-Kordesch, 1998). However, as Gierlowski-Kordesch (1998) emphasized, it is important to understand the source of the carbonate in the lake, as some sources of delivery and mechanisms for precipitation are independent of climate. Potential lacustrine carbonate sources include ions dissolved in stream water delivered by overland flow, ions dissolved in spring waters feeding the basin, and clastic grains of carbonate transported to the basin from the sediment source area.

In general, semiarid conditions are indeed favorable for carbonate precipitation, particularly in closed basins where evaporative concentration results in high levels of alkalinity. These conditions may be met regardless of latitude or altitude. Renaut (1994), for example, described carbonate deposition in a modern ephemeral lake in British Columbia, Canada. Although located at high latitude, orographic effects produce a semiarid climate on the interior plateau where this lake is situated. Evidence of semiaridity is often presented in the lacustrine facies through evaporites or stromatolites interbedded with lacustrine carbonates, recording the climatically driven expansion and contraction of ephemeral water bodies (Platt and Wright, 1991).

However, the presence of lacustrine carbonate sediments by itself is in no way an indicator of climate. Indeed, climate, as measured by the ratio of precipitation to evaporation, fails to correlate with (modern and ancient) lake surface area, depth, or volume (Carroll and Bohacs, 1999; Bohacs et al., 2000). Bohacs et al. (2000), in their review, are quite clear on the point that lakes in any single climatic zone may display all variations of size, chemistry, sediment type, and organic productivity due to the extremely local controls operating on each individual lake; in essence, each lake is unique. De Wet et al. (1998), for example, noted the difficulty of accounting for tectonic activity in controlling both the intersection of base level with the basin floor and the delivery rate of siliciclastic sediment. In their study of the lacustrine carbonates in the Upper Triassic New Oxford Formation, Gettysburg Basin, Pennsylvania, they described how within a single closed basin, a variety of lakes may form that represent locally open or closed hydrologic conditions, demonstrating that overall paleoclimatic conditions cannot be inferred from a single lacustrine deposit.

In fact, carbonate sedimentation takes place in lakes in a wide variety of latitudinal and climatic settings. Perhaps the best known modern lakes in which carbonate sedimentation occurs are those in temperate-humid climatic regimes, where examples abound of water bodies that have sediments that are partially or largely carbonate (see review in Dean and Fouch, 1983). A number of lakes of north-central New York State, for example, are at least partially spring-fed by groundwater enriched by circulation through limestones of Silurian to Devonian age. Green Lake, in Onondaga County, is a particularly well-known meromictic lake in which carbonate precipitation occurs year round (Brunskill and Ludlam, 1969; Dean and Fouch, 1983).

Basinal facies of carbonate lakes often display marl/limestone or mudstone/marl laminae that may be seasonal in origin (i.e., varves; Figure 5A). This cyclical variation in sediment composition in carbonate lakes may reflect a seasonal climate in various ways. In many lakes, seasonality appears to mediate the rates of biotic activity in the epilimnion, which controls carbonate precipitation, either through temperature regulation of productivity or potentially through seasonal changes in the supply of limiting nutrients, for example, through controlling seasonal blooms (Kelts and Hsü, 1978; Glenn

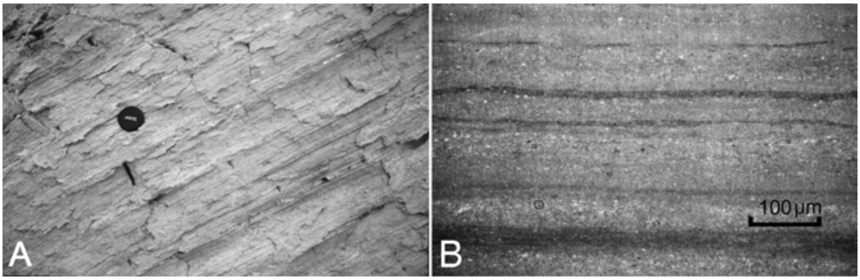

Figure 5 Features of laminated lake sediments of the Miocene–Pliocene Furnace Creek Formation, Death Valley, California. A: Outcrop view of fine lamination in the distal lake deposits. Lightest layers are bedding-parallel veins of secondary gypsum. B: The submillimeter lamination of the Furnace Creek Formation comprises thinner, darker laminae of dense micrite and lighter, coarser laminae that contain fine silt-sized quartz grains.

and Kelts, 1991; Gómez-Fernández and Meléndez, 1991; Tanner, 2002). Alternatively, in some lakes, a siliciclastic-rich component of the couplet is deposited by increased surficial run-off during the wet season, whereas abiotic precipitation is enhanced by evaporative concentration of the surface waters during the dry season (Figure 5B; Dean and Fouch, 1983; Tanner, 2002). Some temperate hard-water lakes have proven value as archives of paleoclimate data. Mullins (1998) used the variation in carbonate content of sediment cores from Cayuga Lake, New York, a northern hard-water lake, to examine a 10,000-year record of climate change. The author demonstrated that Milankovitch forcing of summer insolation during the Holocene Hypsithermal (or Holocene Optimum) created favorable conditions for surface productivity, which resulted in increased biomediated calcite precipitation (up to 55% of the sediment) during this warmer interval.

3.3. Isotopic composition

The isotopic composition of lacustrine primary carbonates (i.e., not of diagenetic origin) has the potential to provide important information on the environmental conditions of the carbonate precipitation. Ideally, the oxygen-isotope composition of abiogenic lacustrine carbonate, which in most ancient lake deposits consists of calcite (Talbot and Kelts, 1990), is controlled solely by the isotopic composition of the lake water and the temperature of precipitation (assuming equilibrium precipitation). The former is a function of the isotopic composition of the inflow into the lake, through precipitation run-off and groundwater flow, and also the residence time of the water. The δ^{18}O of the lake influx is in turn controlled by climatic factors (see Leng and Marshall, 2004, for a thorough review). In general, the δ^{18}O of precipitation ($\delta^{18}O_p$) is related to MAT, which varies strongly by latitude and altitude (Bowen and Wilkinson, 2002). At temperate latitudes, however, $\delta^{18}O_p$ can vary seasonally by 2–8‰, with the greatest variation in continental interiors (Dansgaard, 1964). The impact of seasonal variations on the composition of the lake depends largely on the size of the water body; in large lakes (with residence times of 100+ years), these seasonal changes are averaged out by mixing, but this is not the case in smaller bodies.

As stated above, the δ^{18}O of carbonate precipitated in the lake ($\delta^{18}O_c$) is also dependent on the temperature at which precipitation occurs due to the well-known temperature dependence of isotopic fractionation during equilibrium precipitation. Hence, for abiogenic carbonate precipitated in the surface layer due to photosynthetic mediation, the temperature of precipitation can be calculated, as long as the isotopic composition of the lake waters ($\delta^{18}O_w$) can be estimated. Leng and Marshall (2004) presented the following relationship, derived from the original equations of Craig (1965),

$$T^\circ = 13.8 - 4.5(\delta^{18}O_c - \delta^{18}O_w) + 0.08(\delta^{18}O_c - \delta^{18}O_w)^2$$

where $\delta^{18}O_c$ is measured relative to the standard PDB (or VPDB, for Vienna Peedee Belemnite; Leng and Marshall, 2004) and $\delta^{18}O_w$ is measured relative to SMOW (or VSMOW, for Vienna Standard Mean Ocean Water; Leng and Marshall, 2004). This calculation is intended for calcite only, but it can be adjusted for aragonite and Mg-calcite. Biogenic components of the sediment (e.g., the remains of ostracods) are also likely to have an isotopic signature that differs somewhat from that of abiogenic carbonate. Furthermore, if the remains are of benthic fauna, their composition may be immune to seasonal changes (Leng and Marshall, 2004).

Because evaporation from the surface of a lake preferentially removes lighter molecules, a longer residence time equates with isotopic enrichment with respect to the composition of the inflow (Talbot and Kelts, 1990). Thus, in a hydrologically open basin, where the residence time is short, there will be little isotopic evolution of the $\delta^{18}O$, while the opposite occurs in closed basins. Nevertheless, paleotemperature calculation from $\delta^{18}O_c$ is an important tool in studies of Pleistocene and Holocene climate. For example, Anderson et al. (1997) documented the significant Northern Hemisphere cooling event following the Younger Dryas (at approx. 10–8.2 ka) through the study of the $\delta^{18}O$ of carbonate sediments in Seneca Lake in central New York (Figure 6). A massive influx of isotopically light, glacially derived meltwater through the Great Lakes caused widespread

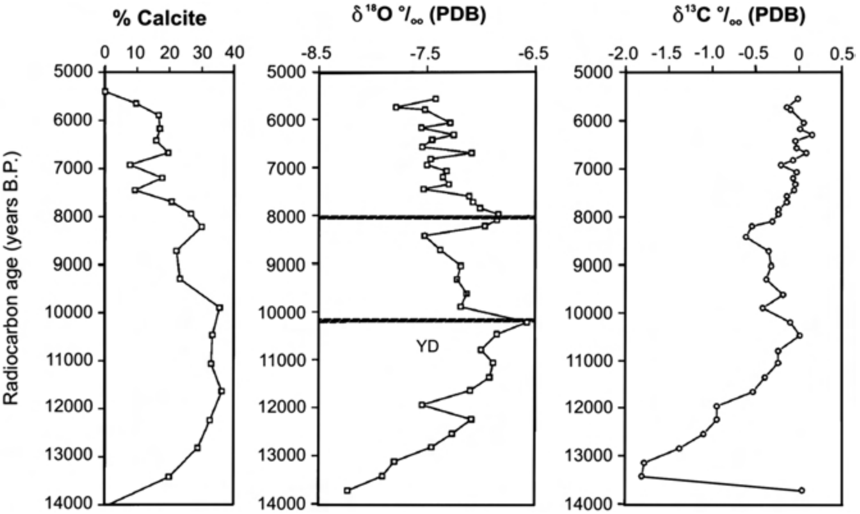

Figure 6 Stable-isotope record of Anderson et al. (1997) obtained from carbonate in a piston core from Seneca Lake, New York. Variations in $\delta^{18}O$ record a weak cooling event between 11 and 10 ka that corresponds to the Younger Dryas (YD), and a stronger regional cooling event between 10.1 and 8.2 ka (bracketed by the horizontal lines).

cooling and led to isotopically light rainfall in downwind areas. Perhaps the true potential of this method for extracting paleoclimatic data is best exemplified by the study of Marshall et al. (2007). In their study of Hawes Water, a hard-water lake in northwest England, the authors combined high-resolution (1-cm intervals) sampling for isotopic analysis with thermal ionization mass spectrometry (TIMS) U-series dating to produce a 2,000-year oxygen-isotope record at a subdecadal scale. Using chironomid midge-larvae population data as an independent temperature control, Marshall et al. (2007) demonstrated a lacustrine record of the 9.3 and 8.2 ka cold events in England. Notably, this study also illustrates the value of multiple paleoclimate proxies.

As there is little temperature-dependent fractionation of carbon isotopes during abiotic precipitation of carbonate, the carbon-isotope composition ($\delta^{13}C$) of lacustrine carbonate is controlled essentially by the isotopic composition of the inorganic carbon (as HCO_3^-) dissolved in the lake. However, this composition is controlled by the complex combination of the isotopic composition of the inflow, the level of biotic productivity, atmospheric exchange, and residence time (Talbot and Kelts, 1990; Leng and Marshall, 2004). The $\delta^{13}C$ of the influx is controlled mainly by geological factors in the catchment. The amount of isotopically depleted soil-respired CO_2 and soil organic carbon that is dissolved in the meteoric waters are important, but bedrock geology is also significant, particularly in the case of isotopically enriched marine limestones that may be dissolved by groundwaters in karst regions. Photosynthetic activity in the surface waters of a lake not only mediates abiotic carbonate precipitation by increasing alkalinity, but also removes isotopically light carbon, thereby causing ^{13}C enrichment of the remaining dissolved HCO_3^-, and subsequently, the precipitated carbonate. Similarly, atmospheric exchange allows diffusion of isotopically light CO_2, with consequent ^{13}C enrichment of the dissolved HCO_3^-.

In general, the carbon- and oxygen-isotope compositions of carbonate precipitated in hydrologically open lakes seem to vary independently of one another (Talbot, 1990; Talbot and Kelts, 1990; Valero-Garcés et al., 1997). Conversely, these isotopes typically display covariance in closed-basin lakes, as evaporation and atmospheric exchange preferentially remove ^{16}O and ^{12}C, respectively, and as carbon-isotope fractionation during photosynthesis further removes ^{12}C. Consequently, the precipitated carbonate is enriched in both ^{18}O and ^{13}C. This covariance between $\delta^{18}O$ and $\delta^{13}C$ is considered a feature that permits the distinction between lakes that are hydrologically open and those that are closed (Alonso-Zarza, 2003). Griffiths et al. (2002) studied the isotopic composition of a sediment core from a lake in central Greece that is palynologically constrained as spanning the last interglacial (MIS 5e) to Early Holocene. The authors noted episodes of covariance that they interpreted as recording periodic hydrologic closure of the basin during arid intervals.

4. PALUSTRINE CARBONATES

4.1. Introduction

The term ‘‘palustrine carbonate’’ often is used to describe the sediments deposited in and around lakes that are ephemeral, resulting in significant episodes of subaerial exposure (Platt, 1989). In fact, the term has broader application to the carbonate muds of low-energy lake margins, ponds in alluvial settings, seasonal wetlands, and even some peritidal settings (Platt and Wright, 1991, 1992; Sanz et al., 1995; see Alonso-Zarza, 2003, for a comprehensive review). It was Freytet (1973) who first suggested that the genesis of palustrine limestones lay in the pedogenic modification of carbonate muds, a concept that was furthered by Esteban and Klappa (1983), who noted that palustrine sediments commonly display pedogenic fabrics similar to those of calcretes.

Palustrine carbonates are frequently associated spatially with lacustrine carbonate facies. Hence, they may be laminated to nonlaminated, and contain charophyte debris, ostracods, gastropods, or other biogenic carbonate grains, but importantly, they display obvious evidence of subaerial exposure, such as microbrecciated to peloidal fabrics with circumgranular cracks, silt-filled fissures, root channels, and mottling (Platt 1989, 1992; Platt and Wright 1992; Armenteros et al., 1997).

4.2. Paleoclimatic significance

The development of palustrine carbonate facies is very sensitive to changes in hydrologic regime, and consequently, to variations in precipitation or groundwater levels. Thus, a spectrum of features record the moisture availability during the formation and subaerial exposure of the sediments; organic-rich facies, for instance, are more likely to be preserved in semi-humid than in semiarid climates. Alternatively, drier climates will cause more intense desiccation, with attendant brecciated and peloidal fabrics, development of microkarst surfaces and, with greater aridity, the formation of evaporites that may be altered subsequently to chert (Platt and Wright, 1992; Alonso-Zarza et al., 1992; Alonso-Zarza, 2003). The isotopic composition of palustrine carbonates does not lend itself to paleoclimatic interpretation, as the potential controlling factors are many, and include the isotopic composition of the original lake waters, the composition of potentially interacting shallow groundwaters, the presence and activity of vegetation on the sediment surface (C_3 or C_4), and the extent and depth of pedogenic modification (Alonso-Zarza, 2003). Several studies have found the isotopic composition of palustrine carbonate to be intermediate between that of contemporaneous lacustrine carbonates and pedogenic carbonates.

Typically, palustrine carbonate is isotopically lighter than the lacustrine carbonate from which it is derived due to pedogenic modification, but the lacustrine origin of the sediments results in the palustrine carbonate being isotopically heavier than laterally equivalent pedogenic carbonate (Platt, 1989; Arenas et al., 1997; Tanner, 2000).

Because many palustrine carbonates appear to be deposited in marginal lacustrine or ephemeral lacustrine settings, stratigraphic sequences containing both lacustrine and palustrine carbonates may be interpreted as the record of climatically driven fluctuations in lake level. For example, in the Lower Cretaceous Rupelo Formation of the West Camaros Basin, northern Spain, Platt (1989) interpreted the association of palustrine and open lacustrine carbonate fabrics as controlled mainly by climatically controlled fluctuations in lake level, with a particularly hyper-arid episode responsible for evaporite deposition.

An interesting case history is provided by the carbonates of the Upper Triassic (Norian) Owl Rock Formation of the Chinle Group, in the Colorado Plateau region of the American Southwest. The upper part of this siliciclastic/carbonate formation is characterized by laterally continuous, meter-scale beds of limestone (Figure 7A). Earlier workers (Blakey and Gubitosa, 1983; Dubiel, 1989, 1993) described these as lacustrine limestones, and interpreted them as deposits of a large lacustrine system centered on the Four Corners region. This interpretation was the basis for an inferred interval of enhanced humidity that interrupted an otherwise semiarid Late Triassic (Dubiel et al., 1991; Parrish, 1993). Other workers, however, recognized pervasive pedogenic fabrics in these beds and suggested that they represented mature (stages III and IV) calcretes and semiarid-to-arid conditions (Lucas and Anderson, 1993; Lucas et al., 1997).

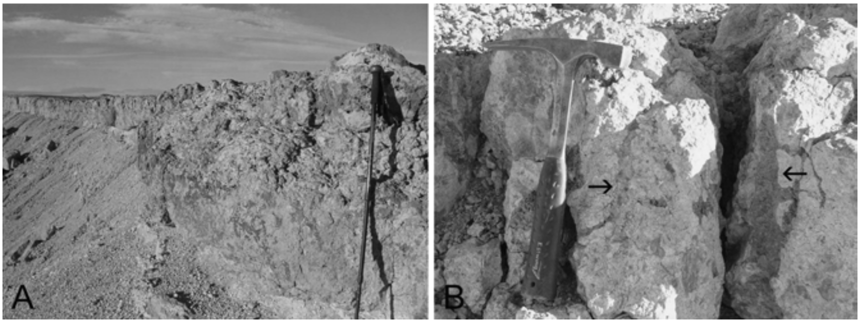

Figure 7 Features of the Upper Triassic Owl Rock Formation, north of Cameron, Arizona. A: Laterally continuous limestone ledges interbedded with redbed mudstones and sandstones characterize the upper part of the formation. The staff is 1.3 m. B: Owl Rock limestones displaying typical brecciated fabrics, root channels (arrows), and mottling.

Tanner (2000) noted the paucity of lacustrine fauna and a lack of open lacustrine fabrics in the Owl Rock limestone, but described the brecciated to peloidal fabrics, pisoliths, spar-filled circumgranular cracks, root channels, and rare calcite pseudomorphs after gypsum (Figure 7B). He interpreted these as palustrine limestones, formed by deposition of carbonates in ponds or wetlands on a sediment-starved floodplain; these sediments were subjected to intense pedogenesis under semiarid conditions during falls in base level. Thus, Tanner (2000) concluded that there was no evidence of a humid interval on the Colorado Plateau during the Norian stage.

5. SPELEOTHEM CARBONATES

5.1. Introduction

The essential mechanics of speleothem formation are quite simple (see review in Fairchild et al., 2006). Speleothems form from the precipitation of $CaCO_3$ (either calcite or aragonite) in subsurface caverns developed in carbonate bedrock, that is, in subsurface karst (Figure 8A). Downward percolating soil waters acidified by dissolved CO_2 (as H_2CO_3) from soil respiration and aerobic decay dissolve $CaCO_3$ in the uppermost zone of the karst aquifer, and continue downward through conduits, becoming supersaturated with respect to carbonate, until they reach cavernous openings. Most caves have near 100% humidity, which prevents evaporation of the drip water.

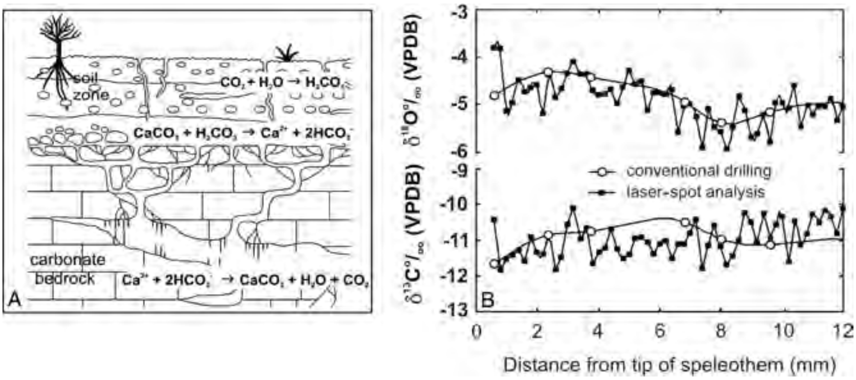

Figure 8 Speleothem carbonate formation and analysis. A: Environment of speleothem carbonate precipitation (adapted from Fairchild et al., 2006). B: Comparison of data obtained by two sampling methods from the top of a speleothem from Gibraltar in which annual laminae are spaced 500—1,000 μm. Conventionally drilled samples obtained at a spacing of 5 mm produced the smoothing trend illustrated. Laser-spot samples were taken at a spacing of 500 μm, with a spot diameter of 250 μm (adapted from Fairchild et al., 2006).

Therefore, CO_2 degassing, not evaporation, causes $CaCO_3$ deposition in isotopic equilibrium with the drip water (McDermott, 2004).

Speleothems, as flowstones, stalactites, and stalagmites typically exhibit growth rates in the range 0.01–1.0 mm per year, depending on cave temperature and the saturation of the drip water. Seasonal changes in water availability may lead to the formation of annual layers, the thickness of which may vary as a response to precipitation changes at the surface. Longer-term decreases in drip water will result in hiatuses in speleothem growth.

5.2. Paleoclimatic significance

Because speleothem carbonates form from $CaCO_3$ precipitated in the subsurface, where the ambient temperature is seasonally stable and near the mean annual surface temperature, speleothem paleoclimate studies initially emphasized attempts to reconstruct paleotemperature time series from the $\delta^{18}O$ of the $CaCO_3$, with age control provided by radiocarbon or U-series dating (see review in Gascoyne, 1992). This is no longer the case, as better understanding of the limitations and complexities of deriving paleotemperature measurements has led to a shift in emphasis. Speleothem isotope measurements now are used for correlating and calibrating records between hemispheres of climate events such as Dansgaard-Oeschger cycles, the Younger Dryas, the 8.2 ka cooling event, and glacial/interglacial transitions (McDermott, 2004; McDermott et al., 2006; Fairchild et al., 2006). Improved sampling and analytical techniques, in particular, precise U-series dating through TIMS, has increased the resolution of the record through decreased sample size (Figure 8B).

Denniston et al. (2007), for example, constructed an approx. 20,000-year Pleistocene $\delta^{18}O$ record, spanning marine isotope stages 5c and 5b, from stalagmites collected in a cave in the Great Basin of the western United States. The authors were able to correlate the observed oxygen-isotope variability in these stalagmites to that of the Greenland ice-core record (GISP2). In particular, they documented isotopic shifts similar in form and duration to Dansgaard-Oeschger events 23 through 21, thus establishing a climate teleconnection between the North Atlantic and the Great Basin. Similarly, Shakun et al. (2007) used an extensive data set (717 analyses) from a single speleothem from Yemen, tied to ^{230}Th dates, to establish a teleconnection between Dansgaard-Oeschger cycles in Greenland and the Indian Ocean.

In theory, changes in $\delta^{18}O$ of meteoric waters, which can be related to a variety of climatic factors (as discussed in Section 3.3 of this chapter), will be recorded in the $\delta^{18}O$ of the speleothem calcite. Ideally, the $\delta^{18}O$ of the water from which the $CaCO_3$ precipitates, the cave drip water, is a weighted annual mean of the $\delta^{18}O$ of the local meteoric water. As well reviewed by McDermott (2004), the local meteoric $\delta^{18}O$ is a function of latitude, altitude, distance to the sea, precipitation volume, and air temperature. Furthermore, this $\delta^{18}O$ is seasonally variable and subject to isotopic enrichment in evaporative environments (cf. Gazis and Feng, 2004). Because speleothems in the same region may form from groundwater traveling different pathways, that is, drip water transferred rapidly from the surface versus water from long-term aquifer storage, some speleothems may record more immediate responses to precipitation events than others. Baker et al. (2007) demonstrated these differences in two contrasting sets of speleothem records from Ethiopia, with one set recording high-frequency climatic "events," and the other low-frequency "storage."

Less commonly applied to paleoclimate study is the $\delta^{13}C$ of the carbonate. In large part, this is because the carbon system for speleothem formation is a partially open system in which the $\delta^{13}C$ of the drip water is derived from a combination of the composition of the dissolved soil-derived CO_2, which in turn is partially a function of the ratio of C_3 to C_4 vegetation and the amount of vegetative cover, in addition to the contribution of the host limestone. However, as noted by McDermott (2004), if the residence time of the soil water is low, these waters may not be in equilibrium with soil–CO_2 and an isotopically heavy atmospheric CO_2 component may be introduced. Nonetheless, the $\delta^{13}C$ of speleothem carbonate does have the potential to document climatic changes by recording climate-driven fluctuations in the soil productivity, the amount of vegetative cover, and/or the C_3/C_4 vegetation ratio.

6. TUFAS

6.1. Introduction

Tufas are bodies of carbonate rock formed by abiogenic or biomediated processes in fresh-water environments under the influence of alkaline-groundwater discharge (*sensu* Pedley et al., 2003). The environments where tufas form include streams, spring margins, lakes, and marshes. In these settings, precipitation takes place at ambient temperatures in water that is in contact with the open air, promoted largely by CO_2 degassing to the atmosphere. For most authors, the temperature of formation distinguishes tufas from travertines, which are considered the deposits of hydrothermal waters (Pedley et al., 2003). Tufas and speleothems are similar in their mechanism of formation, that is, alkalinity rises as CO_2 is lost to the air, promoting the precipitation of $CaCO_3$; additionally, both form at ambient temperatures from meteoric waters, and thus are a proxy record of the same types of environmental information. Commonly, tufas accumulate rapidly, but seasonally, forming millimeter-scale laminations. In temperate climates, these laminae may take the form of annual couplets of alternating dense and porous calcite, potentially reflecting seasonal variations in microbial activity (Andrews, 2006). Tufas differ from speleothems, however, in that they are more rapidly formed, and generally the interval of formation recorded by a single deposit has a shorter duration. Most tufas preserve a record spanning less than 5,000 years, whereas many speleothem records exceed this duration by an order of magnitude or more (Andrews, 2006).

6.2. Isotopic composition

Isotopic analysis of tufas has proven quite useful for paleoclimate research, primarily for studies of the finer details of the Late Pleistocene and Holocene climate (for an excellent review, see Andrews, 2006). Riverine barrage and paludal springline tufas in particular are considered most likely to preserve records of accumulation of sufficient duration and continuity to be appropriate for paleoclimatic analysis (Andrews, 2006). As described above for speleothem carbonates, the δ^{18}O of tufa carbonate is a function of both the temperature at which precipitation occurs and of the δ^{18}O of the water from which the carbonate precipitates. The former is in essence the ambient temperature of the environment of the tufa, while the latter is for the most part the δ^{18}O of the meteoric waters that recharge the aquifer, although this value may be modified (enriched) by evaporation. The δ^{18}O of the meteoric waters (as discussed above) is a regional factor that varies by latitude and altitude, and thus is related to air temperature, although as noted above, the δ^{18}O of precipitation also varies by proximity to the coast, and by "intensity" in the tropics. Most sampling of tufa for isotopic analysis is conducted at the centimeter scale. At this level, variations in δ^{18}O reflect environmental changes that are time-averaged over intervals of years to decades, and so they may be due to either shifts in temperature or the δ^{18}O of the source water.

Ideally, the temperature of precipitation of the tufa carbonate could be calculated through measurement of the $\delta^{18}O_c$ of the carbonate and knowledge of the $\delta^{18}O_w$ of the local meteoric waters. The equation of Hays and Grossman (1991) for meteoric cements, derived from the paleotemperature equation of Craig (1965), is commonly used for this calculation,

$$T^\circ = 15.7 - 4.36(\delta^{18}O_c - \delta^{18}O_w) + 0.12(\delta^{18}O_c - \delta^{18}O_w)^2$$

where $\delta^{18}O_c$ of the tufa calcite is measured relative to the standard PDB (or VPDB) and $\delta^{18}O_w$ of the tufa waters is measured relative to SMOW (or VSMOW). The relationship above assumes equilibrium precipitation. However, this may not be the case very near the discharge source because rapid degassing results in precipitation before the waters have equilibrated to ambient conditions (Andrews, 2006). Equilibration of the groundwaters comes with downstream flow and mixing.

In actual practice, the precise value of $\delta^{18}O_w$ is not known for ancient tufas, but it can be estimated and assumed at a fixed value to allow calculation of the range of local temperature variation. Alternatively, assuming a fixed temperature for tufa formation allows for interpretation of sources of variation of $\delta^{18}O_w$, such as regional climate change or differences in sources of moisture. The uncertainties in the application of the methods and interpretation of the results is well-illustrated by the study of Andrews et al. (2000) of Holocene tufas in southern Spain. Their results, which showed isotopic enrichment of the tufa carbonate in the Middle Holocene (5,000–3,000 radiocarbon years BP), can be interpreted either as a trend of climate warming, or as a shift in the air–mass flow and moisture to a Mediterranean source.

High-resolution (submillimeter) sampling of laminated tufas permits investigation of annual, and even seasonal, changes in the ambient temperature, if the $\delta^{18}O_w$ is known for this time frame. Matsuoka et al. (2001) found, however, that because each lamina represents precipitation across an interval of time during which temperature changes, the temperature recorded by the tufa calcite is time-averaged over a season and that interlayer analyses underestimated the full seasonal range of temperature (Figure 9).

The $\delta^{13}C$ of tufa carbonate is controlled largely by the $\delta^{13}C$ of the dissolved inorganic carbon of the discharge water, which in turn is a function of both the contribution of isotopically light soil carbon and heavy carbon dissolved from the aquifer. Because changes in climate may cause changes in the quantity or type (C_3 vs. C_4) of vegetative cover, these changes may be reflected in the amount or composition of the soil–carbon storage. Andrews et al. (1997) demonstrated this effect in the difference in isotopic composition between contemporaneous high- and low-altitude tufas. Those formed at higher altitudes, where vegetation and soil productivity are lower than at low altitudes, are isotopically heavier due to a smaller contribution of light soil carbon. Zamarreño et al. (1997) interpreted long-term changes (Late Paleocene to Middle Eocene) in tufa carbonate composition as resulting from orogenically triggered orographic effects that altered the extent of vegetative cover. Variations in climate and recharge also can affect the residence time of groundwater in the aquifer, and consequently, the contact time and dissolution of heavy aquifer limestone. Therefore, a drier climate, which equates with decreased recharge rates and longer residence time, will be recorded by increasing $\delta^{13}C$. Garnett et al. (2004) demonstrated this effect in their study of a 4,000-year record from a Holocene tufa from Wateringbury in southern England. Importantly, the authors found that the isotope trend from this tufa matched the trend of Mg/Ca and Sr/Ca. Furthermore, the interpretation of increasingly wet conditions and expansion of forests at the expense of grasslands after 9,050

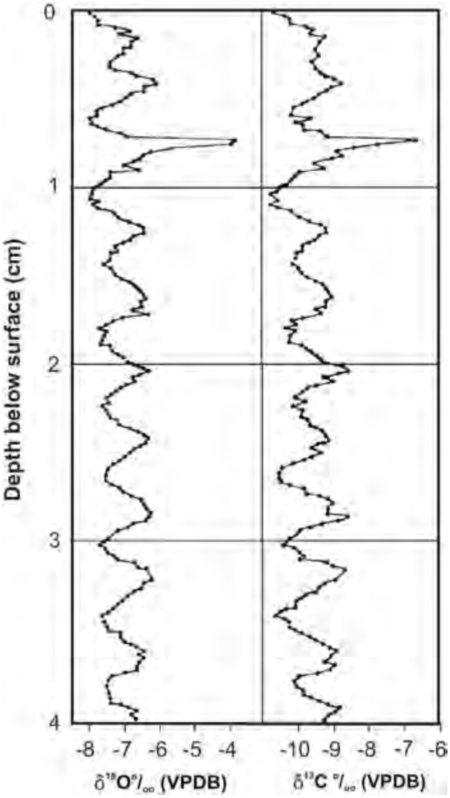

Figure 9 Analysis of tufa by Matsuoka et al. (2001) measured at a resolution of approx. 0.2 mm demonstrates seasonal cycles in isotopic values. Calculation of the seasonal temperature variation from $\delta^{18}O$ underestimated the measured seasonal variation by about 50% (adapted from Andrews, 2006).

years BP is supported by paleontological data, demonstrating again the value of multiple proxies in paleoclimate analysis.

7. SUMMARY

Calcareous paleosols and lacustrine, palustrine, speleothem, and tufa carbonates all have been found particularly useful as paleoclimate proxies. Calcareous paleosols are typically cited as evidence of a semiarid paleoclimate, although calcrete forms in soils under a wide range of conditions of precipitation, seasonality, and temperature. The maturity of calcrete is not by itself useful as a paleoclimate indicator because other variables, such as time and sediment accumulation rate, influence morphology. Micromorphology, however, does show a climatic influence, as alpha fabrics are more clearly associated with drier conditions than beta fabrics. The relationship between the depth to the carbonate horizon and the mean annual precipitation has been a controversial topic, but this relationship has been demonstrated to be applicable to paleosols with complete profiles. The isotopic analysis of pedogenic carbonate is a widely applied tool for paleoenvironmental interpretation. The $\delta^{13}C$ of the carbonate is used to calculate paleo-pCO_2, which provides a broad paleoclimate context. $\delta^{13}C$ also can be used to determine ratios of C_3/C_4 vegetation for soils formed since the advent of the latter. The measurement of $\delta^{18}O$ can be used to calculate the paleo-T° if the $\delta^{18}O$ of the precipitation can be estimated and the carbonate has not been affected by diagenesis.

Lacustrine carbonates in the geological record are often associated with a semiarid climate, although many modern carbonate lakes are found in humid, temperate climates. The $\delta^{18}O$ of lacustrine carbonate may be used for paleotemperature calculations for hydrologically open lakes if the $\delta^{18}O$ of the precipitation can be estimated. In closed-basin lakes, $\delta^{18}O$ and $\delta^{13}C$ typically exhibit covariance due to enrichment from evaporation and atmospheric exchange. Many palustrine carbonates are formed by reworking of lacustrine deposits during lowstands of the base level, which in many instances may be related to climate change (aridification). Specific lithologies associated with palustrine carbonates, such as peat or evaporites, may provide more detailed paleoclimate information. Isotopic analyses of speleothem and tufa carbonates shows that these rocks are important archives of climate data, particularly for the Quaternary. Because $\delta^{18}O$ of these deposits is controlled mainly by the $\delta^{18}O$ of meteoric waters, this measurement is a valuable paleotemperature proxy. Changes in $\delta^{13}C$ over time are linked to changes in vegetative cover, both the density and type (C_3 vs. C_4). Importantly, the information obtained from continental carbonates should be combined with other paleoclimate proxies whenever possible for improved resolution of the paleoclimate record.

ACKNOWLEDGMENT

The success of this manuscript is attributable in part to the editorial assistance of T. van Loon and A. M. Alonso-Zarza, and a helpful review by N. Tabor.

REFERENCES

Allen, J.R.L., 1986. Pedogenic calcretes in the Old Red Sandstone facies (late Silurian-early Carboniferous) of the Anglo-Welsh area, southern Britain. In: Wright, V.P. (Ed.), Paleosols: Their Recognition and Interpretation. Blackwell Scientific, Boston, pp. 58–86.

Alonso-Zarza, A.M., 2003. Palaeoenvironmental significance of palustrine carbonates and calcretes in the geological record. Earth-Science Reviews 60, 261–298.

Alonso-Zarza, A.M., Calvo, J.P., García del Cura, M.A., 1992. Palustrine sedimentation and associated features-grainification and pseudomicrokarst-in the Middle Miocene (Intermediate Unit) of the Madrid Basin, Spain. Sedimentary Geology 76, 43–61.

Alonso-Zarza, A.M, Wright, V.P., 2009a. Calcretes. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Facies, Environments, and Processes. Developments in Sedimentology, Vol. 61, Elsevier, Amsterdam.

Alonso-Zarza, A.M, Wright, V.P., 2009b. Palustrine carbonates. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Facies, Environments, and Processes. Developments in Sedimentology, Vol. 61, Elsevier, Amsterdam.

Anderson, W.T., Mullins, H.T., Ito, E., 1997. Stable isotope record from Seneca Lake, New York; evidence for a cold paleoclimate following the Younger Dryas. Geology 25, 135–138.

Andrews, J.E., 2006. Palaeoclimatic records from stable isotopes in riverine tufas; synthesis and review. Earth-Science Reviews 75, 85–104.

Andrews, J.E., Pedley, H.M., Dennis, P.F., 2000. Palaeoenvironmental records in Holocene Spanish tufas: a stable isotope approach in search of reliable climatic archives. Sedimentology 47, 961–978.

Andrews, J.E., Riding, R., Dennis, P.F., 1997. The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. Palaeogeography, Palaeoclimatology, Palaeoecology 129, 171–189.

Arenas, C., Casanova, J., Pardo, G., 1997. Stable-isotope characterization of the Miocene lacustrine systems of Los Monegros (Ebro Basin, Spain): palaeogeographic and palaeoclimatic implications. Palaeogeography, Palaeoclimatology, Palaeoecology 128, 133–155.

Arenas-Abad, C., Vázquez-Urbez, M., Pardo-Tirapu, G., Sancho-Mercén, C., 2009. Fluvial and associated carbonate deposits. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Facies, Environments, and Processes. Developments in Sedimentology, Vol. 61, Elsevier, Amsterdam.

Armenteros, I., Daley, B., García, E., 1997. Lacustrine and palustrine facies in the Bembridge Limestone (late Eocene, Hampshire Basin) of the Isle of Wight, southern England. Palaeogeography, Palaeoclimatology, Palaeoecology 128, 111–132.

Baker, A., Asrat, A., Fairchild, I.J., Leng, M.J., Wynn, P.M., Bryant, C., Genty, D., Umer, M., 2007. Analysis of the climate signal contained within $\delta^{18}O$ and growth rate parameters in two Ethiopian stalagmites. Geochimica et Cosmochimica Acta 71, 2975–2988.

Behrensmeyer, A.K., Quade, J., Cerling, T.E., Kappelman, J., Khan, I.A., Copeland, P., Roe, L., Hicks, J., Stubblefield, P., Willis, B.J., Latorre, C., 2007. The structure and rate of late Miocene expansion of C_4 plants: evidence from lateral variation in stable isotopes in paleosols of the Siwalik Group, northern Pakistan. Geological Society of America Bulletin 119, 1486–1505.

Berner, R.A., 1994. GEOCARB II: a revised model of atmospheric CO_2 over Phanerozoic time. American Journal of Science 294, 56–91.

Berner, R.A., Kothavala, Z., 2001. GEOCARB III: a revised model of atmospheric CO_2 over Phanerozoic time. American Journal of Science 301, 182–204.

Birkeland, P.W., 1999. Soils and Geomorphology. Oxford University Press, New York, 430 pp.

Blake, W.P., 1902. The caliche of southern Arizona; an example of deposition by the vadose circulation. Transactions of the Society of Mining Engineers of the American Institute of Mining, Metallurgical and Petroleum Engineers, pp. 220–226.

Blakey, R.C., Gubitosa, R., 1983. Late Triassic paleogeography and depositional history of the Chinle Formation, southern Utah and northern Arizona. In: Reynolds, M.W., Dolly, E.D. (Eds), Mesozoic Paleogeography of the West-Central United States. Rocky Mountain Section, Society of Economic Paleontologists and Mineralogists, Denver, pp. 57–76.

Blodgett, R.H., 1988. Calcareous paleosols in the Triassic Dolores Formation, southwestern Colorado. In: Reinhardt, J., Sigleo, W.R. (Eds), Paleosols and Weathering through Time: Principles and Applications. Geological Society of America Special Paper 216, pp. 103–121.

Bohacs, K.M., Carroll, A.R., Neal, J.E., Mankiewicz, P.J., 2000. Lake-basin type, source potential, and hydrocarbon character: an integrated-sequence-stratigraphic – geochemical framework. In: Gierlowski-Kordesch, E.H., Kelts, K.R. (Eds), Lake Basins through Space and Time. American Association of Petroleum Geologists, Studies in Geology 46, pp. 3–34.

Bowen, G.J., Wilkinson, B., 2002. Spatial distribution of $\delta^{18}O$ in meteoric precipitation. Geology 30, 315–318.

Brunskill, G.J., Ludlam, S.D., 1969. Fayetteville Green Lake, New York; physical and chemical limnology. Limnology and Oceanography 14, 817–829.

Buol, S.W., Hole, F.D., McCracken, R.J., Southard, R.J., 1997. Soil Genesis and Classification. Iowa State University Press, Ames, Iowa, 527 pp.

Carroll, A.R., Bohacs, K.M., 1999. Stratigraphic classification of ancient lakes: balancing tectonic and climatic controls. Geology 27, 99–102.

Caudill, M.R., Driese, S.G., Mora, C.I., 1996. Preservation of a paleo-Vertisol and an estimate of late Mississippian paleoprecipitation. Journal of Sedimentary Research 66A, 58–70.

Cecil, C.B., 1990. Paleoclimate controls on stratigraphic repetition of chemical and siliciclastic rocks. Geology 18, 533–536.

Cerling, T.E., 1984. The stable isotopic composition of modern soil carbonate and its relationship to climate. Earth and Planetary Science Letters 71, 229–240.

Cerling, T.E., 1991. Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. American Journal of Science 291, 377–400.

Cerling, T.E., 1999. Stable carbon isotopes in palaeosol carbonates. In: Thiry, M., Simon-Coinçon, R. (Eds), Palaeoweathering, Palaeosurfaces and Related Continental Deposits. International Association of Sedimentologists, Special Publication (Blackwell, Oxford) 27, pp. 43–60.

Cerling, T.E., Quade, J., 1993. Stable carbon and oxygen isotopes in soil carbonates. In: Swart, P.K, Lohmann, K.C., McKenzie, J., Savin, S. (Eds), Climate Change in Continental Isotopic Records. American Geophysical Union, Monograph 78, pp. 217–231.

Craig, H., 1965. The measurement of oxygen isotope palaeotemperatures. In: Tongiorgi, E. (Ed.), Stable Isotopes in Oceanographic Studies and Palaeotemperatures. Consiglio Nazionale Della Richerche, Laboratorio de Geologia Nucleare, Pisa, pp. 161–182.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16, 436–468.

Dean, W.E., 1981. Carbonate minerals and organic matter in sediments of modern north temperate hard-water lakes. Society of Economic Paleontologists and Mineralogists, Special Publication 31, pp. 213–231.

Dean, W.E., Fouch, T.D., 1983. Lacustrine environment. In: Scholle, P.A., Bebout, D.G., Moore, C.H. (Eds), Carbonate Depositional Environments. American Association of Petroleum Geologists Memoir 33, pp. 97–130.

Deines, P., 1980. The isotopic composition of reduced organic carbon. In: Fritz, P., Fontes, J.C. (Eds), Handbook of Environmental Isotope Geochemistry, Volume 1: The Terrestrial Environment. Elsevier, Amsterdam, pp. 329–406.

Denniston, R.F., Asmerom, Y., Polyak, V., Dorale, J.A., Carpenter, S.J., Trodick, C., Hoye, B., Gonzalez, L.A., 2007. Synchronous millennial-scale climatic changes in the Great Basin and the North Atlantic during the last interglacial. Geology 35, 619–622.

Deocampo, D.M., 2009. The geochemistry of continental carbonates. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Geochemistry, Diagenesis and Settings. Developments in Sedimentology (Elsevier, Amsterdam) 62 (this volume).

De Wet, C., Yocum, D.A., Mora, C., 1998. Carbonate lakes in closed basins: sensitive indicators of climate and tectonics: an example from the Gettysburg Basin (Triassic), Pennsylvania, USA. In: Stanley, K.W., McCabe, P.J. (Eds), Role of Eustasy, Climate and Tectonism in Continental Rocks. Society of Economic Paleontologists and Mineralogists Special Publication 59, pp. 191–209.

Driese, S.G., Mora, C.K., 1993. Physico-chemical environment of pedogenic carbonate formation in Devonian vertic paleosols, central Appalachians, USA. Sedimentology 40, 199–216.

Driese, S.G., Mora, C.K., 2002. Paleopedology and stable-isotope geochemistry of Late Triassic (Carnian-Norian) paleosols, Durham sub-basin, North Carolina, USA; implications for paleoclimate and paleoatmospheric pCO_2. In: Renaut, R.W., Ashley, G.M. (Eds), Sedimentation in Continental Rifts. Society for Sedimentary Geology, Special Publication 73, pp. 207–218.

Dubiel, R.F., 1989. Depositional and paleoclimatic setting of the Upper Triassic Chinle Formation, Colorado Plateau. In: Lucas, S.G., Hunt, A.P. (Eds), Dawn of the Age of the Dinosaurs in the American Southwest. New Mexico Museum of Natural History and Science, Albuquerque, New Mexico, pp. 171–187.

Dubiel, R.F., 1993. Depositional setting of the Owl Rock Member of the Upper Triassic Chinle Formation, Petrified Forest National Park and vicinity, Arizona. In: Lucas, S.G., Morales, M. (Eds), The Nonmarine Triassic. New Mexico Museum of Natural History and Science Bulletin 3, pp. 117–121.

Dubiel, R.F., Parrish, J.T., Parrish, J.M., Good, S.C., 1991. The Pangaean megamonsoon: evidence from the Upper Triassic Chinle Formation, Colorado Plateau. Palaios 6, 347–370.

Dworkin, S.I., Nordt, L., Atchley, S., 2005. Determining terrestrial paleotemperatures using the oxygen isotopic composition of pedogenic carbonate. Earth and Planetary Science Letters 237, 56–68.

Ekart, D.D., Cerling, T.E., Montanez, I.P., Tabor, N.J., 1999. A 400-million year carbon isotope record of pedogenic carbonate: implications for paleoatmospheric carbon dioxide. American Journal of Science 299, 805–827.

Esteban, M., Klappa, C.F., 1983. Subaerial exposure environments. In: Scholle, P.A., Bebout, D.G., Moore, C.H. (Eds), Carbonate Depositional Environments. American Association of Petroleum Geologists Memoir 33, pp. 1–96.

Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Mattey, D., McDermott, F., 2006. Modification and preservation of environmental signals in speleothems. Earth-Science Reviews 75, 105–153.

Ferguson, K.M., Gregory, R.T., Constantine, A., 1999. Lower Cretaceous (Aptian-Albian) secular changes in the oxygen and carbon isotope record from high paleolatitude, fluvial sediments, southeast Australia: comparisons to the marine record. In: Barrera, E., Jonson, C.C. (Eds), Evolution of the Cretaceous Ocean-Climate System. Geological Society of America, Special Paper 332, pp. 59–72.

Fox, D.L., Koch, P.L., 2003. Tertiary history of C_4 biomass in the Great Plains, USA. Geology 31, 809–812.

Freytet, P., 1973. Petrography and paleo-environment of continental carbonate deposits with particular reference to the Upper Cretaceous and Lower Eocene of Languedoc (Southern France). Sedimentary Geology 10, 25–60.

Friedman, I., O'Neil, J.R., 1977. Compilation of stable isotopes of geochemical interest. U.S. Geological Survey Professional Paper 440-K, 12 pp.

Frisia, S., Borsato, A., 2009. Karst. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Facies, Environments, and Processes. Developments in Sedimentology, Vol. 61, Elsevier, Amsterdam.

Garnett, E.R., Andrews, J.E., Preece, R.C., Dennis, P.F., 2004. Climatic change recorded by stable isotopes and trace elements in a British Holocene tufa. Journal of Quaternary Science 19, 251–262.

Gascoyne, M., 1992. Palaeoclimate determination from cave calcite deposits. Quaternary Science Reviews 11, 609–632.

Gazis, C., Feng, X., 2004. A stable isotope study of soil water: evidence for mixing and preferential flow paths. Geoderma 119, 97–111.

Ghosh, P., Bhattacharya, S.K., Jani, R.A., 1995. Palaeoclimate and palaeovegetation in Central India during the Upper Cretaceous based on stable isotope composition of the palaeosol carbonates. Palaeogeography, Palaeoclimatology, Palaeoecology 114, 285–296.

Gierlowski-Kordesch, E.H., 1998. Carbonate deposition in an ephemeral siliciclastic alluvial system: Jurassic Shuttle Meadow Formation, Newark Supergroup, Hartford Basin, USA. Palaeogeography, Palaeoclimatology, Palaeoecology 140, 161–184.

Gierlowski-Kordesch, E.H., 2009. Lacustrine carbonates. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Facies, Environments, and Processes. Developments in Sedimentology, Vol. 61, Elsevier, Amsterdam.

Gile, L.H., Peterson, F.F., Grossman, R.B., 1966. Morphological and genetic sequences of accumulation in desert soils. Soil Science 100, 347–360.

Glenn, C.R., Kelts, K., 1991. Sedimentary rhythms in lake deposits. In: Einsele, G., Ricken, W., Seilacher, A. (Eds), Cycles and Events in Stratigraphy. Springer, Berlin, pp. 188–221.

Gómez-Fernández, J.C., Meléndez, N., 1991. Rhythmically laminated lacustrine carbonates in the Lower Cretaceous of La Serranía de Cuenca basin (Iberian Ranges, Spain). In: Anadon, P., Cabrera, L., Kelts, K. (Eds), Lacustrine Facies Analysis. International Association Sedimentologists, Special Publication (Blackwell, Oxford) 13, pp. 245–256.

Goudie, A.S., 1983. Calcrete. In: Goudie, A.S., Pye, K. (Eds), Chemical Sediments and Geomorphology. Academic Press, New York, pp. 93–131.

Griffiths, S.J., Street-Perrott, F.A., Holmes, J.A., Leng, M.J., Tzedakis, C., 2002. Chemical and isotopic composition of modern water bodies in the Lake Kopais Basin, central Greece; analogues for the interpretation of the lacustrine sedimentary sequence. Sedimentary Geology 148, 79–103.

Hays, P.D., Grossman, E.L., 1991. Oxygen isotopes in meteoric calcite cements as indicators of continental palaeoclimate. Geology 19, 441–444.

Hubert, J.F., 1978. Paleosol caliche in the New Haven Arkose, Newark Supergroup, Connecticut. Palaeogeography, Palaeoclimatology, Palaeoecology 24, 151–168.

Jenny, H., 1941. Factors of Soil Formation. McGraw-Hill, New York, 281 pp.

Jenny, H., Leonard, C.D., 1934. Functional relationships between soil properties and rainfall. Soil Science 38, 363–381.

Jones, B., Renaut, R.W., 2009. Calcareous spring deposits in continental settings. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Carbonates in Continental Settings: Facies, Environments, and Processes. Developments in Sedimentology, Vol. 61, Elsevier, Amsterdam.

Kelts, K., Hsü, K.J., 1978. Freshwater carbonate sedimentation. In: Lerman, A. (Ed.), Lakes: Chemistry, Geology, Physics. Springer, Berlin, pp. 295–323.

Koch, P.L., Zachos, J.C., Dettman, D.L., 1995. Stable isotope stratigraphy and paleoclimatology of the Paleogene Bighorn Basin, Wyoming, USA. Palaeogeography, Palaeoclimatology, Palaeoecology 115, 61–89.

Kraus, M.J., 1999. Paleosols in clastic sedimentary rocks: their geologic applications. Earth-Science Reviews 47, 41–70.

Krynine, P.D., 1950. Petrology, stratigraphy, and origin of the Triassic sedimentary rocks of Connecticut. Bulletin of the State Geological and Natural History Survey of Connecticut 73, 1–239.

Leng, M.J., Marshall, J.D., 2004. Palaeoclimate interpretation of stable isotope data from lake sediment archives. Quaternary Science Reviews 23, 811–831.

Levin, N.E., Quade, J., Simpson, S.W., Semaw, S., Rogers, M., 2004. Isotopic evidence for Plio-Pleistocene environmental change at Gona, Ethiopia. Earth and Planetary Science Letters 219, 93–110.

Lucas, S.G., Anderson, O.J., 1993. Calcretes of the Upper Triassic Owl Rock Formation, Colorado Plateau. In: Lucas, S.G., Morales, M. (Eds), The Nonmarine Triassic. New Mexico Museum of Natural History and Science Bulletin 3, pp. G32–G41.

Lucas, S.G., Heckert, A.B., Estep, J.W., Anderson, O.J., 1997. Stratigraphy of the Upper Triassic Chinle Group, Four Corners region. New Mexico Geological Society, Guidebook 48, 81–108.

Machette, M.N., 1985. Calcic soils of the southwestern United States. In: Weide, D.L. (Ed.), Soils and Quaternary Geology of the Southwest United States. Geological Society of America, Special Paper 203, pp. 1–21.

Mack, G.H., 1992. Paleosols as an indicator of climatic change at the Early–Late Cretaceous boundary, southwestern New Mexico. Journal of Sedimentary Petrology 62, 483–494.

Mack, G.H., 1997. Paleosols for Sedimentologists. Geological Society of America, Short Course Notes, 114 pp.

Mack, G.H., Cole, D.R., 2005. Geochemical model of $\delta^{18}O$ of pedogenic calcite versus latitude and its application to Cretaceous palaeoclimate. Sedimentary Geology 174, 122–155.

Mack, G.H., Cole, D.R., James, W.C., Girodano, T.H., Salyards, S.L., 1994. Stable oxygen and carbon isotopes of pedogenic carbonates as indicators of Plio-Pleistocene paleoclimate in the southern Rio Grande rift, south-central New Mexico. American Journal of Science 294, 621–640.

Mack, G.H., James, W.C., Monger, H.C., 1993. Classification of paleosols. Geological Society of America Bulletin 105, 129–136.

Marshall, J.D., Lang, B., Crowley, S.F., Weedon, G.P., Van Calsteren, P., Fisher, E.H., Holme, R., Holmes, J.A., Jones, R.T., Bedford, A., Brookes, S.J., Blomendal, J., Kiriakoulakis, K., Ball, J.D., 2007. Terrestrial impact of abrupt changes in the North Atlantic thermohaline circulation; early Holocene, UK. Geology 35, 639–642.

Matsuoka, J., Kano, A., Oba, T., Watanabe, T., Sakai, S., Seto, K., 2001. Seasonal variation of stable isotopic compositions recorded in a laminated tufa, SW Japan. Earth and Planetary Science Letters 192, 31–44.

McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a review. Quaternary Science Reviews 23, 901–918.

McDermott, F., Schwarcz, H.P., Rowe, P.J., 2006. Isotopes in speleothems. In: Leng, M. (Ed.), Isotopes in Palaeoenvironmental Research, Vol. 10. Springer, Dordrecht, pp. 185–226.

McElwain, J.C., Beerling, D.J., Woodward, F.I., 1999. Fossil plants and global warming at the Triassic-Jurassic boundary. Science 285, 1386–1390.

McFadden, L.D., Tinsley, J.C., 1985. Rate and depth of pedogenic–carbonate accumulation in soils: formulation and testing of a compartment model. In: Weide, D.L. (Ed.), Soil and Quaternary Geology of the Southwestern United States. Geological Society of America, Special Paper 203, pp. 23–41.

Miller, K.B., McCahon, T.J., West, R.R., 1996. Lower Permian-Wolfcampian paleosol-bearing cycles of the U.S. Midcontinent; evidence of climatic cyclicity. Journal of Sedimentary Research 66A, 71–84.

Mullins, H.T., 1998. Environmental change controls of lacustrine carbonate, Cayuga Lake, New York. Geology 26, 443–446.

O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. Journal of Chemical Physics 51, 5547–5558.

Parrish, J.T., 1993. Climate of the supercontinent Pangea. Journal of Geology 101, 215–253.

Pedley, H.M., Martin, J.A.G., Ordóñez Delgado, S., Garcia del Cura, M.A., 2003. Sedimentology of Quaternary perched springline and paludal tufas: criteria for recognition, with examples from Guadalajara Province, Spain. Sedimentology 50, 23–44.

Pimentel, N.L., Wright, V.P., Azevedo, T.M., 1996. Distinguishing early groundwater alteration effects from pedogenesis in ancient alluvial basins: examples from the Palaeogene of southern Portugal. Sedimentary Geology 105, 1–10.

Platt, N.H., 1989. Lacustrine carbonates and pedogenesis: sedimentology and origin of palustrine deposits from the Early Cretaceous Rupelo Formation, W Cameros Basin, N Spain. Sedimentology 36, 665–684.

Platt, N.H., 1992. Fresh-water carbonates from the Lower Freshwater Molasse (Oligocene, western Switzerland); sedimentology and stable isotopes. Sedimentary Geology 78, 81–99.

Platt, N.H., Wright, V.P., 1991. Lacustrine carbonates: facies models, facies distributions and hydrocarbon aspects. In: Anadón, P., Cabrera, L., Kelts, K. (Eds), Lacustrine Facies Analysis. International Association of Sedimentologists, Special Publication 13, pp. 57–74.

Platt, N.H., Wright, V.P., 1992. Palustrine carbonates at the Florida Everglades: towards an exposure index for the fresh-water environment. Journal of Sedimentary Petrology 62, 1058–1071.

Prochnow, S.J., Nordt, L.C., Atchley, S.C., Hudec, M.R., 2006. Multi-proxy paleosol evidence for middle and late Triassic climate trends in eastern Utah. Palaeogeography, Palaeoclimatology, Palaeoecology 232, 53–72.

Quade, J., Cerling, T.E., 1995. Expansion of C4 grasses in the Late Miocene of northern Pakistan: evidence from stable isotopes in paleosols. Palaeogeography, Palaeoclimatology, Palaeoecology 115, 91–116.

Quade, J., Cerling, T.E., Bowman, J.R., 1989. Systematic variations in the carbon and oxygen isotopic composition of pedogenic carbonate along elevation transects in the southern Great Basin, United States. Geological Society of America Bulletin 101, 464–475.

Reeves, C.C., Jr., 1976. Caliche; Origin, Classification, Morphology and Uses. Estacado Books, Lubbock, Texas, 233 pp.

Renaut, R.W., 1994. Carbonate and evaporite sedimentation at Clinton Lake, British Columbia, Canada. In: Rosen, M.R. (Ed.), Paleoclimate and Basin Evolution of Playa Systems. Geological Society of America, Special Paper 289, pp. 49–68.

Retallack, G.J., 1994. The environmental factor approach to the interpretation of palaeosols. In: Amundson, R., Harden, J., Singer, M. (Eds), Factors of Soil Formation: A Fiftieth Anniversary Retrospective. Soil Science Society of America, Madison, Wisconsin, pp. 31–64.

Retallack, G.J., 2000. Depth to pedogenic carbonate horizon as a paleoprecipitation indicator?; discussion. Geology 28, 572–573.

Retallack, G.J., 2005. Pedogenic carbonate proxies for amount and seasonality of precipitation in paleosols. Geology 33, 333–336.

Royer, D.L., 1999. Depth to pedogenic carbonate horizon as a paleoprecipitation indicator?. Geology 27, 1123–1126.

Royer, D.L., 2000. Depth to pedogenic carbonate horizon as a paleoprecipitation indicator?; reply. Geology 28, 573.

Royer, D.L., Berner, R.A., Montanez, I.P., Tabor, N.J., Beerling, D.J., 2004. CO_2 as a primary driver of Phanerozoic climate. GSA Today 14 (3), 4–10.

Ruskin, B.G., Jordan, T.E., 2007. Climate change across continental sequence boundaries; paleopedology and lithofacies of Iglesia basin, northwestern Argentina. Journal of Sedimentary Research 77, 661–679.

Sanz, M.E., Alonso-Zarza, A.M., Calvo, J.P., 1995. Carbonate pond deposits related to semi-arid alluvial systems: examples from the Tertiary Madrid Basin, Spain. Sedimentology 42, 437–452.

Scholz, C.A., Johnson, T.C., Cohen, A.S., Kinge, J.W., Peck, J.A., Overpeck, J.T., Talbot, M.R., Brown, E.T., Kalindekafe, L., Amoako, P.Y.O., Lyons, RP., Shanahan, T.M., Castañeda, I.S., Heil, C.W., Forman, S.L., McHargue, L.R., Beuning, K.R., Gomez, J., Pierson, J., 2007. East African megadroughts between 135 and 75 thousand years ago and bearing on early-modern human origins. Proceedings of the National Academy of Sciences 104, 16416–16421.

Shakun, J.D., Burns, S.J., Fleitmann, D., Kramers, J., Matter, A., Al-Subary, A., 2007. A high-resolution, absolute-dated deglacial speleothem record of Indian Ocean climate from Socotra Island, Yemen. Earth and Planetary Science Letters 259, 442–456.

Slate, J.L., Smith, G.A., Wang, Y., Cerling, T.E., 1996. Carbonate-paleosol genesis in the Plio-Pleistocene St. David Formation, southeastern Arizona. Journal of Sedimentary Research 66, 85–94.

Smith, G.A., 1994. Climatic influences on continental deposition during late-stage filling of an extensional basin, southeastern Arizona. Geological Society of America Bulletin 106, 1212–1228.

Soil Survey Staff, 1998. Keys to Soil Taxonomy, 8th Edition, United States Department of Agriculture, Natural Resources Conservation Service, 321 pp.

Tabor, N.J., Montañez, I.P., 2002. Shifts in Late Paleozoic atmospheric circulation over western equatorial Pangea: insights from pedogenic mineral $\delta^{18}O$ compositions. Geology 30, 1127–1130.

Tabor, N.J., Montanez, I.P., Kelso, K.A., Currie, B., Shipman, T., Colombi, C., 2006. A Late Triassic soil catena: landscape and climate controls on paleosol morphology and chemistry across the Carnian-age Ischigualasto-Villa Union basin, northwestern Argentina. In: Alonso-Zarza, A.M., Tanner, L.H. (Eds), Paleoenvironmental Record and Applications of Calcretes and Palustrine Carbonates. Geological Society of America, Special Paper 416, pp. 17–41.

Talbot, M.R., 1990. A review of the paleohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. Chemical Geology 80, 261–279.

Talbot, M.R., Kelts, K., 1990. Paleolimnological signatures from carbon and oxygen isotopic ratios in carbonates from organic rich lacustrine sediments. In: Katz, B.J. (Ed.), Lacustrine Exploration: Case Studies and Modern Analogues. American Association Petroleum Geologist Memoir 50, pp. 99–112.

Tandon, S.K., Gibling, M.R., 1997. Calcretes at sequence boundaries in Upper Carboniferous cyclothems of the Sydney basin, Atlantic Canada. Sedimentary Geology 112, 43–67.

Tandon, S.K., Kumar, S., 1999. Semi-arid/arid zone calcretes: a review. In: Singhvi, A.K., Derbyshire, E. (Eds), Paleoenvironmental Reconstruction in Arid Lands. A.A. Balkema, Rotterdam, pp. 109–152.

Tanner, L.H., 1996. Pedogenic record of Early Jurassic climate in the Lower Jurassic McCoy Brook Formation, Fundy rift basin, eastern Canada. In: Morales, M. (Ed.), The Continental Jurassic. Museum of Northern Arizona Bulletin 60, pp. 565–574.

Tanner, L.H., 2000. Palustrine-lacustrine and alluvial facies of the (Norian) Owl Rock Formation (Chinle Group), Four Corners Region, southwestern U.S.A.: implications for Late Triassic paleoclimate. Journal of Sedimentary Research 70, 1280–1289.

Tanner, L.H., 2002. Formation of borate deposits in a perennial lacustrine setting, Miocene-Pliocene Furnace Creek Formation, Death Valley Region, USA. Sedimentary Geology 148, 259–273.

Tanner, L.H., Hubert, J.F., Coffey, B.P., McInerney, D.P., 2001. Stability of atmospheric CO_2 levels across the Triassic/Jurassic boundary. Nature 411, 675–677.

Valero-Garcés, B.L., Laird, K., Fritz, S., Kelts, K., Ito, E., Grimm, E., 1997. Holocene climate in the northern Great Plains inferred from sediment stratigraphy, stable isotopes, carbonate geochemistry, diatoms, and pollen at Moon Lake. North Dakota. Quaternary Research 48, 359–369.

Worsley, T.R., Moore, T.L., Fraticelli, C.M., Scotese, C.R., 1994. Phanerozoic CO_2 levels and global temperatures inferred from changing paleogeography. In: Klein, G.D. (Ed.), Pangea: Paleoclimate, Tectonics, and Sedimentation during Accretion, Zenith, and Breakup of a Supercontinent. Geological Society of America, Special Paper 288, pp. 57–73.

Wright, V.P., Tucker, M.E., 1991. Calcretes: an introduction. In: Wright, V.P., Tucker, M.E. (Eds), Calcretes. Blackwell Scientific, New York, pp. 1–22.

Yapp, C.J., 1993. The stable isotope geochemistry of low temperature Fe(III) and Al "Oxides" with implications for continental paleoclimates. In: Swart, P.K, Lohmann, K.C., McKenzie, J., Savin, S. (Eds), Climate Change in Continental Isotopic Records. American Geophysical Union, Monograph 78, pp. 285–294.

Yapp, C.J., 2000. Climatic implications of surface domains in arrays of δD and $\delta^{18}O$ from hydroxyl minerals: goethite as an example. Geochimica et Cosmochimica Acta 64, 2009–2025.

Yapp, C.J., Poths, H., 1996. Carbon isotopes in continental weathering environments and variations in ancient atmospheric CO_2 pressure. Earth and Planetary Science Letters 137, 71–82.

Zamarreño, I., Anadón, P., Utrilla, R., 1997. Sedimentology and isotopic composition of Upper Palaeocene to Eocene non-marine stromatolites, eastern Ebro Basin, NE Spain. Sedimentology 44, 159–176.