Paleoclimatic implications of stable oxygen and carbon isotopes of lacustrine and pedogenic calcite from the Gila Conglomerate (Plio-Pleistocene), Mangas Basin, west-central New Mexico

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PALEOCLIMATIC IMPLICATIONS OF STABLE OXYGEN AND CARBON ISOTOPES OF LACUSTRINE AND PEDOGENIC CALCITE FROM THE GILA CONGLOMERATE (PLIO-PLEISTOCENE), MANGAS BASIN, WEST-CENTRAL NEW MEXICO

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Abstract — Stable carbon and oxygen isotopes of lacustrine (ancient lake Buckhorn) and pedogenic calcite of the Gila Formation (Plio-Pleistocene) in the Mangas Basin, west-central New Mexico, provide information about paleoclimate when compared to similar data from coeval strata in the southern Rio Grande rift near Las Cruces and in the Basin and Range of southeastern Arizona, as well as to modern calcite predicted to precipitate at the sites of the ancient strata. The pedogenic and lacustrine $\delta^{18}O$ values from the ancient strata are more positive than those calculated for corresponding modern sites, implying the existence of air masses whose precipitation was enriched in ^{18}O and/or greater evaporation of lake and soil water during Plio-Pleistocene time compared to today. Although $\delta^{18}O$ values of pedogenic calcite are similar among the ancient strata, the $\delta^{13}C$ values of the Gila Formation are more negative, suggesting a higher proportion of C_3 plants in the Mangas Basin commensurate with cooler and wetter conditions at higher elevation. Differences in $\delta^{13}C$ values of pedogenic calcite *within* the Mangas basin may have resulted from higher water table and concomitant higher percentage of C_3 plants on the river floodplain than on the alluvial fans. The $\delta^{18}O$ and $\delta^{13}C$ values of lake-center ooid limestones of the Gila Formation are more positive than those of the other ancient strata, which could have occurred if lake Buckhorn received precipitation enriched in ^{18}O, had higher rates of evaporation, and/or precipitated limestones during times of diatom and/or algal blooms. In contrast, lake-margin ooid and ostracode limestones of the Gila Formation have significantly lower values of $\delta^{18}O$ and $\delta^{13}C$ compared to the other ancient sites and to the lake-center limestones of the Gila Formation. The low $\delta^{18}O$ values imply that lake-margin sites may have been influenced by water from high-elevation catchments and/or by geothermal waters entering lake Buckhorn via a buried fault, while precipitation of lacustrine calcite during periods of low biological productivity could have produced the low $\delta^{13}C$ values.

INTRODUCTION

Stable carbon and oxygen isotopes of calcite provide important information about the chemical environment from which the calcite precipitated (Bottinga, 1968; O'Neil et al., 1969), and have been applied to lacustrine and pedogenic (soil) calcites as paleoclimate proxies (e.g., Cerling and Hay, 1986; Suchecki et al., 1988; Abell and Williams, 1989; Smith et al., 1993; Mack et al., 1994; Tabor and Montanez, 2002; Nordt et al., 2003). The $\delta^{13}C$ value of pedogenic calcite results from CO_2 that is contributed from oxidation of *in situ* organic matter and from the atmosphere. For late Miocene and younger strata, spatial and temporal variability of pedogenic calcite $\delta^{13}C$ values is controlled by oxidation of organic matter and the relative abundance of plants that use the C_3 and C_4 photosynthetic pathways (Cerling, 1984; Cerling and Quade, 1993). C_4 plants are typically grasses, which have a range of $\delta^{13}C$ values from -10 to -14‰ and are adapted to higher temperature and more moisture-stressed conditions (e.g., Ehleringer, 1991). C_3 plants are typically trees and shrubs, which display a range of $\delta^{13}C$ values from -25 to -30‰ and are adapted to cooler and more humid conditions. Thus, pedogenic calcite that forms in soils with C_3 plants will have more negative $\delta^{13}C$ values than in soils with C_4 plants. The $\delta^{18}O$ of pedogenic calcite is primarily influenced by the isotopic composition of meteoric water, which is related to mean annual temperature and latitude (Fricke and O'Neil, 1999), but may also be affected by soil temperature and evaporation within the soil (Mack and Cole, 2005).

For hydrologically closed lakes, evaporation is the dominant process controlling changes in the $\delta^{13}C$ and $\delta^{18}O$ of the lake water and resultant isotopic composition of lacustrine limestones (Talbot, 1990; Talbot and Kelts, 1990). In addition, the temperature of the lake water affects the isotopic fractionation of oxygen, while biological fractionation of carbon isotopes in the lake water, especially preferential incorporation of ^{12}C into organic matter, may drive the $\delta^{13}C$ values of lacustrine limestones toward more positive values (McKenzie, 1985).

In this study, the concepts described above are applied to the upper Neogene Gila Formation, which was deposited in the Mangas Basin of west-central New Mexico and contains both lacustrine limestones and pedogenic calcite nodules. In order to more fully evaluate the paleoclimatic and paleoenvironmental conditions during deposition of the Gila Formation, isotopic data from calcites in the Gila Formation are compared to data from roughly coeval strata in the southern Rio Grande rift, south-central New Mexico (Mack et al., 1994) and in the southern Basin and Range, southeastern Arizona (Fig. 1; Wang et al., 1993), as well as to modern data from the geographic sites of the older strata.

STRATIGRAPHY AND DEPOSITIONAL SETTING

The Gila Formation (also referred to as Gila Conglomerate) in the Mangas Basin of west-central New Mexico has a maximum exposed thickness of ~280 m and is primarily Pliocene
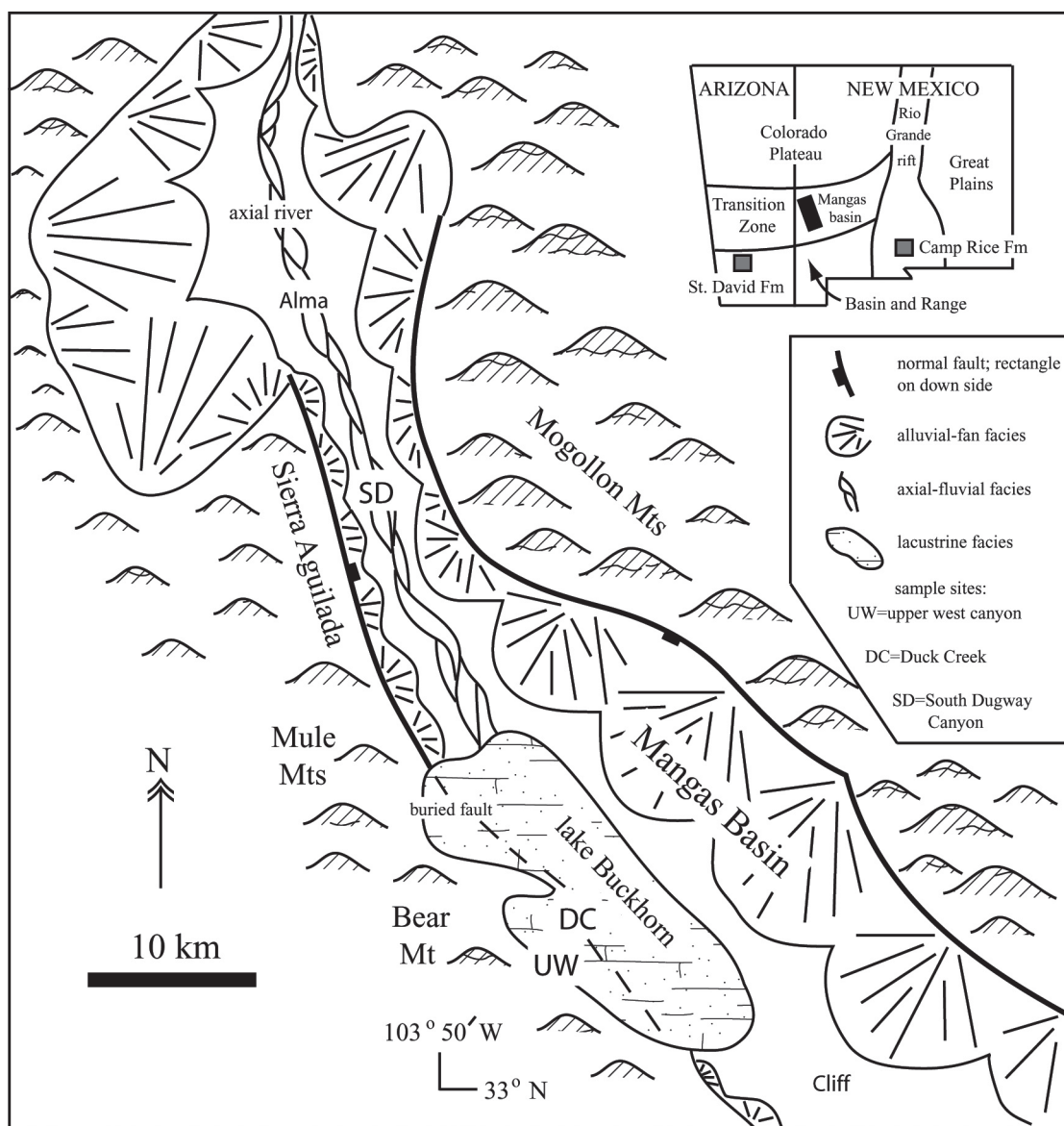
FIGURE 1. Pliocene paleogeographic and paleotectonic map of the Mangas Basin, west-central New Mexico, showing the location of the sample sites from the Gila Formation. Inset map shows the location of the St. David Formation in the Basin and Range of southeastern Arizona and the Camp Rice Formation in the Rio Grande rift of southern New Mexico.

to early Pleistocene in age, although the base may be as old as latest Miocene (Ratte and Finell, 1978; Leopoldt and Kortemeier, 1984; Marvin et al., 1987; Houser, 1987; Morgan et al., 1997). During deposition of the Gila Formation, the Mangas Basin was floored by a closed lake, lake Buckhorn, in which was deposited mudstones, siltstones, sandstones, diatomites, Magadi cherts, and limestones (Figs. 1, 2; Mack and Stout, 2005). Diatomites are most abundant along the western side of the basin, where they contain a high percentage of the species *Denticula thermalis*, which is diagnostic of hot springs (G.W. Andrews, cited in Ratte and Finnell, 1978). This raises the possibility that lake Buckhorn may have been partially fed by geothermal fluids that entered the lake via a buried fault on the western side of the basin (Fig. 1; Mack and Stout, 2005). Lake Buckhorn was flanked by alluvial fans and was fed by a south-flowing axial river, whose deposits

locally display calcic paleosols characterized by stage II morphology calcite nodules and tubules. In addition, paleosols developed in mudstone parent material also display wedge-shaped peds and slickensides, produced by shrinking and swelling of expandable clays (Mack and Stout, 2005).

Samples of the Gila Formation analyzed in this study are from three stratigraphic sections (Fig. 2; Table 1). The upper west canyon and Duck Creek sections display both lacustrine and alluvial-fan facies, and ooid limestones, ostracode limestones, and pedogenic calcite nodules were analyzed. The upper west canyon section is positioned along the western edge of the lake and may overlie a buried fault, while the Duck Creek section occupies a more lake-center location (Mack and Stout, 2005). The South Dugway Canyon section consists of axial-fluvial sediment and was sampled for pedogenic calcite nodules (Fig. 2). Although
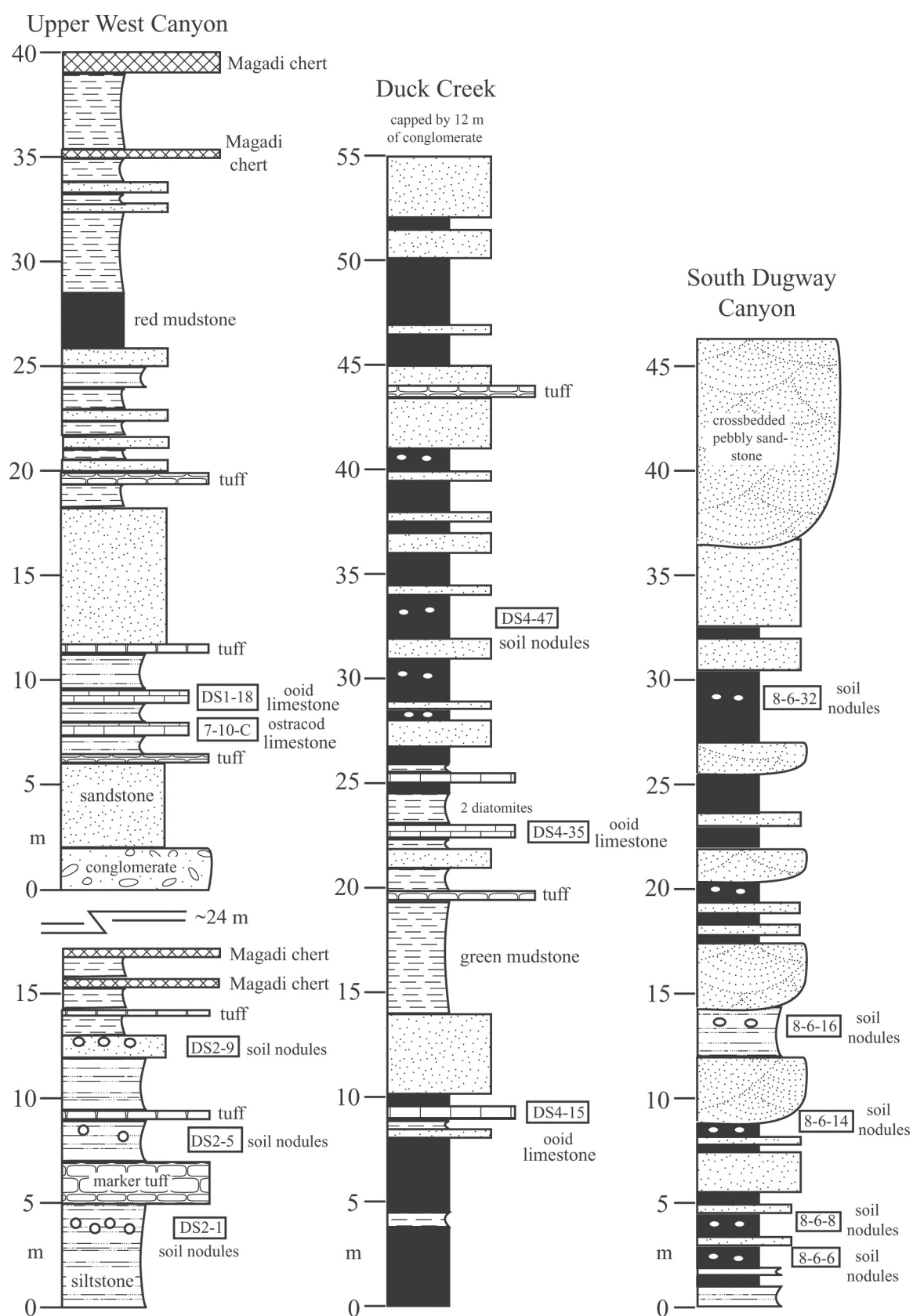
FIGURE 2. Logged sections of the Gila Formation in the Mangas Basin, showing the location of samples of lacustrine limestone and soil (pedogenic) calcite nodules.

age-diagnostic fossils have not been found, the South Dugway Canyon section is considered to be roughly coeval to the lacustrine sections, based on stratigraphic position.

Isotopic data from the Gila Formation are compared to similar data from the Camp Rice Formation in the southern Rio Grande rift and from the St. David Formation in the San Pedro Valley of southeastern Arizona. Both the Camp Rice and St. David formations have been dated as Pliocene to early Pleistocene in age (Wang et al., 1993; Mack et al., 1994). In addition, the isotopic data from lacustrine limestones of the Gila Formation are compared to middle Pleistocene limestones that were fed by springs in the Robledo Mountains, southern Rio Grande rift.

METHODS

Analytical procedures

Lacustrine and pedogenic calcites from the Gila Formation in the Mangas Basin, as well as spring calcites from the Robledo

Mountains in the Rio Grande rift were drilled directly from polished slabs using a table-top drill system with 100 μm diamond bits on an x, y, z stage. X-ray diffraction analysis of these powders confirmed that low-magnesium calcite is the only carbonate present within the samples. Between 5-20 mg of powder was loaded into a reaction vessel and atmospheric gases were evacuated. Samples were then dissolved in 100% H_3PO_4 *in vacuo* at 25° C for ~16 hours to produce CO_2. The CO_2 samples were cryogenically purified and the yield of CO_2 (and weight percent calcite) was determined by mercury manometer. The resulting CO_2 samples were analyzed for carbon and oxygen isotope values using a Finigan MAT 252 isotope ratio mass spectrometer at Southern Methodist University. Isotope values are reported in standard delta notation:

$$\delta^{13}C \text{ (or } \delta^{18}O) = (R_{sample}/R_{standard} - 1) * 1000,$$

where R is the ratio of heavy to light stable isotope present in the sample or standard. The δ values are reported relative to the

TABLE 1. Oxygen and carbon isotope values, as well as wt. % calcite values and stratigraphic information, of samples taken from the Mangas Basin and Robledos Mountains.

Sample Name	$\delta^{18}O$	$\delta^{13}C$	Wt. % Calcite	Stratigaphic Section	Position (m)	Description
Gila Formation, Mangas Basin: axial-fluvial facies (South Dugway Canyon) and alluvial-fan facies (upper west canyon and Duck Creek)						
8-16-14A	-8.5	-8.7	73.8	South Dugway Canyon	9	Paleosol nodules
8-16-14B	-8.8	-8.5	69.5	South Dugway Canyon	9	Paleosol nodules
8-16-16A	-9.9	-8.9	28.6	South Dugway Canyon	14	Paleosol nodules
8-16-16B	-8.9	-9.1	54.7	South Dugway Canyon	14	Paleosol nodules
8-16-32A	-9.1	-8.7	66.4	South Dugway Canyon	29	Paleosol nodules
8-16-32B	-9.0	-9.3	61.3	South Dugway Canyon	29	Paleosol nodules
866-2	-7.6	-8.5	76.4	South Dugway Canyon	2.5	Paleosol nodules
866A	-7.5	-8.8	76.1	South Dugway Canyon	2.5	Paleosol nodules
866B	-8	-8.4	67.4	South Dugway Canyon	2.5	Paleosol nodules
868A	-6.9	-7.8	75.2	South Dugway Canyon	3.5	Paleosol nodules
868B	-7.3	-8.4	75.5	South Dugway Canyon	3.5	Paleosol nodules
DS2-1aA	-7.0	-6.3	69.3	Upper West Canyon	4	Paleosol nodules
DS2-1aB	-8.1	-7.4	75.8	Upper West Canyon	4	Paleosol nodules
DS2-5A	-7.9	-5.2	50.3	Upper West Canyon	8	Paleosol nodules
DS2-5B	-7.4	-5.5	54.8	Upper West Canyon	8	Paleosol nodules
DS2-9A	-5.8	-7.1	47.2	Upper West Canyon	13	Paleosol nodules
DS2-9B	-7.9	-7.5	45.1	Upper West Canyon	13	Paleosol nodules
DS2-9C	-9.1	-7.2	26.3	Upper West Canyon	13	Paleosol nodules
DS4-47	-8.4	-3.3	77.2	Duck Creek	33	Paleosol nodules
DS4-47A	-7.7	-2.4	81.1	Duck Creek	33	Paleosol nodules
Gila Formation, Mangas Basin: lacustrine facies						
7-10-C-1A	-10.2	-7.6	67.4	Upper West Canyon	~48	Oscracode Limestone
7-10-C-1B	-10.2	-7.9	98.9	Upper West Canyon	~48	Oscracode Limestone
7-10-C-1B_2	-10.2	-7.9	83.0	Upper West Canyon	~48	Oscracode Limestone
DS1-18A	-9.4	-4.8	75.0	Upper West Canyon	~50	Ooid Limestone
DS1-18A_2	-9.5	-4.8	76.0	Upper West Canyon	~50	Ooid Limestone
DS1-18B	-9	-4.5	71.7	Upper West Canyon	~50	Ooid Limestone
DS1-18B_2	-9	-4.5	73.3	Upper West Canyon	~50	Ooid Limestone
DS-4-15A	0	0.8	28.5	Duck Creek	9	Ooid Limestone
DS-4-15B	0.7	0.8	23.2	Duck Creek	9	Ooid Limestone
DS4-35_Dust	-1.6	-0.2	61.9	Duck Creek	22.5	Ooid Limestone
Robledos Mountains, southern Rio Grande rift: spring limestones						
RobTuf1	-7.9	1.1	92.3	-	-	Limestone
RobTuf2	-7.7	1.1	95.8	-	-	Limestone
RobTuf3	-8.2	1.4	92.4	-	-	Limestone

Peedee Belemnite standard (PDB; Craig, 1957) for carbon and oxygen isotope values (Table 1).

For pedogenic calcite, there is no correlation between weight percent calcite and $\delta^{18}O$ (R^2=0.12) or $\delta^{13}C$ (R^2=0.02), suggesting that there is no significant contribution of either detrital or diagenetic calcite that is isotopically different from the pedogenic calcite and that the measured isotope values reflect environmental conditions during Plio-Pleistocene soil formation.

Predicted values from modern data

In order to compare the measured Plio-Pleistocene $\delta^{18}O$ values to modern conditions, the $\delta^{18}O$ of calcite predicted to precipitate at the three sample sites (Cliff, New Mexico, Las Cruces, New Mexico, and St. David, Arizona) was calculated, based on modern temperature and meteoric water composition.

The oxygen isotope fractionation factor (Sheppard et al., 1969): $10^3 \ln\alpha = 2.78*10^6/T_{\circ K}^2 - 2.89$, may be restated as:

$$\delta^{18}O_{cc(SMOW)} - \delta^{18}O_{w(SMOW)} = 2.78*10^6/T_{\circ K}^2 - 2.89, \text{ or}$$

$$\delta^{18}O_{cc(SMOW)} = (2.78*10^6/T_{\circ K}^2 - 2.89) + \delta^{18}O_{w(SMOW)},$$

where $\delta^{18}O_{cc(SMOW)}$ is the oxygen isotope value for calcite, $\delta^{18}O_{w(SMOW)}$ is the oxygen isotope value of water from which calcite is precipitated, and $T_{\circ K}^2$ is the temperature of crystallization in degrees Kelvin. Herein, we use mean annual temperature data reported from weather stations near the modern sites, because this temperature very closely approximates the mean annual temperature in the soil (e.g., Buol et al., 1997). The oxygen isotope values of waters have not been measured directly in the study areas. Instead, we estimate the isotope value of precipitation at the modern sites using the *Online Isotopes in Precipitation Calculator* <http://wateriso.eas.purdue.edu/waterisotopes/pages/information/oipc_info.html>. Estimates are calculated from a global data set according to an algorithm developed by Bowen and Wilkinson (2002) and refined by Bowen and Revenaugh (2003) and Bowen et al. (2005). While it is possible that both soil and lake water $\delta^{18}O$ values may be different than regional precipitation $\delta^{18}O$ values as a result of evaporation (e.g., Mack and Cole, 2005), such an effect will drive $\delta^{18}O_w$ toward more positive values. Thus, the estimates of precipitation $\delta^{18}O$ values effectively set a lower limit for $\delta^{18}O_{cc}$ at these modern sites.

DISCUSSION

Oxygen isotopic comparisons

The $\delta^{18}O$ value of calcite is primarily influenced by the temperature during calcite crystallization and the oxygen isotopic value of the water from which the calcite precipitated, neither of which is known with any certainty for the American Southwest during Plio-Pleistocene time. Estimated calcite $\delta^{18}O$ values are similar for all three modern sites and, within analytical uncertainty, the majority of Plio-Pleistocene paleosol and lacustrine calcites have significantly more positive $\delta^{18}O$ values than those
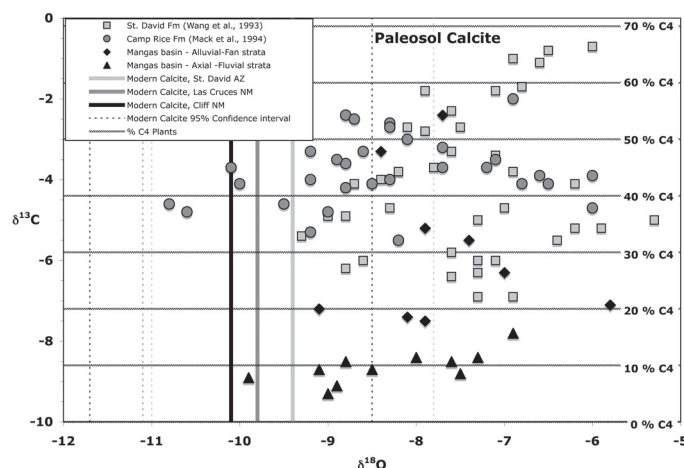

FIGURE 3. Bivariate plot of stable oxygen and carbon isotopes (PDB standard) for paleosol calcite from the Gila Formation in the Mangas Basin, and from the Camp Rice Formation (Mack et al., 1994) and St. David Formation (Wang et al., 1993). Vertical lines are the calculated modern oxygen isotopic values of calcite for the sites of the ancient strata. The percent of C_4 plants is taken from Fox and Koch (2003, 2004).

calculated for equivalent modern sites (Figs. 3, 4). This may indicate the existence of air masses with ^{18}O-enriched precipitation or significant enrichment of ^{18}O in lake and soil waters due to evaporation during Plio-Pleistocene time.

The oxygen isotope values of paleosol calcite from the Plio-Pleistocene Gila Formation in the Mangas Basin are similar to those in the coeval St. David Formation in the Basin and Range of southeastern Arizona and Camp Rice Formation in the southern Rio Grande rift of southern New Mexico (Fig. 3; Table 1). This suggests that the paleosols at the three sites experienced similar soil temperatures and were influenced by meteoric water of similar isotopic composition. However, significant differences exist in lacustrine calcite $\delta^{18}O$ values between the Gila Formation and the other two sample sites and between the two sample sites within the Gila Formation (Fig. 4; Table 1). Lacustrine calcites from the Duck Creek section of the Gila Formation are enriched in ^{18}O compared to the lacustrine calcites of the St. David Formation and spring calcites in the Robledo Mountains, implying precipitation enriched in ^{18}O or higher rates of evaporation in lake Buckhorn in the Mangas Basin. In contrast, lacustrine calcites from the upper west canyon section in the Mangas Basin are slightly depleted in ^{18}O compared to the St. David Formation and Robledo Mountains spring limestones and very depleted in ^{18}O (maximum of ~ 11‰) compared to the Duck Creek samples from the same lake. Because the upper west canyon section is located along the southwestern edge of the basin, the lake waters may have been influenced by surface water or groundwater from local high-elevation catchments and/or by geothermal waters coming up along the inferred buried fault on the southwestern side of the basin, either or both of which could account for ^{18}O depletion. Regardless of the origin, the large disparity in $\delta^{18}O$ values of lacustrine calcites from the two sample sites within the Gila Formation implies that the waters of lake Buckhorn were poorly mixed, an interpretation previously suggested by Mack and Stout
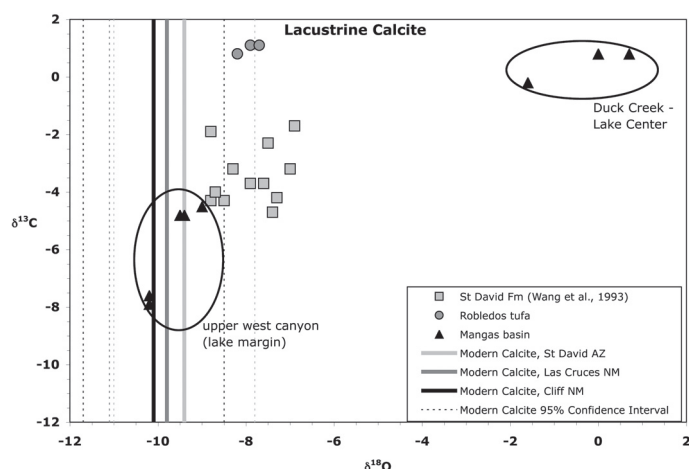
FIGURE 4. Bivariate plot of stable oxygen and carbon isotopes (PDB standard) of lacustrine calcite from the Gila Formation in the Mangas Basin, from the St. David Formation (Wang et al., 1993), and from spring limestones (tufas) in the Robledo Mountains near Las Cruces. Vertical lines are the calculated modern oxygen isotopic values of calcite for the sites of the ancient strata.

(2005) based on the presence of poorly oxygenated green mudstones and uneven geographic distributions of diatomites and Magadi-cherts within the lacustrine strata.

Carbon isotopic comparisons

Variations in $\delta^{13}C$ values of pedogenic calcite in latest Miocene and younger strata is related to the relative abundance of plants colonizing the soil that used the C_3 and C_4 photosynthetic pathways (Cerling, 1984; Cerling and Quade, 1993). In order to estimate the ratio of C_3 and C_4 plants on the paleolandscape, the linear mixing model of Fox and Koch (2003, 2004) is applied (Fig. 3). Based on this approach, the axial-fluvial landscape during deposition of the Gila Formation in the Mangas Basin contained from 5% to16% C_4 plants, while alluvial fans of the Mangas Basin had from 18% to 55% C_4 plants (Fig. 3). Estimates of the relative percentage of C_4 plants on the landscape during deposition of the St. David and Camp Rice formations are 22-67% and 32-58%, respectively (Fig. 3). Although five of the alluvial-fan pedogenic calcite $\delta^{13}C$ values from the Gila Formation are within the range of those of the St. David and Camp Rice formations, the remaining four alluvial-fan values and all of the axial-fluvial values from the Gila Formation are depleted in ^{13}C compared to those of the other ancient sites. This suggests a higher proportion of C_3 trees and shrubs in the Mangas Basin due to higher precipitation and/or cooler temperatures. At least some of this difference may be the result of higher average elevation of the Mangas Basin compared to the southern Rio Grande rift (~150 m lower) and southeastern Basin and Range (~250 m lower).

Variations among axial-fluvial and alluvial-fan pedogenic calcite $\delta^{13}C$ values *within* the Mangas Basin are unlikely to be due to variations in mean annual temperature within the same basin. Instead, it is possible that the river floodplain had a shal-

lower water table than the adjacent alluvial fans, which may have resulted in relatively greater soil moisture, reduced water-stress on plants, and promotion of a greater abundance of C_3 plants among those sites. This isotopic variability within the Mangas Basin highlights the need to consider the role of depositional environment when comparing data among formations or within a single formation.

Like the oxygen isotopic values, the $\delta^{13}C$ values of lake-center limestones in the Mangas Basin (Duck Creek section) are higher than those of the St. David Formation and of spring limestones of the Robledo Mountains in the southern Rio Grande rift (Fig. 4). This may suggest a greater degree of evaporation of lake Buckhorn during limestone formation, and/or precipitation of limestone during times of diatom and/or algal blooms. The opposite interpretation is proposed for the lake-margin limestones of lake Buckhorn (upper west canyon section), whose $\delta^{13}C$ values are somewhat depleted compared to those of the other ancient strata (Fig. 4). The relatively high values of $\delta^{13}C$ of the spring limestones in the Robledo Mountains may reflect a significant contribution of CO_2 from dissolution of Paleozoic marine limestones that comprise much of the mountain range (Wigley et al., 1978).

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