**A molecular isotope record of climate variability and vegetation response in southwestern
North America during mid-Pleistocene glacial/interglacial cycles**

Contreras, Sergio^{1,2,3,a}, Werne, Josef P.¹, Brown, Erik T.², Anderson, R. Scott⁴, Fawcett, Peter J.⁵

(1) Department of Geology and Environmental Science, University of Pittsburgh, Pittsburgh, PA
15260, USA

(2) Large Lakes Observatory and Department of Geological Sciences, University of Minnesota
Duluth, Duluth, MN 55812, USA

(3) *Present Address*: Departamento de Química Ambiental & Centro de Investigación en
Biodiversidad y Ambientes Sustentables (CIBAS), Universidad Católica de la Santísima
Concepción, Casilla 297, Concepción, Chile.

(4) Environmental Programs, School of Earth Sciences and Environmental Sustainability,
Northern Arizona University, Flagstaff, AZ 86011, USA

(5) Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM
87131, USA

(a) *Corresponding author*: scontreras@ucsc.cl; contrerasser@gmail.com

For submission to Palaeo-cubed

June, 2016

ABSTRACT

Climate variability during Pleistocene glacial/interglacial transitions is well documented in marine and ice-sheet isotopic records, but terrestrial records showing the continental response to these transitions are scarce, especially for earlier in the Pleistocene. Cyclic intervals of warm interglacial and cold glacial conditions preserved in terrestrial records such as lake sediments provide opportunities to probe the biosphere's response to climate change. In this study, we track climate and plant type changes, specifically the presence of C3 and C4 plants, using the abundance and $\delta^{13}\text{C}$ signatures of leaf waxes in paleolacustrine sediments from Valles Caldera in New Mexico. Through these changes, we assess the response of vegetation to climate variability in southwestern North America through two mid-Pleistocene glacial/interglacial transitions (Marine Isotope Stage [MIS] 14/13 and 12/11). Leaf wax data show that the C3 forest taxa were dominant through the entire record whereas C4 plants, better adapted to warm conditions and competitive under water stress, are favored during warming and extended arid periods during interglacials. The $\delta^{13}\text{C}$ signature in leaf wax *n*-alkanes suggests that C4 plants persisted in the watershed throughout the interglacials and that some summer rainfall (which is required to support C4 grasses) was maintained even during prolonged dry periods. The abundance and carbon isotope composition of leaf waxes together with new MBT/CBT (methylation index of branched tetraethers/cyclization index of branched tetraethers) temperature data confirm warmer and more arid conditions during MIS 13 than during MIS 11, in spite of relatively low greenhouse gas concentrations during MIS 13. This suggests that variations in incoming solar radiation have played a major role in regulating the surface temperature, regional hydrological systems and vegetation in southwestern North America, likely through changes in the North American Monsoon coupled with variations in the location of the mid-latitude westerlies.

Keywords: Interglacial; leaf waxes; carbon stable isotopes; C3 vs. C4 vegetation; climate change

1. Introduction

Southwestern North America has been identified as a hot spot of climate change due to the potential impacts of warming temperatures on the already limited water availability in the region (Giorgi, 2006; Diffenbaugh et al., 2008; Diffenbaugh and Giorgi, 2012). The main sources of moisture to the region are convective thunderstorms associated with the summer monsoon, and winter precipitation comprised of large-scale frontal systems that often involve snow accumulation at high elevations and locally account for half of the annual precipitation in the Jemez Mountains of New Mexico, the watershed of the former lake in the Valles Caldera (Reneau et al., 2007; Fawcett et al., 2007). Climate models consistently project declines in winter precipitation for the southwest, in response to warming due to rising concentrations of greenhouse gases (Seager et al., 2007; Seager and Vecchi, 2010; Cayan et al., 2010; Seager et al., 2013; Prudhomme et al., 2014). Under these conditions, the sub-tropical dry zones expand poleward where descending air suppresses precipitation by drying the lower atmosphere. Warming also shifts the rain-bearing mid-latitude winter storm tracks towards the poles (Yin, 2005).

Understanding long-term (centennial to glacial-interglacial timescales) natural climate variability of southwestern North America is crucial to disentangle forcing factors and project anthropogenic changes superimposed on natural climate variability. Fawcett et al. (2011) described a lacustrine sediment record (VC-3) from Valle Grande in Valles Caldera National Preserve (New Mexico) (Fig. 1), identifying megadroughts during the warmest phases of two mid-Pleistocene interglacials (MIS 13 and MIS 11). During these intervals the lake became hydrologically closed and evaporated to the extent that centimeter to decimeter-scale mud-cracks were identified. These dry climates were attributed to reduced winter and summer precipitation.

70 Recently, hydrogen isotope (δD) analyses of leaf waxes were used to reconstruct precipitation
71 changes in the same VC-3 core, which were interpreted as indicating greater summer monsoon
72 strength and variability during interglacials than glacials (Cisneros-Dozal et al., 2014). This
73 study identified a precessional signal in monsoon precipitation during the long MIS 11
74 interglacial (Cisneros-Dozal et al., 2014). An increase and subsequent decrease in both organic
75 carbon concentration (%TOC) and carbon stable isotope values in bulk organic matter ($\delta^{13}C_{TOC}$)
76 during the transitions to MIS 11 and MIS 13 were interpreted as an expansion and collapse of C4
77 plant communities in response to changes in summer precipitation (Fawcett et al., 2011).
78 Enhanced summer precipitation due to warmer temperatures could trigger a rise in C4 plant
79 communities. However, the apparent collapse of C4 plants and significant reduction in summer
80 precipitation is not intuitive, and is inconsistent with climate models that predict a significant
81 reduction in winter precipitation for southwestern North America over the next century. The
82 interpretation of carbon isotopic source signals in bulk organic matter can become complicated
83 in areas that receive contributions of organic matter from algae as well as terrestrial C3 and C4
84 plants, as is the case for Valles Caldera. Carbon isotope analysis of terrestrial leaf waxes (long-
85 chain *n*-alkanes; C₂₅ to C₃₃) provides a better approach to interpret such vegetation changes
86 without the complication from multiple sources of organic matter (Eglinton and Calvin, 1967;
87 Collister et al., 1994). Compound specific carbon isotope signatures are less influenced by
88 diagenesis, differential preservation of compound classes, and changes in the sources of organic
89 matter that can complicate interpretations of bulk $\delta^{13}C$ values (e.g., Pancost and Boot, 2004).

90 The present study reconstructs broad-scale plant type changes in the VC-3 lacustrine
91 sedimentary record using the abundance and carbon isotope composition of the long chain *n*-
92 alkanes (C₂₇, C₂₉, C₃₁), which are unambiguous indicators of terrestrial vegetation. The

molecular isotopic data presented reveal details of the response of southwestern North American vegetation to climate change during Pleistocene glacial/interglacial transitions (MIS 14/13 and MIS 12/11). We focus on changes in terrestrial higher plant inputs as well as the $\delta^{13}\text{C}$ signature of the leaf waxes, which can be attributed to terrestrial vegetation changes (i.e. C3 and C4 plants), through glacial/interglacial transitions where abrupt decreases in %TOC and $\delta^{13}\text{C}_{\text{TOC}}$ were interpreted as C4 vegetation decline by Fawcett et al., (2011). In addition, we increased the resolution of the temperature reconstruction based on MBT/CBT from VC-3 to evaluate differences between MIS 13 and MIS 11 in more detail than was possible by Fawcett et al (2011). Such high-resolution temperature reconstructions are needed to understand the natural response of the Earth to climate change, and the VC-3 record is one of a few continental sedimentary records that span MIS 11 and 13.

2. Regional setting

2.1 Study Site

The Valles Caldera complex formed as a result of a large shallow magma chamber eruption 1.23 million years ago (Ma) (Goff and Gardner, 1994). Post-caldera ring-fracture eruptive domes blocked drainages out of the caldera complex, forming several lakes after 0.8 Ma (Reneau et al., 2007). A lake formed in the Valle Grande (35° 52' N, 106° 28' W, 2553 m asl, catchment area 100 km²) during the middle Pleistocene when the South Mountain rhyolite dome erupted and blocked the drainage out of the Valle Grande (Fig. 1). The age of the South Mountain rhyolite was determined to be 552 ± 3 kya on the basis Ar-Ar dating of tephras from core VC- 3 that are geochemically identical to the South Mountain rhyolite (Fawcett et al., 2007; WoldeGabriel et al., 2007) and from a tephra outside the Valles Caldera (Smith et al., 2001).

117

118 **Figure 1.** Map of Valles Caldera in New Mexico showing location of drilling in Valle Grande
 119 (VC-3: 35°52' N, 106°28' W, 2553 m asl).

120 *2.2 Modern Valles Caldera climatology*

121 Modern climate of the Valle Grande is monitored by a USCRN co-op weather station
 122 (NM Los Alamos 13 W) located at the Valles Caldera National Preserve headquarters, on the
 123 flank of the VC-3 paleolake valley. The regional climate is considered semi-arid continental with

more than half of its mean annual precipitation (~ 670 mm) coming through a combination of frontal systems from late fall through early spring (i.e. December to February [DJF] 27 %) and summer convective storms associated with the North American Monsoon (i.e. July to September [JAS] 39 %) with drier spring and fall seasons. Even at the high elevation of the Valles Caldera, summer evaporation amounts are significant so that winter frontal precipitation tends to dominate the annual hydrological cycle. The mean annual temperature (MAT) is 4.8 °C with summer (JAS) temperatures averaging 14.0 °C and winter (DJF) temperatures averaging -4.5 °C.

3. Organic Geochemical Proxies

3.1 Branched GDGTs as temperature proxy

Branched glycerol dialkyl glycerol tetraether lipids (GDGTs) exhibit structural variations (see Appendix for structures) in response to environmental temperatures (Weijers et al., 2007). The extent of methylation (MBT) and cyclization (CBT) of a suite of nine branched GDGTs correlates with the mean annual temperature (MAT) and pH in soils distributed worldwide (Weijers et al., 2007). However, the soil-based MBT-CBT proxy routinely underestimates MAT when applied to lake sediments (Tierney and Russell, 2009; Blaga et al., 2010), likely due to contributions of branched GDGTs from *in situ* production in lake waters and sediments (Buckles et al., 2014; Loomis et al., 2014). This is due to other environmental factors that influence the MBT/CBT proxy (Dirghangi et al. 2013; Naeher et al., 2014; Menges et al., 2014). Nevertheless, the temperature record produced by Fawcett et al. (2011) in VC-3 using the Weijers et al. (2007) soil-derived calibration correlates well with the abundance of temperature sensitive pollen taxa such as *Picea* and *Abies* (cool taxa) and *Juniperus* and *Quercus* (warm taxa) during glacial and interglacial stages, respectively. Thus, temperatures reconstructed using MBT/CBT in Valles

Caldera are likely underestimates and should be considered minimum temperatures, though trends are expected to be robust (Fawcett et al., 2011).

3.2 n-alkanes as aquatic and terrigenous input proxy

Terrestrial plant leaf waxes are dominated by long-chain *n*-alkanes (C₂₅-C₃₃; Eglinton and Hamilton, 1967; Rieley et al., 1991), while aquatic algae are dominated by the short-chain *n*-alkanes (e.g. C₁₇-C₂₁; Giger et al., 1980; Cranwell et al., 1987). The C₁₇ *n*-alkane abundance is often considered to reflect lacustrine paleoproductivity (Meyers, 2003). Terrestrial leaf waxes can be transported to lakes via water or wind (Gagosian et al., 1987), but vegetation in the immediate watershed is typically the predominant source of these long chain *n*-alkanes to lake sediments (Huang et al., 1999; Rieley et al., 1991; Schwark et al., 2002).

3.3 C4 and C3 vegetation changes derived from carbon stable isotopes of long chain n-alkanes (C₂₇, C₂₉, C₃₁)

The abundance and stable carbon isotope composition of leaf waxes can provide additional information about terrestrial inputs and vegetation changes through glacial/interglacial transitions. There are two major photosynthetic carbon fixation pathways in terrestrial plants, the C₄ (Hatch-Slack) and C₃ (Calvin-Benson) pathways (O'Leary, 1981). One major difference in these two enzymatic pathways is an additional carbon concentrating step in the C₄ pathway, which gives C₄ plants an ecological advantage under warm, dry, or low pCO₂ conditions (Bourlière, 1983; Beerling and Osborne, 2006; Tipple and Pagani, 2007). As a consequence of the different carbon fixation pathways, plant tissues in C₄ grasses are relatively enriched in the heavy carbon isotope (¹³C) with a mean δ¹³C value of -13.0 ‰, generally ranging from -9 ‰ to -19 ‰ (Cerling et al., 1997; Ehleringer and Monson, 1993; Ehleringer, 1991; Farquhar et al.,

1989; O’Leary, 1988). C3 vegetation such as trees, shrubs, and cool-season grasses hold a more
 ^{13}C -depleted carbon isotopic signature with a mean $\delta^{13}\text{C}$ value of -27.0‰ and typically range
from -22‰ to -35‰ (Ehleringer and Monson, 1993; Ehleringer, 1991; Farquhar et al., 1989;
O’Leary, 1988). The distinct stable carbon isotope signature in modern plant tissues between C4
and C3 plants is reflected in $\delta^{13}\text{C}$ values of TOC from surface soils and lacustrine sediments, as
well as the sedimentary long chain *n*-alkanes (C_{27} - C_{31}). $\delta^{13}\text{C}_{\text{TOC}}$ values in surface soils from the
North American Great Plains have been used to estimate the relative abundance of C3/C4
vegetation, with values higher than -14‰ and lower than -24‰ interpreted as pure C4 and C3
vegetation, respectively (Rao et al., 2010; Tieszen et al., 1997). The weighted mean average
(WMA) carbon isotope composition of leaf waxes (typically C_{27} , C_{29} , and C_{31} , $\delta^{13}\text{C}_{\text{wax}}$) has been
applied in previous studies to compare the overall leaf-wax isotopic signal between plant taxa or
sediment samples (Street-Perrott et al., 2004; Castañeda et al., 2007; Makou et al., 2007; Vogts
et al., 2009; Feakins and Sessions, 2010). This approach aims to reproduce overall isotopic
variability without focusing on a single *n*-alkane compound, as has been done in some studies
(e.g. Schefuß et al., 2011), because the dominant leaf wax *n*-alkane may vary depending on
vegetation type and/or local climatic influences including aridity (Bush and McInerney, 2013).
 $\delta^{13}\text{C}_{\text{wax}}$ values have been reported to range from -31.4‰ to -38.6‰ for C3 plants and -18.5‰
to -24.5‰ for C4 plants (Rieley et al., 1993, Collister et al., 1994). Here we present both the
 $\delta^{13}\text{C}$ of individual *n*-alkane and that of the WMA as both have advantages and disadvantages.

4. Materials and Methods

4.1 Sediment characteristics and chronology

The 82 m VC-3 lacustrine sediment core was drilled in the Valle Grande in Valles Caldera, New Mexico in 2004 and stored at the National Lacustrine Core Repository (LacCore) at the University of Minnesota. The sediments consist of lacustrine silts and clays with occasional gravels and pumiceous gravels in the lower strata that predate the eruption of the South Mountain rhyolite and subsequent damming of the Valle Grande drainage. Above the basal gravels, two major lithologic cycles of about the same thickness are defined by transitions from silty diatomaceous clays with well-defined, thin (mm-scale) laminations to silty diatomaceous clays with thicker and less well-defined laminations to massive units, with occasional mm-scale silts and sands. The latter units are characterized by the preservation of carbonates and the presence of cm-scale mudcracks. The well-laminated sediments were interpreted as forming under deep lake conditions during glacial periods and the less well-laminated to mudcracked sediments forming in shallower to desiccated lake conditions during drier interglacials (Fawcett et al., 2011).

A detailed description of the age model can be found in Fawcett et al. (2011). Briefly, two basal tephra Ar-Ar dates of 552 ± 3 kyr from a glassy tephra and a well-sorted pumiceous gravel (at 75.8 and 76.0 m depth) constrain the onset of lacustrine sedimentation in core VC-3 to MIS 14 in the middle Pleistocene. Paleomagnetic data (progressive alternating field demagnetization) indicate two short-lived negative magnetic field events (at 17.25 m and 52.3 m depth) that were correlated with globally recognized events 11a (400 kyr) and 14a (536 kyr) (Lund et al., 2006). Two abrupt changes in bulk properties (e.g. increases in TOC, C/N, Si/Ti ratios) were correlated with glacial terminations VI and V, and their globally constrained ages (533 kyr and 426 kyr; Lisiecki and Raymo, 2005). The positions of the dated magnetic field events are consistent with the ages based on glacial terminations.

4.2 Sample collection

A total of 82 sediment samples were taken from the VC-3 core for this study, yielding an average interval of ~2,000 years between samples. Care was taken when sampling to avoid mudcracks, which are in-filled and do not represent primary deposition, and could also be zones of oxidation (Fawcett et al., 2011). All sediment samples were frozen, freeze-dried, and homogenized using an agate mortar and pestle prior to lipid extraction and separation.

4.3. Lipid extraction and separation

Lipid extractions and separations were performed at the Large Lakes Observatory, University of Minnesota Duluth (UMD). Sediment samples were extracted for total lipids using an Accelerated Solvent Extractor (ASE 350, Dionex) with dichloromethane:methanol (9:1 v/v). 5 α -cholestane was added to the total lipid extracts to correct for losses during lipid separation assuming proportional losses for the standard and compounds of interest such as long-chain *n*-alkanes. A blank was included in each sample set, which was taken through the entire procedure and tested for the presence of contaminants prior to sample analysis. Total lipid extracts were separated via short column chromatography with activated alumina (Al₂O₃) as stationary phase into apolar and polar fractions by eluting with hexane/dichloromethane (9:1 v/v) and dichloromethane/methanol (1:1 v/v), respectively. The polar fraction was filtered over a 0.45 μ m PTFE filter, dried under N₂, and re-dissolved in hexane/isopropanol (99:1 v/v) for analysis of branched GDGTs. The apolar fraction was further separated via column chromatography with Ag-impregnated silica gel into saturated and unsaturated hydrocarbons by eluting with hexane

and dichloromethane/methanol (1:1 v/v), respectively. The saturated fractions were dried under N₂ for *n*-alkane analysis.

4.4 GDGT analysis and paleotemperature estimation

Branched GDGTs (see Appendix for structures) were analyzed by high performance liquid chromatography/atmospheric pressure chemical ionization/mass spectrometry (LC/APCI-MS) using an Agilent 1260 LC with an Alltech Prevail Cyano column (3 µm, 2.1 × 150 mm), following procedures modified from Hopmans et al. (2000) and Weijers et al. (2007). Each run (10 µL injection) began with isocratic elution for 5 min with 99 % hexane and 1 % isopropanol, with a flow rate of 0.2 mL/min, followed by a linear gradient to 1.8 % isopropanol in 45 min. GDGT detection was performed on an Agilent 6460 triple quadrupole mass spectrometer using positive-ion APCI in single ion monitoring (SIM) mode to increase sensitivity and reproducibility. SIM was set to scan the *m/z* ratio of protonated GDGTs [M+H]⁺ of the three parent ions (a, b, c) of the branched GDGTs I (*m/z* 1022, *m/z* 1020 and *m/z* 1018), II (*m/z* 1036, *m/z* 1034 and *m/z* 1032) and III (*m/z* 1050, *m/z* 1048 and *m/z* 1046) with a dwell time of 200 ms for each ion. Analytical performance was monitored by injection of GDGTs hydrolyzed from the main phospholipid of *Thermoplasma acidophilum* (Matreya LLC, > 95 % pure) after each ~10 sample injections. Branched GDGTs were quantified by integrating the [M+H]⁺ peaks in the mass chromatograms and mean annual temperature estimated using the MBT and CBT proxy calibrations as defined by Weijers et al. (2007). Each sample was run at least in duplicate with a mean annual temperature error and mean error of all duplicates better than 0.8 °C and 0.25 °C, respectively.

4.5 Analysis of *n*-alkanes

The *n*-alkanes were identified using an Agilent 6890 gas chromatograph (GC) coupled to an Agilent 5973 mass spectrometer (MS). An HP-1 capillary column (30 m length, 0.32 mm inner diameter, 0.25 μ m film thickness) was used with helium as a carrier gas at a flow rate of 2 ml/min. The GC temperature program initiated at 50 °C, increased to 130 °C at 10 °C/min, then to 320 °C at 4 °C/min, and then remained isothermal for 10 min. Quantification of *n*-alkanes was carried out using an Agilent 6890 GC with flame ionization detection (FID) using 5 α -androstane, added before injection. The column type and temperature program were the same as described above for GC-MS. Helium flow rates were set at 1.5 mL/min. Concentration measurements (mg compound per gram sediment dry weight) were reproducible within ± 10 %.

An Agilent 6890N GC (HP-1 column, 60 m length, 0.32 mm ID, 0.25 μ m film thickness) interfaced to Thermo Finnigan Delta^{Plus} XP mass spectrometer was used to determine $\delta^{13}\text{C}$ of *n*-alkanes. The GC temperature program was initiated with a 1 minute isothermal condition at 50 °C, increasing to 130 °C at 50 °C/min and to 320 °C at 4 °C/min, and held isothermally for 6 min. The *n*-alkanes separated by the GC column were oxidized at 940 °C and converted to CO₂. Six pulses of reference CO₂ gas with a known $\delta^{13}\text{C}$ value were injected into the IRMS for determination of the $\delta^{13}\text{C}$. The results were reported as per mil (‰) deviations from Vienna Pee Dee Belemnite (VPDB) in standard delta notation. A standard mixture of *n*-alkanes ("Mix A" containing C₁₆ to C₃₀ *n*-alkanes plus C₃₆ *n*-alkane provided by A. Schimmelmann, Indiana University) with known $\delta^{13}\text{C}$ values were analyzed between a maximum of 6 sample injections to standardize and ensure accuracy in the $\delta^{13}\text{C}$ determination of the *n*-alkanes. Each sample was run at least in duplicate with squalane added before injection as an internal standard to monitor the reproducibility of measurements, which was better than 0.35‰ including the C₂₇, C₂₉ and C₃₁

n-alkanes. The $\delta^{13}\text{C}$ values of leaf waxes are expressed as both individual values and as a single weighted mean average for the odd carbon numbered C_{27} , C_{29} , and C_{31} *n*-alkanes ($\delta^{13}\text{C}_{\text{wax}}$).

To identify changes in the relative proportion of mid-chain (C_{23} and C_{25}) to long chain (C_{29} , C_{31}) *n*-alkanes, the P_{aq} (Ficken et al., 2000) was calculated as follow:

$$P_{\text{aq}} = \frac{(\text{C}_{23} + \text{C}_{25})}{(\text{C}_{23} + \text{C}_{25} + \text{C}_{29} + \text{C}_{31})} \quad \text{Eq. 1}$$

To characterize odd over even chain length predominance, the carbon preference index (CPI) was calculated using the following equation (Eglinton and Hamilton, 1967):

$$\text{CPI}_{25-33} = \frac{1}{2} \left[\left(\frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32}} \right) + \left(\frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34}} \right) \right] \quad \text{Eq. 2}$$

5. Results

5.1 *n*-alkane abundance and $\delta^{13}\text{C}$

The abundance of leaf waxes (C_{27} , C_{29} and C_{31} *n*-alkanes; Fig. 2a) ranged from near zero up to $6.5 \mu\text{g g}^{-1}$ sediment in MIS 11, generally corresponding with the TOC trend (Fig. 3b). The aquatic algae biomarkers (C_{17} , C_{19} , and C_{21} *n*-alkanes; Fig. 2e) were generally found in much lower abundances than the leaf waxes except at the end of MIS 13 through the onset of MIS 12 (Fig. 2), where they reached values of $14 \mu\text{g g}^{-1}$ sediment (in one sample C_{17} reaches nearly $34 \mu\text{g g}^{-1}$). The abundance and temporal trends of mid chain (C_{23} and C_{25}) *n*-alkanes (Fig. 2c) are generally similar to those of leaf waxes, though with lower abundances than the long chain *n*-alkanes especially at the onset of MIS13 and MIS 11 interglacials (e.g. MIS 11 onset at 421 kyr: $[\text{C}_{23}] = 1.7 \mu\text{g g}^{-1}$; $[\text{C}_{25}] = 4.7 \mu\text{g g}^{-1}$; $[\text{C}_{27}] = 4.7 \mu\text{g g}^{-1}$; $[\text{C}_{29}] = 5.1 \mu\text{g g}^{-1}$; $[\text{C}_{31}] = 3.9 \mu\text{g g}^{-1}$).

301 $\delta^{13}\text{C}$ trends are similar for individual leaf waxes, with values ranging from -23‰ to -
 302 33‰, though somewhat greater variability is observed in the C_{27} *n*-alkane (Fig. 2). C_{27} is
 303 generally ^{13}C enriched relative to C_{29} , which is ^{13}C enriched relative to C_{31} . A significant
 304 difference ($\sim 7\text{‰}$) is observed between glacial/interglacial conditions (Fig. 2b). An abrupt
 305 increase in the abundance of leaf waxes in conjunction with more positive $\delta^{13}\text{C}$ values
 306 characterizes the early stages of both interglacials (MIS 13 and 11). Mid chain *n*-alkanes show
 307 broadly similar $\delta^{13}\text{C}$ trends, though with greater variability and generally more ^{13}C enriched
 308 values than leaf waxes, more similar to the C_{27} than the longer chain homologs. Short chain *n*-
 309 alkane $\delta^{13}\text{C}$ values were not reproducible due to low abundance through most of the record
 310 (below the linearity of the mass spectrometer), and are therefore not shown.

311

Figure 2. Abundances and carbon isotope ratio of *n*-alkanes recorded in VC-3 lacustrine sediments. (a) Long chain *n*-alkanes [C_{27} , C_{29} , C_{31}] abundance ($\mu\text{g g}^{-1}$ dry weight sediments [dws]). (b) Carbon isotope ratio of long chain *n*-alkanes [C_{27} , C_{29} , C_{31}] (‰). (c) Mid chain *n*-alkanes [C_{23} , C_{25}] abundance ($\mu\text{g g}^{-1}$ dry weight sediments [dws]). (d) Carbon isotope ratio of long chain *n*-alkanes [C_{23} , C_{25}] (‰). (e) Short chain *n*-alkanes [C_{17} , C_{19} , C_{21}] abundance ($\mu\text{g g}^{-1}$ dry weight sediments [dws]).

5.2 Mean annual temperature (MAT)

We combine our new temperature data with that published in Fawcett et al. (2011). The increased resolution of the MAT reconstruction in the VC-3 sedimentary record confirms that MIS 11 temperatures are close to modern MAT, and that MIS 13 temperatures are the warmest in the entire Valles Caldera record (Fig. 3a). Average glacial MATs of -4.5°C during MIS 12 are similar to present day winter (DJF) temperatures and about 8°C cooler than modern MATs.

6. Discussion

6.1 Long term temperature variability

The amplitude of temperature variation was larger during MIS 13 than MIS 11 (Fig. 3a) which is consistent with the larger variations in local insolation at the precessional scale at 30°N (Fig. 3b; Berger and Loutre, 1991). MIS 13 is characterized by more positive global ocean benthic foraminiferal oxygen isotope values (Lisiecki and Raymo, 2005), cooler Antarctic temperatures (Jouzel et al., 2007) and lower atmospheric CO_2 concentrations (Siegenthaler et al., 2005) than other interglacials of the past 800 kyrs (Figs. 3c and 3d). The greater sensitivity of temperature in southwestern North America to insolation may also explain the large temperature

variability during the second half of MIS 13 when insolation was the greatest of any time in the VC-3 record (Berger and Loutre, 1991). During MIS 13 temperatures reach values greater than during MIS 11 or present-day MAT, and then cooled down to temperatures similar to those observed during MIS 11 (Fig. 3a). These data are consistent with the suggestion by Fawcett et al (2011) that continental temperature in southwestern North America seemed to respond more strongly to insolation than glacial/interglacial trends in greenhouse gases or global ice volume (Figs. 3a, 3b, 3c and 3d). Continental warm conditions during MIS 13 have been recorded across the Northern Hemisphere, in China (Guo et al., 2009), the Tibetan Plateau (Chen et al., 1999), the Lake Baikal region (Prokopenko et al., 2002), Europe (Vandenberghe, 2000; Zagwijn, 1996; Marković et al., 2009) and even in Greenland (de Vernal and Hillaire-Marcel, 2008). Thus, the Valles Caldera temperature record is consistent with the continental northern hemisphere, which experienced a significant warming during MIS 13 under a relatively low concentration of greenhouse gases (~250 ppm, Lüthi et al. 2008), likely due to higher local (30°N) insolation. Paleoclimate studies generally record MIS 11 as warmer and with global sea levels significantly higher than previous interglacials over the past 800 000 years, possibly due to significant collapse of both the Greenland ice sheet and the West Antarctic Ice Sheet (Raymo and Mitrovica, 2012). Furthermore, studies of Lake El'gygytgyn sediments in Siberian Arctic label MIS 11c as a "super" interglacial, significantly warmer than most interglacials (Melles et al., 2012). Recent climate models cannot replicate the extreme warmth of this interval with orbital and greenhouse gas forcings alone. However, vegetation feedbacks and a prescribed lower amount of summer sea-ice can partially explain this interglacial outlier (Coletti et al., 2015). If reduced sea-ice is the reason for the extreme warmth of MIS 11c in the Arctic, it remains unclear whether this forcing

was felt as far south as New Mexico, though local insolation patterns were potentially more important.

Figure 3. Reconstructed temperature and bulk geochemical proxy data from VC-3 record. (a) Mean annual temperature [MAT (°C)] based on branched glycerol dialkyl glycerol tetraether distribution (Weijers et al., 2007). Data shown are from both this study (82 points) and Fawcett et al. (2011) (78 points). Black line indicates the modern MAT of 4.8 °C in the study area. (b) June insolation at latitude 30°N (Berger and Loutre, 1991) (c) Ocean global stack of benthic $\delta^{18}\text{O}$ (‰) records (Lisiecki and Raymo, 2005). (d) Measured atmospheric carbon dioxide concentrations (Siegenthaler et al., 2005) and temperature change estimated with deuterium isotopes on the EPICA (European Project for Ice Coring in Antarctica) Dome Concordia ice core (Jouzel et al, 2007). (e) Total organic carbon concentration. (f) Si:Ti ratio from core scanning X-ray fluorescence (XRF). (g) $\delta^{13}\text{C}_{\text{TOC}}$. (h) Calcium XRF counts and position of mud cracks. (i) C/N ratio.

6.2 Glacial/Interglacial transitions

The temperature record indicates temperature increases of 8 °C and 5 °C during MIS 14/13 and MIS 12/11 glacial/interglacial transitions, respectively (Fig. 3a). At both transitions, deglacial warming is associated with increased TOC (Fig. 3e) and Si/Ti ratio (a proxy of diatom productivity) (Fig. 3f), both of which may be interpreted to indicate increased lake productivity (Fawcett et al., 2011). The increase in lacustrine productivity was followed by increase in the $\delta^{13}\text{C}_{\text{TOC}}$ (Fig. 3g), which was interpreted as an expansion of C4 plants in the watershed by Fawcett et al (2011). During both interglacial periods, an abrupt enrichment in calcium (Fig. 3h) is observed, marking the onset of closed-basin conditions associated with drier conditions (Fawcett et al., 2011). These combined responses to climate change may be explained by different influences of seasonal precipitation, with the C4 grass responding to continued summer (monsoonal) precipitation and lake hydrologic balance responding to reduced winter precipitation.

Mud-cracked facies in MIS 13 and MIS 11 (Fig. 3h) are characterized by negative shifts (6-7 ‰) in $\delta^{13}\text{C}_{\text{TOC}}$ (Fig. 3g) and an abrupt decrease in TOC concentration (Fig. 3d). These intervals were interpreted as a collapse of the interglacial C4 plant community and oxidation of lake sediments due to a significant decrease in summer precipitation associated with aridity (Fawcett et al., 2011). The interpretation of a rise and collapse of C4 vegetation through glacial/interglacial transitions associated with mid-Pleistocene megadroughts (mudcracked intervals) is supported only by the carbon isotope shifts in bulk organic matter (Fig. 3g). However, in-lake productivity based on Si/Ti (Fig. 3f) begins to increase in concert with the rise in temperature (Fig. 3a) and TOC (Fig. 3e), but then Si/Ti decreases while TOC values are still increasing in MIS 11 (as well as during early MIS 12), indicating a mismatch between the bulk

TOC record and lacustrine productivity. The C/N ratio (Fig. 3i) followed the TOC increase beyond the Si/Ti rise, suggesting that an important part of the TOC pool after the lake productivity maxima must be derived from terrestrial higher plant inputs.

The abundance of leaf waxes (C_{27} , C_{29} and C_{31} *n*-alkanes; Fig. 4a) reaches values up to $6.5 \mu\text{g g}^{-1}$ sediment in MIS 11, corresponding with the TOC trend (Fig. 4b), and indicating that terrestrial higher plant inputs represent a dominant fraction of organic carbon (e.g., Rieley et al., 1991; Bird et al., 1995; Lockheart et al., 1997). However, leaf wax abundances show greater variability during MIS12 than TOC values. In contrast, the C_{17} *n*-alkane shows relatively high abundance compared to leaf waxes only at the end of MIS 13 and beginning of MIS12. We speculate that higher in-lake productivity at this time is related to the re-establishment of winter precipitation leading to increased stream flow and open basin conditions (Fig. 4c). The high leaf wax *n*-alkane abundance during early interglacials is likely due to climatic warming stimulating growth of plants that prefer warm conditions (e.g. oak and juniper).

Figure 4. Proxy indicators of plant type change and climate variability recorded in VC-3 lacustrine sediments. (a) Long chain *n*-alkanes [C_{27} , C_{29} , C_{31}] abundance ($\mu\text{g g}^{-1}$ dry weight sediments [dws]) (b) Total organic carbon concentration (%) (c) C_{17} *n*-alkane abundance ($\mu\text{g g}^{-1}$ dry weight sediments [dws]) (d) Weighted mean average of the carbon isotope composition in C_{27} , C_{29} , C_{31} leaf wax *n*-alkanes [$\delta^{13}\text{C}_{\text{wax}}$] (‰). (e) Mean annual temperature [MAT (°C)]. Data shown are from both this study (82 points) and Fawcett et al. (2011) (78 points). (f) $\delta^{13}\text{C}_{\text{TOC}}$ (‰). (g) Calcium XRF counts and position of mud cracks. (h) P_{aq} ratio, based on the relative proportion of midchain (C_{23} , C_{25}) to long chain (C_{29} , C_{31}) *n*-alkane homologues (Eq. 1). (i) Carbon preference index (CPI), an expression of the odd-over-even predominance for long chain of *n*-alkanes (Eq. 2).

The long-term $\delta^{13}\text{C}_{\text{wax}}$ variability follows the glacial-interglacial trend for temperature and is in agreement with the carbon isotope composition of bulk TOC during glacial-interglacial transitions (Fig. 4f). The only exception is during periods when Ca enrichments and mud-cracked facies indicate that the lake level fell significantly (Fig. 4g). This supports the hypothesis that bulk organic carbon concentrations are dominated by terrestrial higher plant input, especially during interglacials. In fact, the shift to ^{13}C -enriched $\delta^{13}\text{C}_{\text{wax}}$ values through the interglacial transitions confirm a shift towards greater contributions of C4 relative to C3 vegetation as suggested by Fawcett et al. (2011). The only clear difference between the long-term trends in $\delta^{13}\text{C}_{\text{wax}}$ (Fig. 4d) and $\delta^{13}\text{C}_{\text{TOC}}$ (Fig. 4f) is observed during MIS 12 with a larger and more gradual decrease in $\delta^{13}\text{C}_{\text{wax}}$. This decrease seems to record a global climatic trend (Figs. 2c and 2d) consistent with the benthic foraminiferal oxygen isotope increase (Lisiecki and Raymo, 2005) and atmospheric CO_2 drawdown during MIS 12 (Siegenthaler et al., 2005). We interpret the range and variability of $\delta^{13}\text{C}_{\text{wax}}$ as a mixture of C3 and C4 vegetation where C3 plants dominated

the landscape and C4 plants expanded during warming and extended periods of aridity during interglacials, in agreement with the interpretation based on carbon isotope composition of bulk TOC (Fawcett et al., 2011) and surface soil end members (Rao et al., 2010; Tieszen et al., 1997).

Mid chain n-alkanes (C_{20} – C_{25}) have been observed to be the dominant n-alkanes in aquatic macrophytes, but long chain homologues are also synthesized in shallower lakes possibly due to adaptation to partial exposure to air (Eglinton and Calvin, 1967; Huang et al., 1999; Ficken et al., 2000; Aichner et al., 2010). Ficken et al. (2000) proposed an n-alkane ratio (P_{aq} ; Eq. 1) for discriminating the input between terrestrial plants and aquatic macrophytes where values <0.25 indicate predominantly higher terrestrial plant input. The P_{aq} ratio takes advantage of the fact that submerged/floating species have abundant mid chain n-alkanes relative to emergent macrophytes and terrestrial plant vegetation. There are few studies reporting the bulk $\delta^{13}C$ of macrophytes but $\delta^{13}C$ values are generally within the range of C3 plants (Aichner et al., 2010; Liu et al., 2013; Liu et al., 2015). Limited CO_2 availability as a result of high pH, alkalinity, or high CO_2 consumption might lead to HCO_3^- assimilation and lead to ^{13}C enrichment (Allen and Spence, 1981; Prins and Elzenga, 1989; Keeley and Sandquist, 1992; Aichner et al., 2010). In fact, bulk $\delta^{13}C$ values reported for submerged aquatic plants suggest that they might behave more like C4 plants, and emergent aquatic plants more like C3 plants (Aichner et al., 2010; Liu et al., 2013; Liu et al., 2015). Therefore, a shift towards higher $\delta^{13}C_{wax}$ values in the Valles Caldera record might be triggered by higher relative amounts of long chain n-alkanes from aquatic macrophytes (if they were present) responding to a low lake level conditions, rather than greater relative abundance of C4 plants.

In order to assess the potential input of aquatic plants, we examine the P_{aq} (Fig. 4h) together with the $\delta^{13}C$ of the individual long chain n-alkane compounds (C_{27} , C_{29} , C_{31}) (Fig. 2b). The $\delta^{13}C$

values of C₂₇ n-alkane are higher than the others and are a major factor driving variability in $\delta^{13}\text{C}_{\text{wax}}$, which could indicate a significant influence from aquatic macrophytes. However, the $\delta^{13}\text{C}_{\text{wax}}$ enrichment through the glacial/interglacial transitions during dry periods is associated with a decrease in P_{aq} values, which is the opposite of what we would expect from elevated inputs from aquatic macrophytes. Therefore, the ^{13}C enrichment is most likely being driven by increased relative contribution of C4 land plants. Furthermore, because inputs from aquatic plants would drive the $\delta^{13}\text{C}$ values in the opposite direction of what we observe, our binary estimate of C3/C4 contributions represents a minimum, conservative estimate of relative C4 inputs. If we could remove the influence of aquatic plants the estimate of C4 inputs would likely be much larger.

The $\delta^{13}\text{C}_{\text{wax}}$ does not follow the abrupt decrease in $\delta^{13}\text{C}_{\text{TOC}}$ observed during the MIS 11, which was interpreted as a collapse of C4 vegetation and attributed to reduced summer monsoon by Fawcett et al (2011). Instead, ^{13}C -enriched $\delta^{13}\text{C}_{\text{wax}}$ values characterize the entire warming phase of the interglacial stage compared to the glacial stage (MIS 12), suggesting that C4 plants were comparatively more abundant throughout the interglacial. The observed decline in $\delta^{13}\text{C}_{\text{TOC}}$ can either be explained by the preferential removal of an organic matter fraction enriched in ^{13}C or the addition of components depleted in ^{13}C , most likely associated with closed basin conditions and desiccation of the lake during these intervals. Carbohydrates and proteins are generally ^{13}C -enriched and lipids are ^{13}C -depleted compared to total plant tissue (Degens, 1969; Deines, 1980; Lehmann et al., 2002). Loss of carbohydrates and proteins is more likely, because they are more susceptible to microbial degradation than lipids (Hedges et al., 1988; Harvey et al., 1995; Lehmann et al., 2002). This would lead to a decrease in the $\delta^{13}\text{C}_{\text{TOC}}$ value of residual organic matter. Alternatively, organic matter derived from microorganisms using a ^{13}C -depleted

carbon source (i.e. methane or organic matter) for biomass synthesis during closed basin conditions and desiccation of the lake might be an explanation for the observed depleted $\delta^{13}\text{C}_{\text{TOC}}$ values (Spooner et al., 1994; Hollander and Smith, 2001; Neunlist et al., 2002).

Significant organic matter degradation or microbial activity, raises concern that diagenetic alteration of *n*-alkanes during droughts (i.e. periods of Ca enrichment and mudcracks) might limit paleoclimate interpretations, especially during MIS 13. In order to characterize the potential diagenetic alteration of long chain *n*-alkanes, we calculated the carbon preference index (CPI, Eq. 2) (Eglinton and Hamilton, 1967). Long-chain *n*-alkanes are refractory and have a strong predominance of odd over even carbon chain lengths in fresh (undegraded) organic matter, typically expressed as high CPI values (e.g. >5) compared to petroleum (highly degraded organic matter) with CPI values near 1 (Wang et al, 2014; Chikaraishi & Naraoka, 2007; Collister et al, 1994). The CPI of higher-plant *n*-alkanes gradually decreases with algal input, microbial reworking and diagenesis, approaching CPI values of 1 (Bray and Evans, 1961, Kvenvolden, 1966). In core VC-3, CPI values range from 4 to 8.4 with almost all data above 5 (Fig. 4i), and are consistent with a terrestrial higher plant origin of the long-chain *n*-alkanes with no evidence of diagenetic alteration. In fact, Bush & McInerney (2013) suggest that, due to the tremendous diversity of CPI values in modern plants, it seems prudent to use CPI as an indicator of terrestrial plant origin in a more binary sense (either the *n*-alkanes indicate well preserved source material or do not due to diagenesis) than to attempt to quantitatively determine the degree of *n*-alkane degradation as in some studies (Buggle et al., 2010; Zech et al., 2013). In the Valles Caldera sedimentary record, CPI values do not follow a glacial-interglacial trend, in contrast to MAT and $\delta^{13}\text{C}_{\text{wax}}$. In addition, a lack of correlation between CPI values and long-chain *n*-alkane abundance ($r = 0.19$ with C_{27} ; $r = 0.17$ with C_{29} and $r = 0.12$ with C_{31}) suggests

that *n*-alkane distribution is not significantly affected by the glacial-interglacial variability. Distinct C₁₇ *n*-alkane and leaf wax distributions also suggest that degradation does not strongly affect the VC-3 sedimentary *n*-alkane record, as these compounds would be similarly impacted by diagenesis. An exception to this is the observed decrease in *n*-alkane abundance (Fig. 4a and 4c), especially of n-C₁₇ (zero values), through the MIS 13 interval where deep mudcracks were reported (Fig. 4g). Although this must be related to some extent to organic matter degradation under shallow lake conditions, this degradation apparently did not greatly affect the more refractory terrestrial *n*-alkanes judging by the CPI values through this interval. Thus our interpretations are not likely to be influenced by the oxidative degradation of organic matter.

6.3 Using variability among interglacials as a key to understanding southwestern North American climate

Pleistocene interglacials are highly diverse, and several have been suggested as analogues to the Holocene (Tzedakis et al., 2009; Tzedakis, 2010; Yin and Berger, 2015). MIS 11 has been considered a good analogue to the current Holocene warming with both high greenhouse gas concentration and prolonged duration, as opposed to MIS 13, which was thought to have been cooler with low greenhouse gas concentration and persistent continental ice in the Northern Hemisphere (Loutre and Berger, 2003; Tzedakis et al., 2012). Fawcett et al. (2011) concluded that if MIS 11 is considered to be an analogue for the Holocene, then climate in southwestern North America would naturally be trending towards a somewhat cooler and wetter stage if not for the influence of anthropogenic CO₂ emissions on climate. According to this hypothesis, the drying expected for the twenty-first century can be mainly attributed to increased greenhouse forcing, with a lesser role for orbital forcing/insolation in the near future (Seager et al., 2007;

Woodhouse et al., 2010). However, Fawcett et al. (2011) emphasized a reduction in both winter and summer monsoon rainfall, and that the summer monsoon strength reduction could not be predicted by models of near future climate change (Seager et al., 2007; Seager and Vecchi, 2010; Cayan et al., 2010; Seager et al., 2013; Prudhomme et al., 2014). The present study suggests that the extended dry episodes recorded in MIS 11 and MIS 13 (megadroughts) were in fact best characterized by reductions primarily in winter precipitation.

The molecular isotopic record presented here provides evidence that MIS 13, a time when atmospheric greenhouse gas concentrations were relatively low for an interglacial (250 ppmv), was warmer and drier than MIS 11 in southwestern North America. Our data are consistent with the hypothesis of Cisneros-Dozal et al (2014) that summer monsoon precipitation was present throughout both dry interglacial intervals (MIS 13 and MIS 11). While warmer temperatures likely influenced the increase in C4 contributions, we attribute the majority of this shift to changes in aridity. Dry interglacials (including the extreme megadroughts) were times of reduced annual precipitation most likely due to decreased winter precipitation, but summer monsoon precipitation likely continued during these intervals at a level high enough to support land plants like C4 grasses (Cisneros-Dozal et al, 2014). A reduction in annual precipitation while maintaining summer monsoon rainfall could be driven by a reduction in winter precipitation due to the poleward shifting of the rain-bearing mid-latitude winter storm tracks, as predicted in models (Yin, 2005). Winter rainfall is driven by shifts in the westerly storm tracks, and appears to be more strongly tied to glacial/interglacial conditions driven by high-latitude ice volume while summer rainfall is more strongly influenced by local insolation.

Clearly, there is still more to learn about the influence of climate change on vegetation in southwestern North America considering the variability among warm stages leading to very

different hydrological regimes and related changes in biota. These data suggest that plant type changes responded to long-term glacial-interglacial climate variability in a manner similar to current climate changes in southwestern North America.

7. Conclusions

Continental records showing mid-Pleistocene glacial/interglacial transitions are scarce. The present study shows climate and environmental changes through two glacial/interglacial transitions in southwestern North America, where droughts are predicted by recent projections of anthropogenic warming (Intergovernmental Panel on Climate Change, 2014).

The abundance and carbon isotope composition of leaf waxes together with the new temperature data indicate that MIS 13 was warmer and drier than MIS 11 in southwestern North America, despite relatively low concentrations of greenhouse gases. The environmental response to warming through glacial/interglacial transitions is expressed as an increasing relative abundance of C4 vegetation (e.g. grasses), which are better adapted to warmer, more water-stressed conditions, during relatively dry interglacials. We attribute this shift to a combination of reduced winter precipitation (from northward migration of winter storm tracks) and continued summer precipitation (from local insolation driving the North American Monsoon). The carbon isotope and leaf wax data from Valles Caldera suggest that summer (monsoon) precipitation continued throughout even periods of “megadrought”, whereas winter precipitation was greatly reduced. This interpretation is consistent with model projections for southwestern North America in the near future (IPCC, 2014).

These observations support the hypothesis that climate of southwestern North America responds strongly to local insolation through the influence of the North American Monsoon on summer precipitation, but was also sensitive to variations in greenhouse gases and/or ice volume during Pleistocene glacial/interglacial transitions through the influence of westerly storm tracks on winter precipitation. Our study shows that the influence of natural climate variability on terrestrial ecosystems is not easy to predict by simple responses to insolation forcing or greenhouse gas variations, but rather is a complex response to the relative influences of greenhouse gases and insolation on the intensity of monsoonal and winter (westerly) precipitation in the region.

Acknowledgments

We thank the National Lacustrine Core Repository (LacCore) at the University of Minnesota for core access and assistance. We thank Julia Halbur, Sarah Grosshuesch and Koushik Dutta for laboratory assistance and Matthew Finkenbinder for graphics assistance. This research was supported by the National Science Foundation proposal #EAR-0902888 to PJF, JPW, ETB, and RSA. SC received funding during the writing of this article from the CONICYT Grant 79130036 through the “Programa Atracción e Inserción de Capital Humano Avanzado (PAI)”.

References

- Allen, E.D., Spence, D.H.N., 1981. The differential ability of aquatic plants to utilize the inorganic carbon supply in fresh water. *New Phytologist* 87, 269–283.
- Aichner, B., Herzsuh, U., Wilkes, H., 2010. Influence of aquatic macrophytes on the stable carbon isotopic signatures of sedimentary organic matter in lakes on the Tibetan Plateau. *Org Geochem* 41, 706–718.
- Beerling, D.J., Osborne, C.P. 2006. The origin of the savanna biome. *Glob Change Biol* 12, 2023–2031.
- Berger, A., Loutre, M.F. 1991. Insolation values for the climate of the last 10 million years. *Quaternary Sci Rev* 10, 297–317.
- Bird, M.I., Summons, R.E., Gagan, M.K., Roksandic, Z., Dowling, L., Head, J., Keith Fifield, L., Cresswell, R.G., Johnson, D.P., 1995. Terrestrial vegetation change inferred from n-alkane $\delta^{13}\text{C}$ analysis in the marine environment. *Geochim Cosmochim Acta* 59(13), 2853–2857.
- Blaga, C. I., G.-J. Reichert, S. Schouten, A.F. Lotter, J.P. Werne, J.S. Sinninghe Damsté (2010) Branched glycerol dialkyl glycerol tetraethers in lake sediments: Can they be used as temperature and pH proxies? *Org Geochem*, 41:1225-1234.
- Bourlière, F., 1983. Tropical Savannas. In: Goodall, D.W. (ed.) *Ecosystems of the World* 13, 1–730.
- Bray, E.E., Evans, E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. *Geochim Cosmochim Acta* 22, 2–15.
- Buckles, L.K., J.W.H. Weijers, D. Verschuren, J.S. Sinninghe Damsté (2014) Sources of core and intact branched tetraether membrane lipids in the lacustrine environment: Anatomy of

611 Lake Challa and its catchment, equatorial East Africa. *Geochim. Cosmochim. Acta*
 612 140:106-126.

613 Buggle B., Wiesenberg G. L. B., Glaser B., 2010. Is there a possibility to correct fossil n-alkane
 614 data for postsedimentary alteration effects? *Appl Geochem* 25, 947–957.

615 Bush, R.T., McInerney, F.A., 2013. Leaf wax n-alkane distributions in and across modern plants:
 616 Implications for paleoecology and chemotaxonomy. *Geochim Cosmochim Acta* 117, 161–
 617 179.

618 Castañeda, I., Werne, J.P., Johnson, T.C., 2007. Wet and arid phases in the southeast African
 619 tropics since the Last Glacial Maximum. *Geology* 35(9), 823–826.

620 Cayan, D.R., Dasa, T., Pierce, D.W., Barnett, T.P., Tyree, M., Gershunov, A., 2010. Future
 621 dryness in the southwest US and the hydrology of the early 21st century drought. *Proc Natl*
 622 *Acad Sci USA* 107(50), 21271–21276.

623 Cerling, T.E., Harris, J.M., MacFadden, B.J., Leakey, M-G., Quadek, J., Eisenmann, V.,
 624 Ehleringer, J.R., 1997. Global vegetation change through the Miocene/Pliocene boundary.
 625 *Nature* 389, 153–158.

626 Chen, F.H., Bloemendal, J., Zhang, P.Z., Liu, G.X., 1999. An 800 ky proxy record of climate
 627 from lake sediments of the Zoige Basin, eastern Tibetan Plateau, *Palaeogeogr*
 628 *Palaeoclimatol Palaeoecol* 151, 307–320.

629 Chikaraishi, Y, Naraoka, H., 2007. $\delta^{13}\text{C}$ and δD relationships among three n-alkyl compound
 630 classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. *Org Geochem*
 631 38, 198–215

632 Cisneros-Dozal, L.M., Huang, Y., Heikoopa, J.M., Fawcett, P.J., Fessenden, J., Anderson, R.S.,
 633 Meyers, P.A., Larsona, T., Perkin, G., Toney, J., Werne, J.P., F. Goff, WoldeGabriel, G.,

634 Allen, C.D., Berke, M.A., 2014. Assessing the strength of the monsoon during the mid-
 635 Pleistocene in southwestern United States. *Quaternary Sci Rev* 103, 81–90.

636 Colletti, A.J., DeConto, R.M., Brigham-Grette, J., and Melles, J., 2015. A GCM comparison of
 637 Pleistocene super-interglacial periods in relation to Lake El'gygytgyn, NE Arctic Russia
 638 *Climates of the Past* 11, 979–989.

639 Collister, J.W., Rieley, G., Stern, B., Eglinton, G., Fry, B., 1994. Compound-specific $\delta^{13}\text{C}$
 640 analyses of leaf lipids from plants with differing carbon dioxide metabolisms. *Org*
 641 *Geochem* 21, 619–627.

642 Cranwell, P.A., Eglinton, G., Robinson, N., 1987. Lipids of aquatic organisms as potential
 643 contributors to lacustrine sediments—II. *Org Geochem* 11, 513–527.

644 de Vernal, A. Hillaire-Marcel, C., 2008. Natural variability of Greenland climate, vegetation, and
 645 ice volume during the past million years. *Science* 320, 1622–1625.

646 Degens, E.T., 1969. Biogeochemistry of stable carbon isotopes. In Eglinton, E., Murphy, M.T.J.
 647 (editors), *Organic Geochemistry*. Springer-Verlag, New York. 304–329.

648 Deines, P., 1980. The isotopic composition of reduced organic carbon. In Fritz, P., Fontes, J.C.
 649 (editors), *Handbook of Environmental Isotope Geochemistry*. Elsevier, Amsterdam. 329–
 650 406.

651 Diffenbaugh, N.S., Giorgi, F., 2012, Climate change hotspots in the CMIP5 global climate model
 652 ensemble. *Clim Change* 114(3-4), 813–822.

653 Diffenbaugh, N.S., Giorgi, F., Pal, J.S., 2008. Climate change hotspots in the United States.
 654 *Geophys Res Lett* 35(16), L16709.

655 Dirghangi S.S., Pagani, M., Hren, M.T., and Tipple, B.J. 2013 Distribution of glycerol dialkyl
 656 glycerol tetraethers in soils from two environmental transects in the USA, *Organ Geochem*
 657 59, 49–60.

658 Eglinton, G., Calvin, M., 1967. Chemical fossils. *Sci Amer* 261, 32–43.

659 Eglinton, G., Hamilton, R.J., 1967. Leaf Epicuticular Waxes. *Science* 156, 1322–1335.

660 $^{13}\text{C}/^{12}\text{C}$ fractionation and its utility in terrestrial plant studies

661 Ehleringer, J.R., 1991. $^{13}\text{C}/^{12}\text{C}$ fractionation and its utility in terrestrial plant studies. In: *Carbon*
 662 *isotope techniques*, edited by Coleman, D.C and Fry B., 274 pp.

663 Ehleringer, J.R., Monson, R.K., 1993. Evolutionary and ecological aspects of photosynthetic
 664 pathway variation. *Annu.Rev. Ecol Syst* 24, 411–439

665 Farquhar, G. D., Ehleringer, J. R., Hubick, K. T., 1989. Carbon isotope discrimination and
 666 photosynthesis. *Annu. Rev. Plant Physiol. Plant Mol Biol* 40, 503–537.

667 Fawcett, P.J., Heikoop, J., Goff, F., Anderson, R.S., Donohoo-Hurley, L., Geissman, J.W.,
 668 WoldeGabriel, G., Allen, C.D., Johnson, C.M., Smith, S.J., and Fessenden-Rahn, J., 2007.
 669 Two Middle Pleistocene Glacial-Interglacial Cycles from the Valle Grande, Jemez
 670 Mountains, northern New Mexico; *New Mexico Geological Society Guidebook*, 58th Field
 671 Conference, *Geology of the Jemez Mountains Region II*, 409–417.

672 Fawcett, P.J., Werne, J.P., Anderson, R.S., Heikoop, J.M., Brown, E.T., Berke, M.A., Smith,
 673 S.J., Goff, F., Donohoo-Hurley, L., Cisneros-Dozal, L.M., Schouten, S., Sinninghe Damste,
 674 J.S., Huang, Y., Toney, J., Fessenden, J., WoldeGabriel, G., Atudorei, V., Geissman J.W.,
 675 Allen. C.D., 2011. Extended megadroughts in the southwestern United States during
 676 Pleistocene interglacials. *Nature* 470, 518–521.

677 Feakins, S.J., Sessions, A.L., 2010. Controls on the D/H ratios of plant leaf waxes in an arid
 678 ecosystem. *Geochim Cosmochim Acta* 74(7), 2128–2141.

679 Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An n-alkane proxy for the sedimentary
 680 input of submerged/floating freshwater aquatic macrophytes. *Org Geochem* 31, 745–749.

681 Gagosian, R.B., Peltzer, E.T., Merrill, J.T., 1987. Long range transport of terrestrially derived
 682 lipids in aerosols from the south Pacific. *Nature* 325, 800–803.

683 Giger, W., Schaffner, C., Wakeham, S.G., 1980. Aliphatic and olefinic hydrocarbons in recent
 684 sediments of Greifensee, Switzerland. *Geochim Cosmochim Acta* 44, 119–129.

685 Giorgi, F., 2006. Climate change hot-spots. *Geophys Res Lett* 33(8), L08707.

686 Goff, F., Gardner, J.N., 1994. Evolution of a mineralized geothermal system, Valles Caldera,
 687 New Mexico. *Econ Geol* 89, 1803–1832.

688 Guo, Z.T., Berger, A., Yin, Q.Z., Qin, L., 2009. Strong asymmetry of hemispheric climates
 689 during MIS-13 inferred from correlating China loess and Antarctica ice records. *Clim Past*
 690 5, 21–31.

691 Harvey H. R., Tuttle J. H., and Bell J. T. (1995) Kinetics of phytoplankton decay during
 692 simulated sedimentation: Changes in biochemical composition and microbial activity under
 693 oxic and anoxic conditions. *Geochim Cosmochim Acta* 59(16), 3367–3377.

694 Hedges J.I., Clark W.A., Cowie G.L., 1988. Fluxes and reactivities of organic matter in a coastal
 695 marine bay. *Limnol. Oceanogr.* 33(5), 1137–1152.

696 Hollander, D.J., Smith, M.A., 2001. Microbially mediated carbon cycling as a control on the
 697 $\delta^{13}\text{C}$ of sedimentary carbon in eutrophic Lake Mendota (USA): New models for
 698 interpreting isotopic excursions in the sedimentary record. *Geochim Cosmochim Acta* 65:
 699 4321–4337.

Hopmans, E.C., Weijers, J.W.H., Schefuss, E., Herfort, L., Damste, J.S.S., Schouten, S., 2000. A
 novel proxy for terrestrial organic matter in sediments based on branched and isoprenoid
 tetraether lipids. *Earth Planet Sc Lett* 224, 107–116.

Huang, Y., Street-Perrott, F.A., Perrott, R.A., Metzger, P., Eglinton, G., 1999. Glacial-
 interglacial environmental changes inferred from molecular and compound-specific $\delta^{13}\text{C}$
 analyses of sediment from Sacred Lake, Mt. Kenya. *Geochim Cosmochim Acta* 63, 1383–
 1404.

IPCC, 2014: Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part B: Regional
 Aspects. Contribution of Working Group II to the Fifth Assessment Report of the
 Intergovernmental Panel on Climate Change [Barros, V.R., C.B. Field, D.J. Dokken, M.D.
 Mastrandrea, K.J. Mach, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B.
 Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White (eds.)].
 Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 688
 pp.

Jouzel, J., Masson-Delmotte, V., Cattani, O., Dreyfus, G., Falourd, S., Hoffmann, G., Minster,
 B., Nouet, J., Barnola, J.M., Chappellaz, J., Fischer, H., Gallet, J.C., Johnsen, S.,
 Leuenberger, M., Loulergue, L., Luethi, D., Oerter, H., Parrenin, F., Raisbeck, G.,
 Raynaud, D., Schilt, A., Schwander, J., Selmo, E., Souchez, R., Spahni, R., Stauffer, B.,
 Steffensen, J.P., Stenni, B., Stocker, T.F., Tison, J.L., Werner, M., Wolff, E.W., 2007.
 Orbital and Millennial Antarctic Climate Variability over the Past 800,000 Years. *Science*
 317, 793–797.

Keeley, J.E., Sandquist, D.R., 1992. Carbon: freshwater plants. *Plant Cell and Environment* 15,
 1021–1035.

723 Kvenvolden, K., 1966. Molecular distribution of normal fatty acids and paraffins in some lower
724 Cretaceous sediments. *Nature* 209, 573–577.

725 Lehmann, M.F., Bernasconi, S.M., Barbieri, A., McKenzie, J., 2002. Preservation of organic
726 matter and alteration of its carbon and nitrogen isotope composition during simulated and
727 in situ early sedimentary diagenesis. *Geochim Cosmochim Acta* 66(20) 3573–3584.

728 Lisiecki, L.E., Raymo, M.E., 2005. A Pliocene-Pleistocene stack of 57 globally distributed
729 benthic $\delta^{18}\text{O}$ records. *Paleoceanography* 20, PA1003.

730 Liu, W., Li, X., An, Z., Xu, L., Zhang, Q., 2013. Total organic carbon isotopes: A novel proxy of
731 lake level from Lake Qinghai in the Qinghai–Tibet Plateau, China. *Chem Geol* 347, 153–
732 160.

733 Liu, W., Yang, H., Wang, H., An, Z., Wang, Z., Leng, Q., 2015. Carbon isotope composition of
734 long chain leaf wax n-alkanes in lake sediments: A dual indicator of paleoenvironment in
735 the Qinghai-Tibet Plateau. *Org Geochem* 83-84, 190–201.

736 Lockheart, M.J., Van Bergen, P.F., Evershed, R.P., 1997. Variations in the stable carbon isotope
737 compositions of individual lipids from the leaves of modern angiosperms: Implications for
738 the study of higher land plant-derived sedimentary organic matter. *Org Geochem* 26, 137–
739 153.

740 Loomis, S.E., J.M. Russell, A.M. Heurreux, W.J. D’Andrea, J.S. Sinninghe Damste (2014)
741 Seasonal variability of branched glycerol dialkyl glycerol tetraethers (brGDGTs) in a
742 temperate lake system. *Geochim. Cosmochim. Acta* 144:173-187.

743 Loutre, M.F., Berger, A., 2003. Marine Isotope Stage 11 as an analogue for the present
744 interglacial. *Global Planet. Change* 36, 209–217.

745 Lund, S., Stoner, J.S., Channell, J.E.T., Acton, G., 2006. A summary of Bruhnes paleomagnetic
 746 field variability recorded in Ocean Drilling Program cores. *Phy Earth Planet* 156, 194–204.
 747 Lüthi, D., Le Floch, M., Bereiter, B., Blunier, T., Barnola, J-M, Siegenthaler, U., Raynaud, D.,
 748 Jouzel, J., Fischer, H., Kawamura, K., Stocker, T., 2008. High-resolution carbon dioxide
 749 concentration record 650,000–800,000 years before present. *Nature* 453, 379–382.
 750 Makou, M.C., Hughen, K.A., Xu, L., Sylva, S.P., Eglinton, T.I., 2007. Isotopic records of
 751 tropical vegetation and climate change from terrestrial vascular plant biomarkers preserved
 752 in Cariaco Basin sediments. *Org Geochem* 38, 1680–1691.
 753 Marković, S.B., Hambach, U., Catto, N., Jovanović, M., Bugge, B., Machalett, B., Zöller, L.,
 754 Glaser, B., Frechen, M., 2009. The middle and late Pleistocene loess sequences at
 755 Batajnica, Vojvodina, Serbia. *Quat Int* 198, 255–266.
 756 Melles, M.C., et al., 2012. 2.8 Million Years of Arctic Climate Change from Lake El’gygytyn,
 757 NE Russia. *Science* 337, 315–320.
 758 Menges, J., Huguet, C., Alcañiz, J. M., Fietz, S., Sachse, D., Rosell-Melé, A. 2014. Influence of
 759 water availability in the distributions of branched glycerol dialkyl glycerol tetraether in
 760 soils of the Iberian Peninsula. *Biogeosciences* 11, 2571–2581.
 761 Meyers, P.A., 2003. Applications of organic geochemistry to paleolimnological reconstructions:
 762 a summary of examples from the Laurentian Great Lakes. *Org Geochem* 34, 261–289.
 763 Naeher, S., Peterse, F., Smittenberg, R.H., Niemann, H., Zigah, P.K., Schubert, C.J., 2014.
 764 Sources of glycerol dialkyl glycerol tetraethers (GDGTs) in catchment soils, water column
 765 and sediments of Lake Rotsee (Switzerland) - Implications for the application of GDGT-
 766 based proxies for lakes. *Org. Geochem.* 66: 164–173.

767 Neunlist, S., Rodier, C., Llopy, P., 2002. Isotopic biogeochemistry of the lipids in recent
 768 sediment of Lake Bled (Slovenia) and Baldeggersee (Switzerland). *Org Geochem* 33:
 769 1183–1195.

770 O’Leary, M.H., 1981. Carbon isotope fractionation in plants. *Phytochemistry* 20, 553e567.

771 O’Leary, M.H., 1988. Carbon isotopes in photosynthesis. *Bioscience* 38, 328–336.

772 Pancost, R.D. and Boot, C.S., 2004. The palaeoclimatic utility of terrestrial biomarkers in marine
 773 sediments. *Mar Chem* 92(1-4), 239–261.

774 Prins, H.B.A., Elzenga, J.T.M., 1989. Bicarbonate utilization: function and mechanism. *Aquatic*
 775 *Botany* 34, 59–83.

776 Prokopenko, A.A., Williams, D.F., Kuzmin, M.I., Karabanov, E.B., Khursevich, G.K., Peck,
 777 J.A., 2002. Muted climate variations in continental Siberia during the mid-Pleistocene
 778 epoch. *Nature* 418, 65–68.

779 Prudhomme, C., Giuntolia, I., Robinson, E.L., Clark, D.B., Arnell, N.W., Dankers, R., Fekete,
 780 B.M., Franssen, W., Gerten, D., Goslingh, S.N., Hagemann, S., Hannahb, D.M., Kim, H.,
 781 Masakik, Y., Satohl, Y., Stacke, T., Wadam, Y., Wissern, D., 2014. Hydrological droughts
 782 in the 21st century, hotspots and uncertainties from a global multimodel ensemble
 783 experiment. *Proc Natl Acad Sci USA* 111(9), 3262–3267.

784 Rao, Z., Zhu, Z.Y., Jia, G., Chen, F., Barton, L., Zhang, J., Qiang, M., 2010. Relationship
 785 between climatic conditions and the relative abundance of modern C3 and C4 plants in
 786 three regions around the North Pacific. *Chinese Sci Bull* 55(18), 1931–1936.

787 Raymo, M.E., Mitrovica, J.X., 2012. Collapse of polar ice sheets during the stage 11 interglacial.
 788 *Nature* 483, 453–456.

789 Reneau, S.L., Drakos, P.G., Katzman, D., 2007. Post-resurgence lakes in the Valles Caldera,
790 New Mexico, New Mexico Geological Society Guidebook, 58th Field Conference,
791 Geology of the Jemez Mountains Region II, 398–408.

792 Rieley, G., Collier, R.P., Jones, D.M., Eglinton, G., Eakin, P.A., Fallick, A.E. 1991. Sources of
793 sedimentary lipids deduced from stable carbon-isotope analyses of individual compounds.
794 Nature 352, 425–427.

795 Rieley, G., Collister, J.W., Stern B., Eglinton, G. 1993. Gas Chromatography /Isotope Ratio
796 Mass Spectrometry of Leaf Wax n-Alkanes from Plants of Differing Carbon Dioxide
797 Metabolisms. Rapid Communications in Mass Spectrometry 7, 488–491.

798 Schefuß, E., Kuhlmann, H., Mollenhauer, G., Prange, M., Pätzold, J., 2011. Forcing of wet
799 phases in southeast Africa over the past 17,000 years. Nature 480, 509–512.

800 Schwark, L., Zink, K., Lechterbeck, J., 2002. Reconstruction of postglacial to early Holocene
801 vegetation history in terrestrial Central Europe via cuticular lipid biomarkers and pollen
802 records from lake sediments. Geology 30, 463–466.

803 Seager, R. and Vecchi, G.A., 2010. Greenhouse warming and the 21st Century hydroclimate of
804 southwestern North America. Proc Natl Acad Sci USA 107(50), 21277–21282.

805 Seager, R., Goddard, L., Nakamura, J., Henderson, N., Lee, D., 2013. Dynamical causes of the
806 2010/11 Texas-northern Mexico drought. J. Hydrometeorology 15, 39–68

807 Seager, R., Ting, M.F., Held, I.M., Kushnir, Y., Lu, J., Vecchi, G., Huang, H.-P., Harnik, N.,
808 Leetmaa, A., Lau, N.-C., Li, C., Velez, J., Naik, N., 2007. Model Projections of an
809 Imminent Transition to a More Arid Climate in Southwestern North America. Science 316,
810 1181–1184.

811 Siegenthaler, U., Stocker, T.F., Monnin, E., Lüthi, D., Schwander, J., Stauffer, B., Raynaud, D.,
 812 Barnola, J-M, Fischer, H., Masson-Delmotte, V., Jouzel, J., 2005. Stable Carbon Cycle-
 813 Climate Relationship During the Late Pleistocene. *Science* 310, 1313–1317.
 814 Smith, G.A., McIntosh, W., and Kuhle, A.J., 2001. Sedimentologic and geomorphic evidence for
 815 seesaw subsidence of the Santo Domingo accommodation-zone basin, Rio Grande rift,
 816 New Mexico, *Geol Soc America Bull* 113, 561–574.
 817 Spooner, N., Rieley, G., Collister, J.W., Lander, M., Cranwell, P.A., 1994. Stable carbon isotopic
 818 correlations of individual biolipids in aquatic organisms and a lake bottom sediment. *Org*
 819 *Geochem* 21: 823–827.
 820 Street-Perrott, F.A., Ficken, K.J., Huang, Y., Eglinton, G., 2004. Late Quaternary changes in
 821 carbon cycling on Mt. Kenya, East Africa: an overview of the $\delta^{13}\text{C}$ record in lacustrine
 822 organic matter. *Quaternary Sci Rev* 23(7), 861–879.
 823 Tipple, B.J., Pagani, M., 2007. The early origins of terrestrial C4 photosynthesis. *Annu Rev*
 824 *Earth Planet Sci* 35, 435–461.
 825 Tierney, J.E., J.M. Russell (2009) Distributions of branched GDGTs in a tropical lake system:
 826 Implications for lacustrine application of the MBT/CBT paleoproxy. *Org Geochem* 40,
 827 1032–1036.
 828 Tieszen, L.L., Reed, B.C., Bliss, N.B., Dejong, D.D., Wylie, B.K., DeJong, D.D., 1997. NDVI,
 829 C3 and C4 production and distributions in Great Plains grassland land cover classes. *Ecol*
 830 *Appl* 7(1), 59–78.
 831 Tzedakis, P. C., 2010. The MIS 11 – MIS 1 analogy, southern European vegetation, atmospheric
 832 methane and the “early anthropogenic hypothesis”. *Clim Past* 6, 131–144.

833 Tzedakis, P. C., Raynaud, D., McManus, J., Berger, A., Brovkin, V., Kiefer, T., 2009.
834 Interglacial diversity. *Nature Geosci* 2, 751–755.

835 Tzedakis, P.C., Channell, J.E.T., Hodell, D.A., Kleiven, H.F., Skinner, L.C., 2012. Determining
836 the natural length of the current interglacial. *Nature Geosci* 5, 138–141.

837 Vandenberghe, J., 2000. A global perspective of the European chronostratigraphy for the past
838 650 ka. *Quat Sci Rev* 19, 1701–1707.

839 Vogts, A., Moossen, H., Rommerskirchen, F., Rullkötter, J., 2009. Distribution patterns and
840 stable carbon isotopic composition of alkanes and alkan-1-ols from plant waxes of African
841 rain forest and savanna C3 species. *Org Geochem* 40, 1037–1054.

842 Wang, N., Zong, Y., Brodie, C.R., Zheng, Z., 2014. An examinatio of the fidelity of n-alkanes as
843 a palaeoclimate proxy from sediments of Palaeolake Tianyang, South China. *Quat Int* 333,
844 100–109.

845 Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Sinninghe Damsté, J.S.,
846 2007. Environmental controls on bacterial tetraether membrane lipid distribution in soils.
847 *Geochim Cosmochim Ac* 71, 703–713.

848 WoldeGabriel, G., Heikoop, J., Goff, F., Counce, D., Fawcett, P.J., and Fessenden-Rahn, J.,
849 2007. Appraisal of post-South Mountain volcanism lacustrinesedimentation in the Valles
850 Caldera using tephra units. *New Mexico Geological Society Guidebook*, 58th Field
851 Conference, *Geology of the Jemez Mountains Region II*, 83–85.

852 Woodhouse, C.A., Meko, D.M., MacDonald, G.M., Stahled, D.W., Cook, E.R., 2010. A 1,200-
853 year perspective of 21st century drought in southwestern North America. *Proc Natl Acad*
854 *Sci USA* 107, 21283–21288.

855 Yin, J., 2005. A consistent poleward shift of the storm tracks in simulations of 21st century
856 climate. *Geophys Res Lett* 32(18), L18701.

857 Yin, Q., Berger, A., 2015. Interglacial analogues of the Holocene and its natural near future.
858 *Quaternary Sci Rev* 120, 28–46.

859 Zagwijn, W., 1996. The Cromerian complex stage of the Netherlands and correlation with other
860 areas in Europe, in: *The early Middle Pleistocene in Europe*, edited by: Turner, C.,
861 Balkema, Rotterdam, 145–172.

862 Zech M., Krause T., Meszner S., and Faust D. (2013) Incorrect when uncorrected:
863 Reconstructing vegetation history using n-alkane biomarkers in loess-paleosol sequences–
864 A case study from the Saxonian loess region, Germany. *Quaternary Int* 296, 108–116.

865

866

867

Appendix. Molecular structures of the branched glycerol dialkyl glycerol tetraether (GDGTs).

Figure

Figure

Figure

Figure

Figure