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Will animal subjects be used? ☐ Yes ☒ No

APPROVAL DATE: _____ PROTOCOL #: _____ PENDING: _____

Does this application involve any recombinant DNA technology or resea ☐ Yes ☒ No

Reconstructing climate variability, aridity and water availability in the Sacramento-San Joaquin watershed based on isotopic evidence in sediments from Swamp Lake, Yosemite NP

A research proposal by Joseph H. Street, Stanford University & University of California, Santa Cruz

INTRODUCTION & MOTIVATION

As the evidence for anthropogenic influence on global climate has solidified, increasing attention has been devoted to developing a predictive understanding of the climate system on ever more detailed regional scales. A first step toward this goal is to understand the patterns, timescales and drivers of past climatic changes as recorded in geological and biological archives. Paleoclimatological approaches extend our knowledge of the climate system over a vastly longer period of time than the instrumental record, and as a result provide a more complete picture of the range of climatic variability and of the processes driving climate changes. Both historical and proxy records demonstrate that climate change is often expressed most acutely as rearrangements in the hydrological cycle on regional and local scales (Hodell et al. 1995; Gleick et al. 2000; Benson et al. 2007). Changes in the amount, timing and form of precipitation have direct but at times non-linear effects on hydrologic variables – e.g., streamflow, groundwater recharge, soil moisture – that determine the availability of water for ecosystems and human communities (Alverson and Edwards 2003; Knox 2003).

Recent decades have seen an explosion in our understanding of the drivers of hydroclimatic variability on interannual timescales, with a particular emphasis on the global influence of the El Niño-Southern Oscillation (ENSO) cycle arising in the tropical Pacific Ocean. A century of direct observations has been sufficient to assign a host of generalized regional responses to both El Niño events (positive ENSO) (e.g., drought in Australia, wet conditions in Peru) and La Niña (negative ENSO) conditions, particularly in the tropics and sub-tropics (Allan 2000). However, it has become increasingly apparent that regional climates also vary on longer sub-orbital timescales – decadal, centennial, and millennial – and that these slower changes in "baseline" conditions interact with annual and interannual processes to amplify or damp climatic responses (e.g., McCabe and Dettinger 1999). Reconstructions of the ENSO phenomenon reveal continual shifts in ENSO behavior – regime shifts between periods of strong or frequent ENSO cycles and periods of relative quiescence that far exceed the modern range of variability – occurring on decadal to millennial timescales (e.g., Stahle et al. 1998; Moy et al. 2002; Cobb et al. 2003; Rein et al. 2005). Understanding lower frequency climatic variability is crucial because processes on these timescales determine water supplies, influence the distribution of plants and animals, and modulate the occurrence of higher-frequency events such as floods and droughts. In addition, low-frequency natural variability may obscure or intensify the human influence on global climate.

An understanding of natural hydroclimatic variability is of particular importance in California, where agriculture, environmental resources and a growing urban population compete for a limited water supply that is heavily dependent on snowmelt runoff from the Sierra Nevada. Recent history has demonstrated that just a few years of drought can lead to severe water shortages, restricted agricultural uses and the decline of aquatic resources in the Sacramento-San Joaquin River Delta. Climate models suggest that under global warming conditions impacts to the California water supply, and to the ecosystems that depend on water availability, may stem predominantly from shifts in the rain/snow balance of precipitation, the timing of Sierra snowmelt and peak runoff, and the frequency of extreme events (floods & droughts) (e.g., Knowles and Cayan 2004; VanRheenen et al. 2004). The history and causes of decadal, centennial, and millennial-scale fluctuations in California hydroclimate are largely unresolved, particularly prior to the latest Holocene, due in part to a shortage of long, high resolution paleoclimatic records in the Sierra Nevada watershed. The degree to which California climate has been controlled by ENSO and multidecadal-scale variability in the North Pacific remains an open question, as is the long-term influence of more distant potential teleconnections with North Atlantic climate (McCabe et al. 2004).

The research proposed here will address these gaps in our understanding through the development of a new record of California hydroclimate since the last glacial maximum (LGM). This record will be based on the hydrogen (δ^2H, or δD), carbon (δ^{13}C), and nitrogen (δ^{15}N) isotopic compositions and elemental abundances (TOC, TN, C/N) of organic matter preserved in the sediments of Swamp Lake, a mid-elevation lake in the central Sierra Nevada. Compound-specific δD analyses of both aquatic and terrestrial plant leaf-

wax biomarkers will provide an index of lake hydrologic balance and aridity, while the carbon and nitrogen proxies will provide a record of ecosystem responses to changing precipitation and temperature conditions. The combined record will be of sufficient resolution (~20-50 years) to reconstruct patterns of climatic variability and lake response on decadal to millennial timescales, and to evaluate the influence of proposed climate drivers (e.g., ENSO, PDO) over the entire Holocene.

BACKGROUND

Drivers of Precipitation in California: California's climate is marked by steep precipitation gradients (decreasing north-south, west-east), a high degree of spatial heterogeneity, and strong seasonality (85-90% of precipitation in the winter-spring wet season). In snow-dominated mountain watersheds, such as the large Sacramento-San Joaquin River system draining the Sierra Nevada, streamflow trails precipitation, with peak discharge typically occurring three to six months after peak snowfall, in the late spring and early summer. The amount and seasonality of precipitation in California is governed by atmospheric circulation patterns in the North Pacific, specifically the development and persistence of a negative sea level pressure (SLP) anomaly off the coast of Northern California in response to the weakening and southward shift of the Pacific Subtropical High, allowing moisture-bearing storms to reach California (Cayan and Peterson 1989; Cayan and Peterson 1993; Peterson et al. 1995). The intensity of the basic seasonal pattern, and hence precipitation in California, varies on interannual, decadal, and potentially much longer timescales, but the relatively local nature of the winter circulation governing California ensures that the effects of basin-scale and global ocean-atmosphere processes, including ENSO and the lower-frequency Pacific Decadal Oscillation (PDO) (Mantua and Hare 2002), remain indirect (Schonher and Nicholson 1989; Cayan and Peterson 1993). Major climate drivers such as ENSO modulate, rather than dictate, atmospheric circulation in north-central California, producing an inconsistent precipitation response (Ropelewski and Halpert 1986; Cayan and Peterson 1989; Cayan et al. 1998; Schonher and Nicholson 1989).

On average, El Niño events are linked with above normal rainfall in California (Dai and Wiggley 2000), but this generalization masks a bimodal response: Strong El Niños producing large, extensive, and persistent sea surface temperature (SST) anomalies in the tropical and subtropical Pacific consistently result in high precipitation in California; moderate or weak El Niños are more often associated with slightly below normal precipitation or even drought (Schonher and Nicholson 1989). La Niña years tend to be dryer than normal in California, but this response is also inconsistent (Cole et al. 2002). Recent research has demonstrated that decadal-scale oscillations in the Pacific and Atlantic oceans influence the intensity and spatial pattern of climatic responses to ENSO in western North America (Gershunov and Barnett 1998; Cole et al. 2002; McCabe et al. 2004); for example, several major regional droughts since 1850 corresponded to La Niña years occurring during cold phases of the PDO (Cole et al. 2002). Prior to the instrumental record, the influence of these oceanic drivers of climate remains poorly understood, particularly in north-central California.

Paleoclimate research in California*:* High-resolution climate records in the California region are for the most part limited to tree-ring studies extending several hundred to a thousand years into the past (e.g., Earle 1993, Graumlich 1993, Scuderi 1993, Meko et al. 2001, 2002). Longer high-resolution records exist for the Southern Sierra (Hughes and Brown 1992), western Great Basin (LaMarche 1974; Benson et al. 1996; Benson et al. 2002; Mensing et al. 2004) and Southern California coastal margin (Kennett and Ingram 1995), but are otherwise lacking. Within the area encompassed by the Sacramento-San Joaquin watershed, including the western slope of the Sierra Nevada, few paleoclimatic records of decadal- or even centennial-scale resolution extend past the late Holocene. In the absence of such records, it has been difficult to evaluate the long-term influence of ENSO on water resources in California, or to draw useful lessons about regional climate variability during past warm intervals (e.g., the mid-Holocene).

Hydrogen Isotopes in Paleoclimatic Research*:* Variations in the hydrogen isotope composition of water are observed in every stage of the hydrologic cycle, from cloud formation to precipitation to biological utilization, making the the deuterium/hydrogen ratio (D/H, δD) a potentially powerful tracer of paleohydrologic processes. The initial δD of water vapor in an air mass is set by evaporation from the ocean,

which produces vapor depleted in deuterium. Further depletion occurs as an air mass moves inland through progressive cycles of precipitation and evaporative inputs from the land surface (Dansgaard 1964; Ingraham and Taylor 1991). δD of precipitation is positively related to air temperature (4 to 6 ‰ per ºC at mid-latitudes), giving rise to broad geographical and seasonal patterns (Craig 1961; Kendall and Coplen 2001). Accordingly, proxy records of changes in the δD of precipitation at a site could provide information about paleotemperature and/or the sources and seasonality of precipitation.

Lake sediments provide one potential archive of paleohydrological information in the form of sedimentary organic matter (OM), but the isotopic heterogeneity of lake OM (deriving from many plant, algal, and microbial sources) and the problem of selective diagenesis in ancient sediments hampered early attempts to use the δD of bulk materials or kerogen in paleoclimatic reconstructions (e.g., Krishnamurthy et al. 1995). More recent analytical techniques for measuring δD of individual hydrogen-bearing organic compounds have eliminated many of the factors confounding interpretation of lake sediment records. Lakes integrate the δD signals of their meteoric water sources -- surface runoff, groundwater and direct precipitation – over timescales related to the water residence time. Subsequent increases in lake water δD driven by evaporation are minor in humid environments but may become important in arid or highly seasonal environments (Sachse et al. 2004, Huang et al. 2004; Sachse et al. 2006, Sachs 2006). Lipid biomarkers produced by lake algae and aquatic plants record the δD value of their water source with systematic fractionations (-100 to -400 ‰) determined by the specific biochemical pathways and intracellular H pools utilized during lipid biosynthesis (Sternberg 1988; Sessions et al. 1999; Sauer et al. 2001; Sachse et al. 2004; Zhang and Sachs 2007). Where aquatic lipid biomarkers are preserved in sediments they may provide the means of reconstructing the δD of precipitation and/or lake evaporation/precipitation balance in the past (Huang et al. 2002).

Compounds derived from terrestrial plants may also be present in lake OM, and may provide additional hydrological information. The δD of plant leaf water is generally modified from local precipitation by evapotranspiration occurring in the soil and from leaf stomata (Fig. 1); δD of leaf water is usually 20 to 80‰ greater than soil water (Ziegler et al 1989). Thus, the apparent fractionation ($\varepsilon_{plant/H2O}$) between the δD of plant tissues and δD of precipitation may be smaller than expected based on biochemical fractionations alone (Fig. 1). The relative importance of evapotranspiration (i.e., relative humidity) versus air temperature in modifying the source water isotopic signal in plant tissues has been explored in multiple studies of δD and $\delta^{18}O$ in tree ring cellulose (e.g., Epstein and Yapp 1976; Feng and Epstein 1994, 1995). Cellulose, however, contains a significant amount of exchangeable H, and is subject to degradation in sedimentary records. The work proposed here will instead utilize both aquatic and terrestrial lipid biomarkers -- which are more refractory and contain more carbon-bound, non-exchangeable hydrogen than cellulose -- to develop δD records of hydrologic variability at our study site.

<u>*Biomarkers:*</u> Long-chain, odd-numbered ($C_{25} – C_{33}$) *n*-alkanes have long been recognized as biomarkers for terrestrial vegetation, deriving from plant leaf-waxes (e.g., Eglinton and Hamilton 1967; Cranwell et al. 1987). Shorter-chain *n*-alkanes, *n*-alkadienes and *n*-acids have been identified as biomarkers for submerged aquatic plants (C_{21}, C_{23}, C_{25} *n*-alkanes; C_{22} behenic acid) (Ficken et al. 2000; Hou et al. 2006) and aquatic algae and photosynthetic bacteria (C_{17}, C_{19} *n*-alkane; C_{25} - C_{31} *n*-alkadiene; C_{14} - C_{20} fatty acids) (Cranwell et al. 1987; Huang et al. 2004; Zhang and Sachs 2007). Other biomarkers for various classes of aquatic algae include dinosterol (dinoflagellates) (Sauer et al. 2001), alkenones (haptophyte algae) (Englebrecht and Sachs 2005), and a class of C_{30-37} polymethylated triterpenes, termed 'botryococcenes", produced by the freshwater colonial green alga *Botryococcus braunii* (Zhang and Sachs 2007). A compound-specific approach provides a potentially powerful means of ensuring that the δD values measured apply to material of specific origin, and thus of isolating particular components of the hydroclimatic system.

<u>*Previous Studies:*</u> Multiple field studies have demonstrated strong correlations between δD values of specific compounds and δD values of meteoric and lake water, which in turn correlate with mean annual temperature, over a wide range of lakes and climatic regimes (Sauer et al. 2001; Huang et al. 2004; Sachse et al. 2004; Hou et al. 2006). These studies document have documented consistent apparent fractionations

($\varepsilon_{compound/H2O}$) between lakewater and individual aquatic biomarkers extracted from surface sediments, supporting the notion that these offsets are dominated by the biosynthetic fractionation rather than environmental variables. Though several recent studies have observed somewhat variable biosynthetic fractionations between different species, between geographically distinct strains of the same species (Table 1), and in response to physiological and environmental variables (Schouten et al. 2006; Zhang and Sachs 2007; Sachse and Sachs 2007), these sources of variation tend to be small and in general algal biomarkers appear to faithfully capture the isotopic composition of source water.

Though long-chain *n*-alkanes derived from leaf waxes also record source water δD values, the observed apparent fractionations in these and other studies are smaller (and somewhat more variable) than for short-chain *n*-alkanes, in the range of -115 to -140 ‰ (Sternberg 1988; Sauer et al. 2001; Chikaraishi & Naraoka 2003; Sachse et al. 2004; Sachse et al. 2006). Using the consistently observed value of -160‰ as the "baseline" biosynthetic fractionation for *n*-alkanes, Sachse et al. (2004) and (2006) attributed the lower apparent fractionations of long-chain *n*-alkanes to evaporative enrichment of deuterium in soil or leaf water, as illustrated in Fig. 1. Phrased differently, these *n*-alkanes displayed evapotranspirative fractionations (ε_{ET}), calculated as the difference between the apparent fractionation (-115 to -140‰) and the biosynthetic fractionation (-160‰), in the range of 20-45‰. Employing a similar set of assumptions, Feakins et al. (2006) measured increasing ε_{ET} values in leaf wax *n*-alkanes across a decreasing moisture gradient in Southern California. As with algal biomarkers, interspecific variability among *n*-alkane sources sources – in terms of leaf-wax *n*-alkane distributions and a species' susceptibility to evapotranspirative water loss -- may complicate the interpretation of sedimentary *n*-alkane δD records. Nonetheless, available evidence suggests that a combined approach utilizing aquatic biomarkers and leaf-waxes can be used to reconstruct changes in the δD of both lake water and plant leaf water, records which would in turn yield information about precipitation patterns and aridity at a study site (Sachse et al. 2006). The proposed research will test and then utilize this general approach as a means of better understanding paleoprecipitation and patterns of drought in California.

Carbon & nitrogen isotopes in lake sedimentary OM: Work proposed here will also utilize more traditional measurements of bulk sedimentary OM as a means of reconstructing ecological and biogeochemical responses to climatic variability in the Swamp Lake watershed. Many previous studies have demonstrated the utility of carbon and nitrogen elemental abundances (total organic carbon, TOC; total nitrogen, TN; carbon/nitrogen ratio, C/N) and isotopic compositions ($\delta^{13}C_{org}$, $\delta^{15}N$) in bulk OM as tracers of organic matter sources (C/N, $\delta^{13}C_{org}$), nutrient sources and cycling ($\delta^{15}N$), and lake primary productivity and eutrophication (TOC, TN, ($\delta^{13}C_{org}$, $\delta^{15}N$), all of which respond to ecological and climatic changes (e.g., Hodell and Schelske 1998; Brenner et al. 1999; Herczeg et al. 2001; Meyers 2003). Because each of these bulk OM tracers may respond to multiple controls, the interpretation of the downcore records to be developed in this study will be informed by a survey of modern conditions and intercomparison among the various tracers.

PROPOSED WORK

The development of a decadally- to centennially-resolved record of Late Pleistocene-Holocene climatic variability for the Sierra Nevada would represent a major step forward for paleoclimatic research in California. No record of comparable length and temporal resolution exists in the Sacramento-San Joaquin watershed, the largest in California. The Swamp Lake record would reveal the last 19,000 years of climate history in the western Sierra at a level of detail that has to this point been restricted to the latest Holocene, and would complement existing long, high resolution records from the western Great Basin. Previous work, discussed above, suggests that isotopic and elemental analysis of lake sedimentary organic matter provides a useful suite of tools for reconstructing past lake environments. Compound-specific hydrogen isotopes in particular are likely to provide detailed hydroclimatic information that has typically been unavailable from sediments lacking carbonate minerals. Our overall research objective is to develop a high-resolution record of Sierra Nevada paleoclimate since the last glaciation based on organic geochemical proxies. The research can be further divided into three major objectives:

A. *Complete a detailed modern calibration study providing a basis for interpreting the down-core records;*
B. *Develop a record of paleoprecipitation/aridity based on hydrogen isotopes in individual lipid compounds derived from both terrestrial plant and aquatic sources;*
C. *Develop a record of ecosystem response to water balance and temperature changes based on carbon and nitrogen isotopes and elemental abundances in bulk sedimentary organic matter.*

This work is governed by the following hypotheses: (H1) Compound specific isotope records of plant and aquatic material are controlled by the hydrogen isotopic composition of precipitation and fractionation during evaporative water loss related to aridity; (H2) ecosystem responses to changes in precipitation and/or temperature are reflected in the C and N elemental and isotopic composition of sedimentary organic matter; and (H3) these proxy records can be recovered from sediments at Swamp Lake. Results of this research will reveal, in greater detail than has been possible in all but a handful of previous records, the nature of climate variability in California since the LGM, especially past cycles of precipitation and water availability, and will provide a basis for evaluating the past influence of ENSO and other Pacific basin oscillations as drivers of this variability. Much of the work proposed here will be completed in the laboratory using pre-existing core samples collected from Swamp Lake in 2002. A limited amount of field sampling, necessary as part of the calibration study of objective (A), will take place in the summer seasons (May – Oct.) of 2008 and 2009. More specific details of the research follow.

Work Plan

Research proposed here can be broken into several phases or components, each contributing to the achievement of the major project objectives listed above. The largest, most labor-intensive component is the development of the downcore proxy records using sediment cores from Swamp Lake for the isolation of biomarker compounds from the bulk organic matter and analyses of (a) H isotopes (δD) in individual biomarker and (b) C and N abundance and isotopes in bulk OM. The interpretation of the downcore records will be supported by a field study to determine (a) the modern systematics of H isotopes in the Swamp Lake watershed in relation to the seasonal cycle and (b) the modern source signatures (in terms of biomarkers and C and N proxies) of organic matter components (e.g., algae, aquatic and terrestrial plants). A second foundation of the interpretation will be provided by a comparison of the recent Swamp Lake proxy records with instrumental and high resolution late-Holocene climate records in the Sierra Nevada, which will establish the relationship between the chosen proxies and climate variables. The final component of the proposed research will be to interpret the downcore record in light of the evidence provided in the field and calibration studies, and to evaluate potential drivers of the observed climate patterns through comparison with existing records of California climate, as well as records of ENSO and North Pacific variability. Future work to follow (not part of the current project) will incorporate the data set in regional climate models (see letter of support and collaboration from Dr. Lisa Sloan).

Field and Laboratory Studies

<u>*Samples:*</u> A series of sediment cores was collected from the deep basin of Swamp Lake, located in northwestern Yosemite National Park (map) in 2002, by R.S. Anderson of Northern Arizona University. These cores include a multi-drive Livingstone core extending 10 m into glacial till at its base (core 02-5), as well as a frozen finger preserving intact the sediment-water interface and unconsolidated sediment down to a depth of 73 cm (core 02-8a). Age control is provided by 13 AMS ^{14}C measurements, two tephra layers, and ^{210}Pb and ^{137}Cs dating of the upper interval of the freeze core (J. Barron, pers. comm.) (Fig. 2). Sedimentation has remained relatively stable, at or near 50.5 cm/kyr, through most of the record, with somewhat higher rates (up to 85 cm/kyr) calculated for the less compacted freeze core. The continuous, undisturbed nature of this sedimentary record is confirmed by the presence of fine (100 – 1000 μm) laminae extending through the entire Holocene interval (Fig. 3). Sediment samples from these cores, sectioned at 1 cm (~20 yr) intervals, are available for the proposed research and are already archived in our laboratory at UCSC.

<u>*Lipid extraction & compound-specific δD analysis:*</u>

Lipid biomarkers will be separated from bulk sediment and biomass (plant & planktonic) samples following standard organic geochemical techniques. Initial work has focused focus on the *n*-alkanes, which encompass biomarkers produced by lake algae (n-$C_{17,19}$), submerged aquatic plants (n-C_{21-25}), and terrestrial vegetation (n-C_{25-33}), are generally abundant and well-preserved in lake sediments (Schimmelmann et al. 1999; Sachse et al. 2006) and are relatively easy to extract and purify from bulk lipids (Sauer et al. 2001; Sachse et al. 2006); other algal-derived compounds (e.g., *n*-alkanoic acids, alkadienes, botryococcenes) will be examined in the coming year. Soluble lipids are extracted from 0.5 – 3 g of dried material using a microwave extraction system with successive treatments of 1:1 hexane/acetone and 2:1 dichloromethane/methanol at 95° C, and separated into aliphatic, aromatic, ketone/aldehyde and sterol/fatty acid fractions with specific solvent mixtures on a glass chromatographic column filled with activated silica gel (*see* Lorenson et al. 2002; Nilsen et al. 2005). Where necessary, aliphatic fractions will be subjected to a urea adduction procedure (Wakeham and Pease 2004) to isolate straight-chain *n*-alkanes from co-eluting branched and cyclic hydrocarbons. *n*-Alkanes are identified using a Shimadzu gas chromatograph (GC-FID) at the U.S. Geological Survey, Menlo Park, and quantified by comparison to an external *n*-alkane standard mixture (n-C_{10} to n-C_{36}). H isotope ratios will be measured on a Finnigan DeltaXL isotope-ratio mass spectrometer (IRMS) coupled to an Agilent 6890 GC at the California Institute of Technology (described fully in Sessions et al. 1999), and expressed in standard δ notation as

$$\delta D = [(D/H_{sample})/(D/H_{standard}) - 1] \times 1000,$$

relative to VSMOW. The accuracy of δD measurements for the preliminary set of *n*-alkane samples, estimated on the basis of duplicate runs, is ± 4‰, with improvements expected for future samples (to ± 2-3‰) as injection volumes are optimized (A. L. Sessions, pers. comm.).

Bulk Sediment Analyses (TOC, TN, $\delta^{13}C$, $\delta^{15}N$): Total organic carbon (TOC), total nitrogen, $\delta^{13}C$ and $\delta^{15}N$ of bulk sediment, vegetation, and POM samples will be measured on a Carlo Erba elemental analyzer interfaced with an Optima gas source isotope-ratio mass spectrometer (IRMS) at UCSC. All C and N isotope measurements are expressed in standard delta notation relative to the PDB and air standards, respectively. Analytical precision based on repeated standard runs is ± 0.1‰ for $\delta^{13}C$ and ± 0.2‰ for $\delta^{15}N$ (1 SD). Measurement of a subset of previously acidified sample splits indicates that carbonate minerals are absent from Swamp Lake sediments and do not contribute to bulk sediment $\delta^{13}C$ values.

Field Study -- H Isotope Systematics: Previous studies of compound-specific H isotopes in lake sediments have observed close linear relationships between the δD of biomarker compounds, lake water and precipitation, and with mean annual temperatures across a wide range of sites (Huang et al. 2002, 2004; Sachse et al. 2004, 2006; Hou et al. 2006). In these studies, down-core variations in lipid δD have been interpreted as reflecting changes in the mean annual temperature. None of these studies, however, was conducted in an environment with extreme seasonality in precipitation and humidity as the central Sierra Nevada. Approximately 85% of the precipitation Yosemite NP occurs between November and April (WRCC, online data). At a mid-elevation site such as Swamp Lake (~1550 m), most of this precipitation falls as snow, and is delivered to the watershed as an extended pulse of meltwater over the course of the late spring and early summer. Much of the precipitation reaching the lake will have condensed at cold temperatures that do not reflect the annual mean or the summer growing season for plants and algae. In addition, evapotranspiration during the dry summer months is likely to progressively increase the D/H of both lake and leaf water to an extent not observed at more humid sites (Sachse et al. 2006). Under such conditions we might expect to see a seasonal oscillation in δD of both lake and leaf water, with peak values in the late fall and lowest values in the late spring. However, the actual response of the Swamp Lake system and the surrounding biota to the seasonal cycle is unknown. The sensitivity of Swamp Lake to evaporative deuterium enrichment may be limited if, as has been suggested, the lake receives much of its water through groundwater input (G. Stock, pers. comm.). Likewise, many plants in semi-arid environments possess physiological adaptations that reduce water loss, or phenological adaptations that confine growth (and possibly leaf wax production) to periods of high soil moisture, which would limit isotopic enrichment of leaf water during the dry season (O'Leary 1988). In light of these considerations, a threshold question underlying

the proposed research is: *What is the extent of dry season deuterium enrichment in Swamp Lake water and plant leaf wax compounds above the δD of winter precipitation?* To address this question, the proposed research will include monthly sampling of lake water, lake algae, and leaves of terrestrial and aquatic plants over the summer season (approx. May-Oct), followed by determination of δD values for water samples and individual biomarker compounds. The average δD value of winter precipitation is likely to be best represented by the initial spring lake water samples; seasonal variability in δD of precipitation will be evaluated by analysis of precipitation samples being collected within Yosemite National Park by park staff (C. Stott, pers. comm.). *n*-Alkane distributions of plant and algal samples will also be determined to confirm that the particular chain lengths are indeed diagnostic of particular sources in this system.

Field Study – Organic Matter Sources: While a compound-specific approach allows for the isolation of particular components (e.g., aquatic plants) of sedimentary OM, the use of bulk organic proxies integrates all sources. If the sources have and retain distinct geochemical or isotopic signatures, relevant information on source variability, which is likely to be related to climatic or ecological changes, can be inferred. To better interpret the downcore C and N record, we will determine the geochemical signatures – in terms of C/N, $\delta^{13}C$ and $\delta^{15}N$ – of modern sources of OM to Swamp Lake sediments. Samples of the dominant species of terrestrial and aquatic vegetation, as well as samples of POM and plankton tows, will be collected three times during the summer and analyzed for C and N isotopes and elemental abundances as described above. Sampling of multiple species will allow for the characterization of the different classes of OM sources, while the time series, covering the environmental extremes of the modern growing season, will provide insight into any ecophysiological effects on the geochemical signatures.

Downcore Analyses: Downcore analyses (δD of individual biomarkers, bulk $\delta^{13}C_{org}$,$\delta^{15}N$, TOC, TN) will provide data that will be interpreted in terms of climatic variability (see below). Compound-specific δD measurements will be made on approximately 225 downcore samples, sampled at 2-5 cm (50 – 100 yr) intervals, spanning the last 17.3 kyr. Due to very low organic contents, samples older than this will likely need to be combined to yield sufficient quantities of biomarkers, resulting in lower time resolution. Bulk sediment elemental (TOC, TN, C/N) and isotopic ($\delta^{13}C$, $\delta^{15}N$) analyses will be completed on 475 down-core samples spanning the entire 18.8 kyr record at 1 to 2.5 cm (20-50 yr) intervals. The sampling intervals described above reflect a balance between the goal of the project – to produce a decadal to multi-decadal resolution climate reconstruction – and the relatively labor-intensive sample preparation (described above) involved in the compound-specific isotope measurements. However, if results reveal periods of rapid change these sections will be analyzed at higher resolution (as available material allows).

Interpretation and Modeling

Interpreting the Compound-specific δD Record: Our preferred interpretive framework for the downcore compound-specific δD record is that of Sachse et al. (2006) and Feakins et al. (2006), which uses the difference between the apparent fractionation from precipitation to leaf-wax *n*-alkanes ($\varepsilon_{n\text{-alk}}$) and the alkane biosynthetic fractionation of -160‰ to calculate an "evapotranspirative fractionation" (ε_{ET}) tracking the degree of evaporative water loss from soils and leaves prior to biosynthesis (Fig. 1), which in turn would reflect the relative humidity and availability of soil moisture during the growing season. This approach requires knowledge of the δD of past precipitation, which is assumed to be similar to the lake water δD values preserved in the δD signatures of algal and aquatic plant biomarkers. However, in a seasonal, semi-arid environment such as the Sierra Nevada, this assumption may not hold, and the precipitation signal in lake water δD may be modified by dry season evaporation. A key goal of the calibration study described above is to determine the importance of evaporative enrichment in the modern lake and among terrestrial plants in the watershed. If dry season evapotranspiration is found to have a negligible effect on lake water δD, but causes deuterium enrichment of plant *n*-alkanes, we can have some confidence that the interpretive framework described above is valid, at least for climatic regimes similar to the modern, and that the δD of leaf wax *n*-alkanes can be used to reconstruct a record of water availability in the Sierra. If deuterium enrichment is observed in both the lake and leaf waxes, then the downcore δD records may both reflect

aridity, but separating this signal from changes in the δD of precipitation would require comparison with other records and/or modeling approaches.

It is likely that δD measured in both leaf waxes and aquatic compounds would, on some timescale, respond to past changes in the balance or seasonality of precipitation sources, for instance, between winter storms sourced in the North Pacific approaching the Sierra along more northerly or southerly tracks, which are likely to have distinct temperatures and δD signatures (Ingraham and Taylor, 1991; Feng and Epstein 1994). Changes in the dominant storm track may also be related to the frequency of ENSO events, or phase of the PDO (Dettinger 2007), and could appear in the δD record as baseline shifts, possibly distinguishable from other higher-frequency sources of variability. If the modern seasonal study suggests that the δD of lake water and/or plant leaf waxes is insensitive to evaporative enrichment, one or both of the downcore records may be interpretable in terms of the δD of precipitation, winter temperature, and the relative influence of warm and cold Pacific storms in the Sierra.

Interpreting the Bulk C and N Records: Of the bulk OM proxies used in this study, only the C/N ratio can be considered an unambiguous source tracer (Meyers 2003). TOC and TN integrate OM inputs from all sources and can be diluted by inorganic debris. $\delta^{13}C$ and $\delta^{15}N$ values can identify different OM sources, but they can also vary within a single OM component (e.g., land plants) in response to environmental conditions, biogeochemical processes, and species-specific physiological differences (O'Leary 1988; Meyers 2003). While it may not be possible to disentangle all sources of variability in the sedimentary record, the dominant controls on proxy abundances can be constrained by establishing the geochemical signatures of potential end-members (algae, aquatic and land plants) and by comparing the various proxy records. As discussed above, the source signatures of modern OM components will be established during the field study, allowing for the application of simple source mixing models to the downcore data. Where sediment proxy values fall within the mixing space of known endmembers, this provides strong evidence that source mixing is the dominant control on the downcore record; where proxy values fall outside the mixing space, other explanations – e.g., changes in the biogeochemical cycling of C or N, the emergence of an uncharacterized OM source, post-depositional processes – may be suggested. In addition, determining the relationships of the various proxy records to less ambiguous tracers (e.g., C/N ratios, biogenic silica for diatom productivity) and to one another will limit the field of possible interpretations.

Calibration with Instrumental & Late-Holocene Proxy Records: Because a single season of field observations cannot hope to capture the full range of environmental conditions Swamp Lake has experienced over time, the proxy records proposed here will be further calibrated by comparison with instrumental records, and with high-resolution dendroclimatic records extending back much further in time. Several such records, specific to the central and southern Sierra Nevada, are available in the literature (e.g., Hughes and Brown 1992; Graumlich 1993), and track both precipitation and temperature effects on tree growth. These annually-resolved records will be smoothed to match the multi-decadal resolution of our proxy records. Correlations with the Swamp Lake records will be evaluated. In this way, the relative influence of climatic variables – precipitation, aridity (e.g., Palmer Drought Severity Index), temperature (seasonal and annual mean) -- on the proxies used in this study can be tested against our expectations, and on a more appropriate timescale than is possible using the summer field study alone. Combined with the results of the field study, this calibration exercise will guide the interpretation of the Swamp Lake proxy records in the more distant past.

Comparison with Holocene Records of ENSO Variability and Low Frequency North Pacific Climate: A final component of the proposed research will be to compare the calibrated proxy records from Swamp Lake with existing records of ENSO variability (e.g., Moy et al. 2002, Rein et al. 2005) and decadal- and centennial-scale variability in the North Pacific (e.g., MacDonald and Case 2005; Barron et al. 2003). Of particular interest will be to compare the Swamp Lake records with late-Holocene tree-ring reconstructions of the PDO (e.g., MacDonald and Case 2005; Biondi et al. 2001; D'Arrigo et al. 2001), which will help define the degree of influence that this major decadal oscillation has had in California beyond the short, inconclusive instrumental record. Though the complex responses of California precipitation to ENSO events the 20th century are generally established (Schonher and Nicholson 1989), the comparisons proposed here

will explore the influence of ENSO over a much longer timeframe, and provide a means for evaluating previous suggestions of non-stationary ENSO effects in California and the West (e.g., Meko and Woodhouse 2005). Explicit comparisons of this sort have not, to our knowledge, been attempted for a continental climate record in north-central California, and will provide a baseline for evaluating the pattern of influence of major, basin-scale processes on California climate over the course of the Holocene.

Future Regional Climate Modeling: While pre-mature at this stage , we ultimately we hope to use the records from Swamp Lake to understand present and future regional climate trends. To achieve this goal we will work in collaboration with other researchers to utilize this record to validate and test regional climate models.

PRELIMINARY RESULTS

Preliminary results (summarized below) confirm the hypothesis (H3) that OM proxies are well-preserved in Swamp Lake sediments, and most importantly, that terrestrial and aquatic biomarker compounds can be extracted in sufficient quantities for δD analysis. Our data reveal significant variability in a multi-century to millennial scale, preliminary record of δD of leaf-wax *n*-alkanes, and in centennially-resolved records of bulk TOC, TN, C/N, $\delta^{13}C$, and $\delta^{15}N$ (Fig. 4a-h). The preliminary records are consistent with climate-driven interpretations, and provide strong support for the eventual success of the proposed work.

Hydrogen Isotopes in Individual Lipid Compounds: To examine the relationship between climate and local vegetation response to climate variability and to evaluate the feasibility of this project, lipid extractions have been completed on select samples spanning the last 15 kyr. All samples analyzed to date contain measurable quantities (0.8 - 15 ug/g) of odd *n*-alkanes between C_{21} and C_{31}. Chain-lengths of C_{27} and C_{29} (mostly terrestrial plant origin) and C_{23} and C_{25} (mostly aquatic macrophyte origin) are the most abundant and least impacted by co-eluting compounds. A preliminary set of *n*-alkane extracts has been analyzed for compound-specific δD (Fig. 4e-h). The range of variation in these samples is >30‰, well above the analytical error (± 4‰), and the long-term pattern is consistent with a dryer early- to mid-Holocene (higher δD values) relative to a wetter late Holocene (lower δD values), as seen in other records. The greater degree of more rapid, high amplitude variability seen in the C_{21}, C_{23}, and C_{25} *n*-alkane records may indicate that aquatic plants respond more sensitively to changes in the local water balance, or that terrestrial plant *n*-alkanes have a longer residence time in the watershed, in effect "smoothing" the record. If this is true, developing a concurrent δD record based on lake algal biomarkers will be important for evaluating the sensitivity of this climate proxy. The mid-Holocene δD peak at 405 cm (7.7 cal kyr BP) corresponds to a multi-point peak in bulk $\delta^{13}C$ and C/N and abrupt changes in TOC and BSi – indicative of reduced algal productivity, altered carbon chemistry and perhaps increased dominance of emergent swamp vegetation consistent with a dramatic lowering of lake level at this time.

Carbon & Nitrogen in Bulk Organic Matter: Sub-samples from collected at 5 cm (~100 year) intervals from the full 18.8 kyr record have been analyzed for TOC, TN, C/N, $\delta^{13}C$, and $\delta^{15}N$ of bulk organic matter. These data, along with a record of biogenic silica (BSi), a proxy for diatom productivity, are shown in Fig. 4a-d. Key features of this record are highlighted below:

- C/N ratios have fluctuated between extreme values of 7 and 21, indicating that during most intervals both higher plants (C/N >20) and lake algae (C/N ~3-10) have contributed organic matter to the sediments.
- Coherent variability on centennial and millennial timescales is evident in each of the records, with multi-centennial (200-400 yr period) oscillations especially apparent over the Holocene.
- Correlation (or anti-correlation) between C/N ratios the other proxies ($\delta^{13}C$, $\delta^{15}N$, TOC, BSi) records suggests that variability largely reflects the balance of algal and plant OM inputs; this interpretation is bolstered by the results of a mixing analysis (Fig. 5) in which sediment samples from most core intervals fall within the $\delta^{13}C$ and C/N mixing space of algal (POM), aquatic plant, and terrestrial plant end-members, with algal sources generally dominant. Exceptions include late glacial samples (for which a different relationship between C/N and $\delta^{13}C$ prevails) and a handful of mid-Holocene samples (7.5 – 8.0

cal kyr BP) that plot much closer to the aquatic plant end-member.

- General coherence between the TOC and BSi proxies suggests that OM accumulation has been largely, if not exclusively, controlled by lake algal productivity.

An underlying climatic control for these paleoecological fluctuations is suggested by strong variations in the late Holocene corresponding to the LIA and MCA (Fig. 4, highlighted), the effects of which are well-studied in the Sierra Nevada (Graumlich 1993; Stine 1994; Benson et al. 2002). The MCA was marked by warm summer temperatures and extended droughts, while the LIA was cooler than present, with a higher frequency of wet winters. Both temperature and precipitation are likely to modulate algal productivity and OM input to Swamp Lake (e.g., via temperature controls on algal growth rates, the length of the growing season and the number of ice-free days; precipitation controls on snowpack, terrigenous inputs, and nutrient availability), with the expected responses matching those observed in the proxy records. Completion of a higher resolution carbon and nitrogen record will allow for calibration with the instrumental record and a more precise interpretation of the observed Holocene variability and its links to regional climate.

ANTICIPATED PRODUCTS AND BENEFITS

Results of the bulk C and N measurements were presented at the AGU conference in San Francisco in December 2007. We anticipate being able to present the preliminary results of the compound-specific δD measurements beginning in late 2008 at appropriate forums, such as professional meetings or the CALFED-sponsored conferences. Although it may be necessary to collect more samples or perform further analyses in order to better understand or interpret our results during 2009, we anticipate submitting manuscripts for publication in peer-reviewed journals in early 2009 (bulk C and N data) and late 2009 or early 2010 (compound-specific δD data). The reviewed, revised version of these manuscripts would also form the basis of the final completion report required by CALFED. Efforts to apply our data sets in predictive modeling efforts would begin once data collection has been completed, and reasonably solid interpretations of the downcore data developed, perhaps at the beginning of year two (summer/fall of 2009).

The research proposed here will form the foundation (2-3 chapters) of the applicant's doctoral dissertation, and will represent a successful new extension of the isotopic tools typically utilized by the research mentor to a new sub-discipline (recent paleoclimatology). Upon completion of this study, the CALFED priority to ensure an adequate water supply for both human and environmental uses will benefit from a better, more detailed understanding of how decadal to centennial climate processes have affected precipitation and water supply in the Sacramento-San Joaquin watershed over the Holocene. The particular, unique benefits of this study stem from its promise to extend a decadally-resolved climate record over the past 19,000 years, a period far longer than has previously been available for the watershed at comparable resolution. When completed, our record will allow for the close examination of hydrologic conditions in the watershed during past warm periods (e.g., early-mid Holocene) and multiple climatic transitions. These results will be directly applicable to water supply forecasting through incorporation into climate models, and in a more indirect sense, in defining extreme scenarios and system thresholds.

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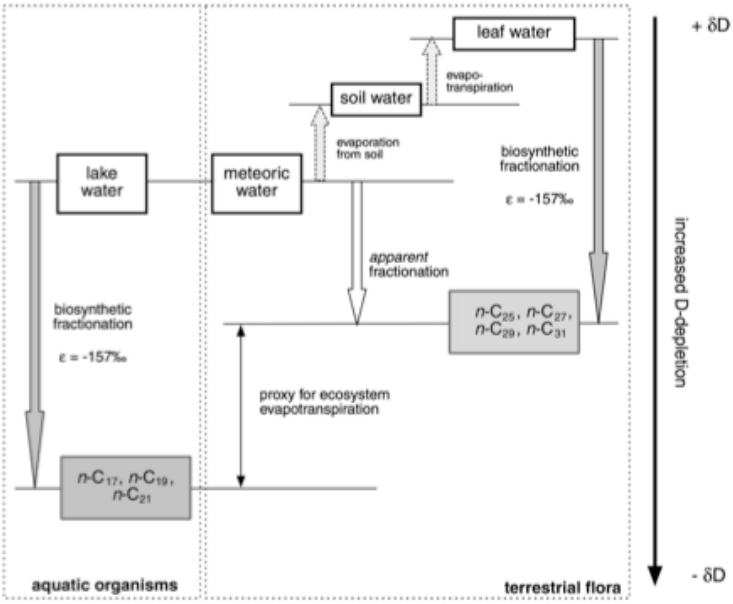

Figure 1 (right): Conceptual diagram of the isotopic relationships between source water and n-alkanes of aquatic and terrestrial origin in sediments (Sachse et al. 2006)

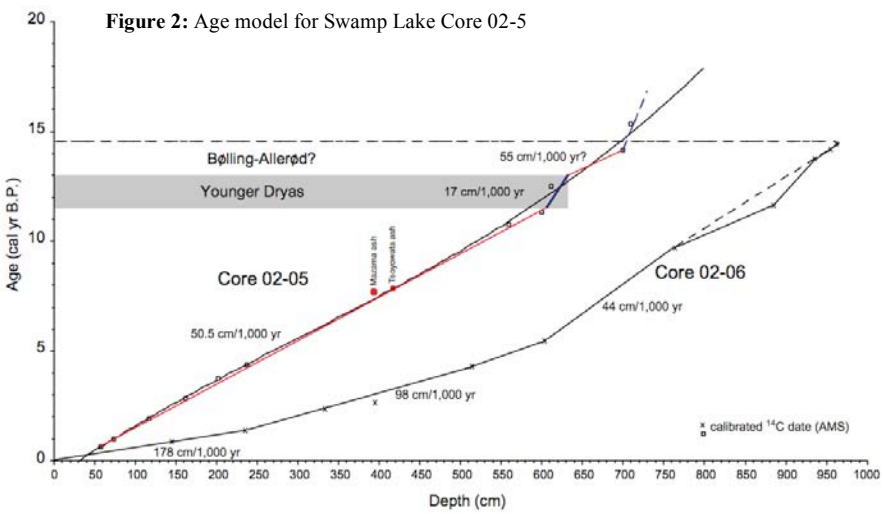

Figure 2: Age model for Swamp Lake Core 02-5

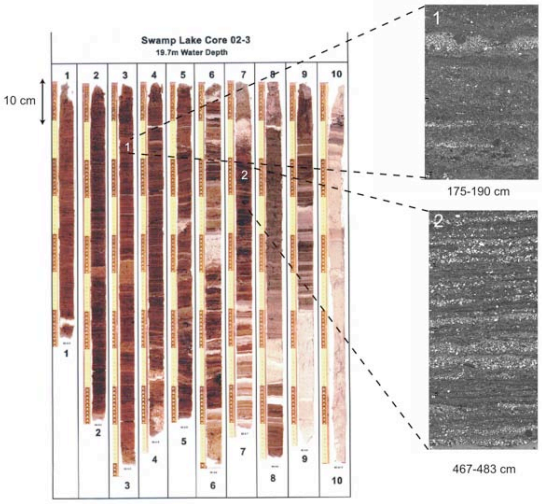

Figure 3: Core 02-5. Laminations visible in details (1) and (2), right.
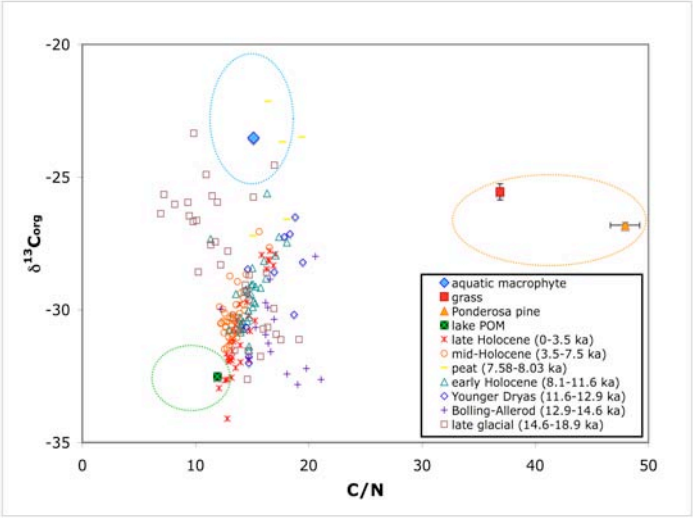
Figure 5 (right): $\delta^{13}C$ and C/N values for Swamp Lake sediments and representative modern OM sources.