The influence of hydrology and climate on the isotope geochemistry of playa carbonates: a study from Pilot Valley, NV, USA

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ABSTRACT

Carbonates often accompany lake and lake-margin deposits in both modern and ancient geological settings. If these carbonates are formed in standing water, their stable isotope values reflect the aquatic chemistry at the time of precipitation and may provide a proxy for determining regional hydrologic conditions. Carbonate rhizoliths and water samples were collected from a playa lake in eastern Nevada. Pilot Valley ($\sim$43°N) is a closed-basin, remnant playa from the Quaternary desiccation of palaeo-Lake Bonneville. Water is added to the playa margin by free convection of dense brines to the east and forced convection of freshwater off the alluvial fan to the west. Both freshwater and saline springs dot the playa margin at the base of an alluvial fan. Water samples collected from seven springs show a range from −16 to −0·2‰ (Vienna Standard Mean Ocean Water), and are consistent with published values. The $\delta^{18}O_{calcite}$ values from rhizolith samples range from −18·3 to −6·7‰ (Vienna Pee Dee Belemnite), and the average is −12‰ V-PDB (1 − σ SD 2‰). With the exception of samples from Little Salt Spring, the range in the $\delta^{18}O_{calcite}$ values collected from the rhizoliths confirms that they form in equilibrium with ambient water conditions on the playa. The initial geochemical conditions for the spring waters are dictated by local hydrology: freshwater springs emerge in the northern part of the basin to the east of a broad alluvial fan, and more saline springs emerge to the south where the influence of the alluvial fan diminishes. Rhizoliths are only found near the southern saline springs and their $\delta^{13}C_{calcite}$ values, along with their morphology, indicate that they only form around saltgrass (*Distichlis* sp.). As the residence time of water on the playa increases, evaporation, temperature change and biological processes alter the aquatic chemistry and initiate calcite precipitation around the plant stems. The range in $\delta^{18}O_{calcite}$ values from each location reflects environmental controls (e.g. evaporation and temperature change). These rhizoliths faithfully record ambient aquatic conditions during formation (e.g. geochemistry and water depth), but only record a partial annual signal that is constrained by saltgrass growth and the presence of standing water on the playa margin.

Keywords Carbon isotopes, oxygen isotopes, phytocast, playa, rhizoliths.

INTRODUCTION

Lake and lake-margin environments, often containing wetlands and/or springs, are dynamic features on the landscape that are sensitive to climate changes that affect water level, aquatic chemistry and their resulting geological deposits (Pedley *et al.*, 1996; Andrews *et al.*, 2000; Manga, 2001; Saez & Cabrera, 2002). The precipitation and preservation of calcium carbonate in

palustrine and lacustrine deposits afford researchers the opportunity to reconstruct regional-scale palaeoenvironments by analysing the stable isotopic composition in these carbonate samples (Botz *et al.*, 1988; Talbot, 1990; Chavetz *et al.*, 1991; Johnson *et al.*, 1991; Fontes *et al.*, 1996; Li & Ku, 1997; Deocampo & Ashley, 1999; Andrews *et al.*, 2000; Saez & Cabrera, 2002; Andrews *et al.*, 2004). Terrestrial stable isotope records are used to reconstruct conditions, such as water temperature, evaporation/precipitation ratios, biological productivity and chemistry (e.g. pH), that can help to recreate the ancient landscape (Cerling & Hay, 1986; Cerling & Quade, 1993; Smith *et al.*, 1993; Li & Ku, 1997; Koch, 1998; Sikes *et al.*, 1999; Andrews *et al.*, 2000; Wynn, 2000; Saez & Cabrera, 2002; Watanabe *et al.*, 2003; Levin *et al.*, 2004).

Reconstructing lake and lake-margin deposits of the past 2·5 Myr are of interest because of the resources they provided to our human ancestors (Hay, 1976; Cerling *et al.*, 1988; Hay, 1990; Ashley, 1996; Wynn, 2000; Feibel, 2001; Hay & Kyser, 2001; Deocampo *et al.*, 2002; Liutkus *et al.*, 2005). Liutkus *et al.* (2005) used the relationship between stable isotope values from rhizoliths and clay mineralogy to construct a model for interpreting the stable isotopic signature in terms of climate change. The results of Liutkus *et al.* showed that rhizoliths are sensitive to both large and small changes in lake and lake-margin environments due to their location within the hydrological system and because their preservation potential is good throughout the geological record. The stable isotopic signature in rhizoliths is readily attained and may provide sub-annual resolution when they form quickly in an aquatic environment.

Two variables influence stable oxygen isotope composition in carbonate material: (i) the temperature at which the carbonate precipitated; and (ii) the $\delta^{18}O$ value of the water from which the carbonate formed (Craig, 1965). For palaeoenvironmental reconstructions, there are three important considerations. Firstly, the scientist is left with one equation and two unknowns because the $\delta^{18}O_{calcite}$ is measured, but either the temperature or $\delta^{18}O_{water}$ variable must be estimated or constrained by another proxy. Secondly, the origin of the carbonate deposits must be distinguished (e.g. did the calcite precipitate pedogenically, or in standing water?). Finally, it must be determined whether the type of carbonate sample (e.g. taxa and mineral phase) faithfully records the ambient environmental conditions.

The results of a stable isotopic investigation of modern calcitic rhizoliths from Pilot Valley, NV, are reported in this study with the goal of investigating the conditions that affect the isotopic signature of modern, arid-region carbonates that form in standing water. The use of the term 'rhizolith' is expanded to describe calcite that has encrusted plant stems, and the use of the term 'phreatic' is applied to all carbonates that form in standing water above the sediment surface, rather than simply as a result of groundwater. This type of phytocast (i.e. stem cast) is a relatively under-described feature in the geological record, and may have been previously lumped together with pedogenic carbonates, unknowingly. The field of geology has not developed the appropriate terminology to accurately describe their formation, and at present, the origin of the rhizolith carbonate (whether precipitated directly from playa waters or pedogenic), the timing of their formation and regional environmental conditions during carbonate precipitation are not well-known. This study, therefore, seeks to describe the formation processes surrounding such phreatic carbonate precipitates by analysing their isotopic composition in comparison with local geochemical parameters. Unlike pedogenic rhizoliths, which form within the soil profile during dry periods, phreatic rhizoliths form during wetter conditions and thus can record a separate suite of environmental characteristics.

The rhizoliths were collected from the perimeter of groundwater-fed springs on the valley floor. Suites of physical and chemical proxies were measured on spring and groundwater samples to help establish the baseline conditions. These values are then used to establish equilibrium isotopic conditions for carbonate samples forming under phreatic and pedogenic conditions to infer origin. The proportion of the annual cycle that is recorded by the stable isotope record in modern arid-region rhizoliths is also determined. By understanding the formation process, timing and rate of modern phreatic carbonates in a playa setting, more accurate interpretations of isotope data collected from ancient carbonates can be made.

GEOLOGICAL SETTING

Site description and geology

Pilot Valley is located on the western edge of the Great Salt Lake Desert in eastern Nevada, and is
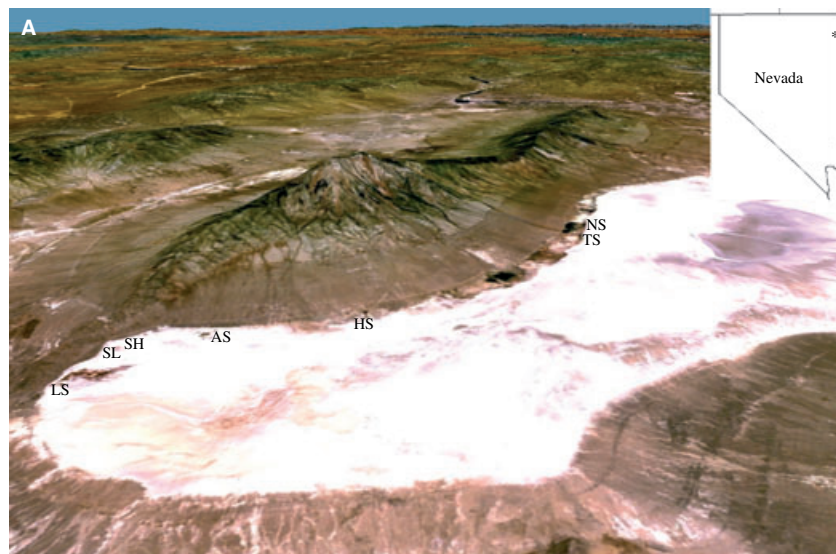
Fig. 1. (A) Visible colour Landsat 7 image of Pilot Valley area. Inset map shows the location of the site within the north-eastern corner of Nevada. The valley sits between the Pilot Range to the west and the Silver Island Mountains to the east. The location of each spring is noted on the edge of the playa. LS, Little Salt Spring; SL, Slope Spring; AS, Agony Springs; SH, Sinkhole Spring; HS, Halls Spring; TS, Tessa Spring; NS, New Spring. No springs were located on the east side of the valley. Image cached from NASA World Wind v1.4 (public domain). (B) Model of groundwater circulation in a playa lake system developed originally by Duffy & Al-Hassan (1988) and modified from Fan *et al.* (1997). The right side of the diagram shows free convective flow of dense water sinking in the playa centre. Near the drainage divide, forced convective flow results from hydraulic head in the uplands forcing water down the alluvial fan. Map courtesy of Geography at About.com - http://geography.about.com.
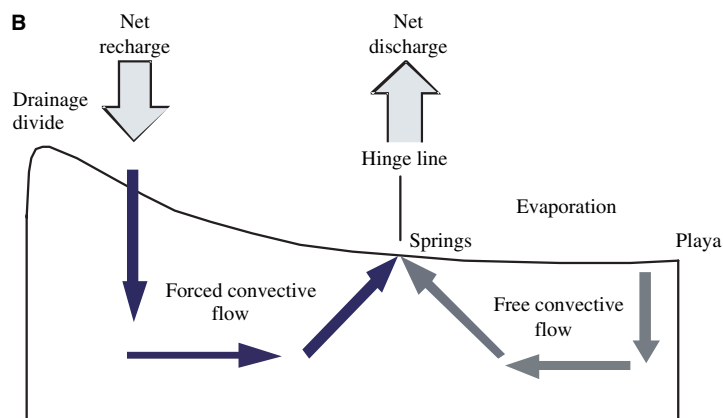
separated from the Bonneville Salt Flats by the Silver Island Mountains (Fig. 1A). Lacustrine sediments cover the valley floor, but are also found above on the mountain slope, recording higher levels of Lake Bonneville (32 to 14 ka) (Lines, 1979). By 10 ka, Lake Bonneville had receded to ~15 m above the modern Great Salt Lake leaving Pilot Valley as a closed-basin remnant. Since that time, the lake level has continued to fall and, at present, only a playa exists on the Pilot Valley floor.

Bedrock in the area is comprised of limestone, dolomite, shale and quartzite, and calcareous tufas are found along the western edge of the Bonneville flats along the Silver Island Mountains (Lines, 1979). Ephemeral streams, resulting from snowmelt and thunderstorm events, flow off the Pilot Range and the Silver Island Mountains, intermittently filling the playa.

Precipitation in the region is low (<150 mm year^{-1}) with rainfall peaking in the spring around April/May (Lines, 1979; Fan *et al.*,

1997). Evaporation peaks in the summer (>2300 mm year^{-1}) with rates temporarily increasing after individual rain events (Malek *et al.*, 1990; Menking *et al.*, 2000). The annual mean temperature range varies from 17 to 33 °C, and moderately high wind speeds are common during the spring (Lines, 1979; Fan *et al.*, 1997).

Regional hydrology

Pilot Valley is considered a closed and undrained system, and is categorized as a 'wet playa', meaning that it maintains a shallow water table (Snyder, 1962; Rosen, 1994; Fan *et al.*, 1997). Three distinct aquifers bring groundwater to the western edge of the playa: an alluvial fan aquifer, a shallow brine aquifer and a basin fill aquifer (Lines, 1979). The alluvial fan aquifer delivers water to the playa at the toe of the fans, while the shallow brine aquifer maintains the presence of a brine near the surface of the playa (Lines, 1979; Fan *et al.*, 1997). The basin-fill aquifer is too deep

to influence the playa surface (Lines, 1979; Fan *et al.*, 1997).

Sand and gravel deposits within the alluvial fan complex channel water off the highlands into the basin. At times of high run-off, the capacity of the alluvial fan aquifer is exceeded (due to the presence of confining units, probably lacustrine clays), causing water to be discharged in springs at the toe of the alluvial fan (Lines, 1979). At Pilot Valley, springs emerge along the 1298 m elevation. Recharge of this aquifer is by infiltration of precipitation and by brine contamination; discharge is dominated by evapotranspiration by phreatophytes and spring discharge (Lines, 1979). Recharge of the shallow brine aquifer is dominated by precipitation infiltration and surface run-off, while evaporation and transpiration are the two means of discharge (Lines, 1979).

Two types of circulation dominate the hydrologic mixing at Pilot Valley; free convection and forced convection (Fan *et al.*, 1997) (Fig. 1B). Free convective flow occurs as evaporation concentrates the brine on the playa, forcing it to sink into fresher groundwater below. Fan *et al.* (1997) suggest that eventually the sinking brine will reach the bottom of the basin, extend outward and mix with fresh groundwater, causing the brine to 'dilute' and flow upward to the surface again. Forced convection occurs as precipitation drains into the sub-surface of an alluvial fan and migrates towards the toe of the fan under a hydraulic gradient. The water then emerges in springs along the hinge line and evaporates back into the atmosphere (Fan *et al.*, 1997).

Pilot Valley geochemistry

Snow $\delta^{18}O_{water}$ values lie on or near the meteoric water line (Fig. 2) (Fan *et al.*, 1997). Spring and stream $\delta^{18}O_{water}$ values are only slightly more positive than the snow values (−8 to −16‰ versus Vienna Standard Mean Ocean Water, V-SMOW), indicating that they are relatively fresh and predominantly precipitation derived and/or run-off derived (Fan *et al.*, 1997). Brine samples have more positive $\delta^{18}O_{water}$ and δD values with respect to the spring and stream values ($\delta^{18}O_{water}$ = −7·5 to −3·5‰ V-SMOW), suggesting evaporation as the dominant control on brine oxygen isotope values (Fan *et al.*, 1997) (Fig. 2).

Description of rhizoliths

Rhizoliths are found on the playa adjacent to several springs. The rhizoliths consist of an
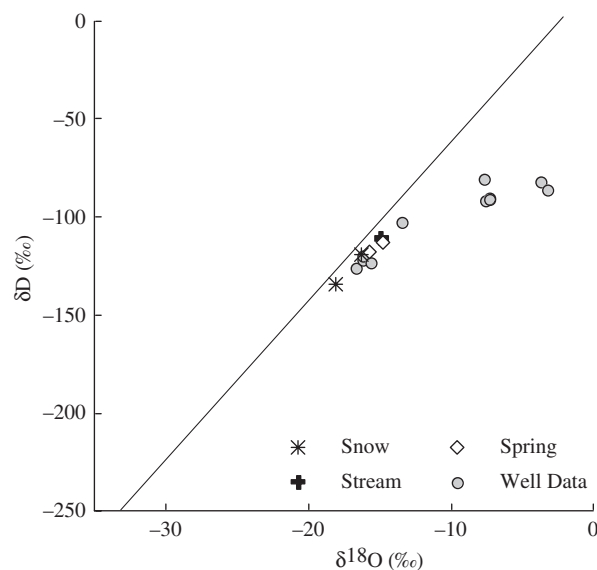
Fig. 2. Stable isotope values ($\delta^{18}O_{water}$ and δD) of waters in the Pilot Valley region. Data re-plotted from Fan *et al.* (1997). Well data that have high $\delta^{18}O_{water}$ values were found out on the playa and probably experienced evaporative concentration (Fan *et al.*, 1997). The solid line represents the meteoric water line.

indurated calcite 'tube' that is either filled with unconsolidated (or weakly cemented) sediment or left open (Fig. 3). The vegetation found on the playa mudflats consists of a variety of C_3 shrubs, such as rabbitbrush (*Chrysothamnus* sp.), greasewood (*Sacrobatus* sp.) and sagebrush (*Artemisia* sp.). Pickleweed (*Salicornia* sp.), a salt-tolerant Crassulacean acid metabolism (CAM) plant, and saltgrass (*Distichlis* sp.), a C_4 halophytic grass, are found on the margins of the more saline springs and on the adjacent mudflats. Evaporation in the area is high and most plants on the mudflat are crusted with salt and, sometimes, carbonate.

The morphology of most of the plants excludes them as the host of the Pilot Valley rhizoliths, however. Cracks in the playa flat are also calcified with micritic sediment, and rhizolith tubules are found *in situ* within the calcified cracks (Fig. 4A). These cracks are not continuous in the shape of desiccation polygons and are instead short, isolated lineaments (<20 to 25 cm). Saltgrass (*Distichlis sp.*) preferentially grows in these lineaments due to rhizome propagation and, due to its stem diameter and morphology, is the likely host plant for the rhizoliths on the Pilot Valley playa (Fig. 4B and C). The 'spiky' nature of the sprout of the plant means it can push up through clay-rich soils, and its hardiness allows it to colonize saline, alkaline environments.

Most of the rhizolith tubules found in Pilot Valley are in the order of 1 or 2 cm long, but
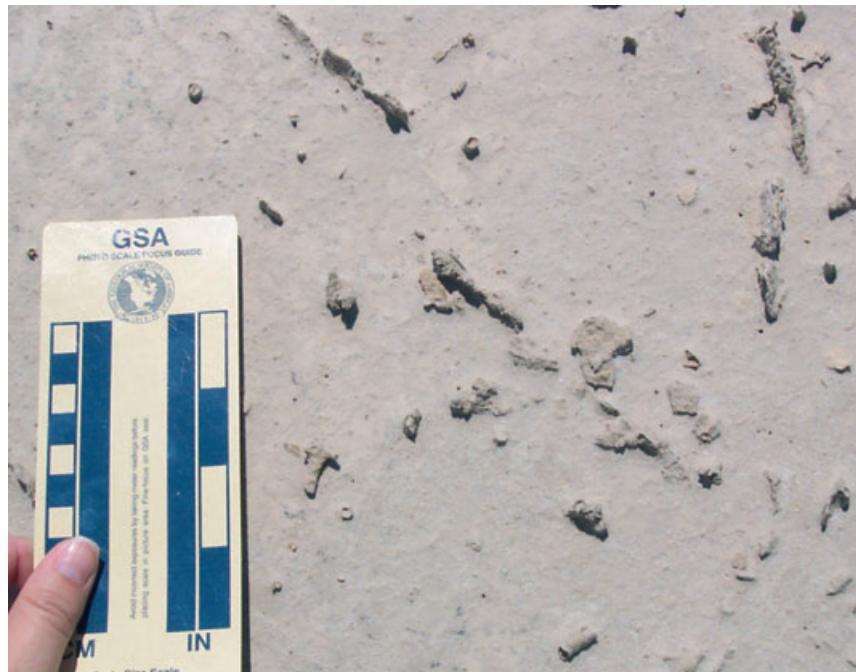
Fig. 3. Rhizolith distribution on the Pilot Valley playa near Agony Spring. Scale shows centimetres (left) and inches (right). Note that some rhizoliths are still upright in the substrate.

can be up to 5 or 6 cm long in rare instances (Fig. 3). Tubules do not extend more than a few millimetres below the sediment–air surface, except in crack-fill situations where carbonate may extend up to a centimetre or more below the surface. Precipitated carbonate extends laterally at the base of the rhizoliths (outward) like an apron, as if to follow the sediment surface (Fig. 3). Furthermore, all of the rhizoliths found at Pilot Valley are concentrated on the sediment surface; no rhizoliths were found buried in the sediment.

METHODS

Field methods

Geochemical data, and water and carbonate samples for $\delta^{18}O$ analysis
To determine baseline conditions for calcite precipitation, temperature values were needed in addition to samples of carbonate and water. Temperature measurements were made to the nearest 0·1 °C in the field at each location where water samples were collected. Also, to determine the conditions under which calcite precipitation is initiated, pH and electrical conductivity (EC) measurements were taken at each sample site using an instant-read Hanna Instruments HI9811 pH-EC-TDS meter (Hanna Instruments, Woonsocket, RI, USA). Geochemical data from source

and ground waters in Pilot Valley have been previously documented by Oliver (1992).

Water samples were collected from each spring source (when possible) as well as adjacent pools and drainage channels, to constrain the influence of temperature and evaporation on shallow versus deeper bodies of water. Each water sample was collected through a sterile 60 ml syringe and filtered through a 0·45 m filter to remove detritus. All water samples were then loaded into 20 ml glass vials with minimal headspace, closed with polyethylene cone caps, and wrapped in Parafilm® (Pechiney Plastic Packaging Company, Menasha, WI, USA), to reduce degassing.

All rhizoliths were collected (*in situ*) from the surface of the playa, either adjacent to the springs or on the playa proper. The number of rhizoliths collected at each site is a proxy for their abundance at each locality. No springs (and no rhizolith carbonates) were found on the eastern edge of the playa. Locations of the spring sites described in this paper are shown in Fig. 1A.

Laboratory methods

Isotopic composition of water
The three variables needed to determine whether a carbonate sample has precipitated in isotopic equilibrium with its surrounding waters are the $\delta^{18}O_{water}$, the $\delta^{18}O_{calcite}$ and the temperature at which the calcite forms. Temperature measurements were made in the field, and the isotopic
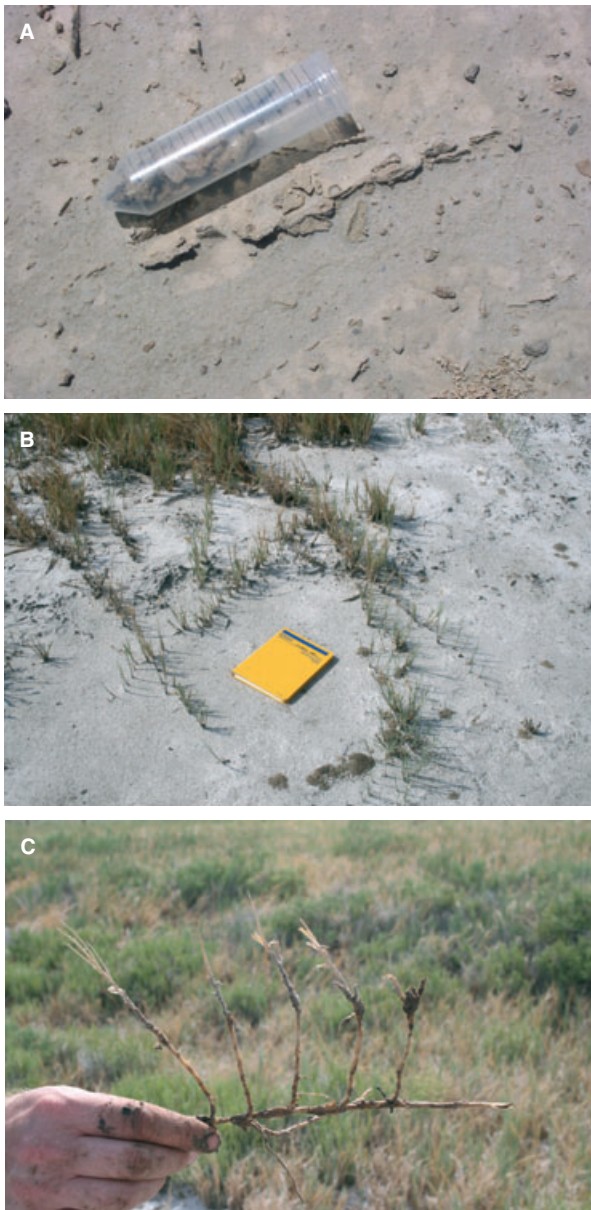
Fig. 4. (A) Rhizoliths found in calcified cracks on Pilot Valley playa. Fifty-millilitre vial shown for scale is 11·5 cm long. (B) Saltgrass plants growing adjacent to Agony Springs. The notebook for scale is 22 cm long. (C) Rhizomes beneath the surface create lineaments of saltgrass plants that mimic the rhizoliths found in calcified cracks.

variables were determined at the Stable Isotope Laboratory at Rutgers University in the Department of Geological Sciences. Preparation of the $\delta^{18}O_{water}$ samples involved pipetting 2 ml of the water sample into a 5 ml vial, flushing the sample by slowly bubbling CO_2 through the water for 10 seconds in a glove bag, and then capping the vial. The CO_2 in the headspace above the water samples was allowed to equilibrate isotopically at

40 °C for eight hours before analysis on a Micromass (Optima) dual-inlet mass spectrometer (Micromass UK Limited, Manchester, UK) with an attached multi-Prep device (GV Instruments, Wythenshawe, Manchester, UK). Samples of water from seven springs throughout Pilot Valley were analysed for oxygen isotope composition and reported as V-SMOW (Table 1). Duplicate samples from each site were run and the values averaged. When the difference between the duplicate samples was greater than 0·2‰, the samples were re-analysed. The 1-σ standard deviation of the $\delta^{18}O_{water}$ standards analysed with the samples was 0·07‰.

Isotopic composition of carbonate
Stable isotope values for Pilot Valley carbonates were derived from 28 different rhizolith samples (148 analyses) and one bulk carbonate sample (Halls Spring). Prior to analysis, all rhizoliths were washed and sonicated in distilled water at room temperature for 10 minutes to remove detritus and to dissolve any remnant salt. A clean surface of each rhizolith was uncovered by sawing off the rough end of the rhizolith perpendicular to its long axis. Using a high-speed drill fitted with a 0·5 mm drill bit, powdered samples of carbonate were taken at 0·5 mm intervals staggered across a transect of the clean surface (from edge to centre to opposite edge). Stable isotope analyses were run in the Stable Isotope Laboratory at Rutgers University in the Department of Geological Sciences. Samples were loaded into a multi-prep device and were reacted in 100% phosphoric acid at 90 °C for 13 minutes before being analysed on the Micromass (Optima) dual-inlet mass spectrometer. Both $\delta^{13}C$ and $\delta^{18}O$ values were obtained and the values reported versus the Vienna Pee Dee Belemnite (V-PDB) by analysis of a laboratory standard calibrated to the National Bureau of Standards (NBS) #19 with values of 1·95 and −2·20‰ for $\delta^{13}C$ and $\delta^{18}O$ respectively (Coplen *et al.,* 1983). Standard deviation (1-σ) of the standards was 0·08 and 0·05‰ for $\delta^{18}O$ and $\delta^{13}C$, respectively. Isotopic values with precision error greater than 0·01 were excluded from the data set.

RESULTS

Geochemical results for Pilot Valley waters

Temperature, pH and EC measurements for each spring from various field visits are presented in

Table 1. Data collected from Pilot Valley Springs from 2002 to 2006.

Spring name	Date sampled	Temperature (°C)	pH	Conductivity (mS cm^{-1})
Halls Spring	July 2002	16	7·0 to 8·9	N/A
	August 2003	16	7·4	2·04
	July 2004	16	6·4	2·02
	May 2006	16	8·7*	0·75*
	July 2006	15	7·9	2·08
New Spring	August 2003	22	6·7	0·75
	July 2004	28	6·8	1·18
	May 2006	Dry	N/A	N/A
	July 2006	17	4·5	0·49
Tessa Spring	August 2003	17	6·4	0·67
	July 2004	14	6·5	0·63
	May 2006	14	6·0	0·60
	July 2006	15	6·1	0·66
Agony Spring	August 2003	24	7·0	17·40
	July 2004	29	7·2	15·50
	May 2006	17 to 22	7·4 to 8·0	15·60 to 16·86
	July 2006	27 to 31	6·3 to 9·0	17·40 to 19·70
Agony Spring SW	July 2004	30 to 33	7·9 to 8·8	15·35 to 16·00
Slope Spring	August 2003	28	7·9	14·60
	July 2004	28	8·0	13·70
	May 2006	22 to 25	8·4	11·96
	July 2006	26	8·3	15·20
Little Salt Spring	July 2004	28	7·8	10·25 g l^{-1}†
	May 2006	23	6·4	10·66 g l^{-1}†
	July 2006	28	10·9	11·10 g l^{-1}†
Sinkhole Spring	July 2004	N/A	7·0	11·81
	May 2006	20	8·8	11·46
	July 2006	26	8·0	13·50

*Possible equipment malfunction due to low battery.
†Values recorded as grams per litre because conductivity exceeded metre range.

Table 1. Geochemical measurements from each of the springs reflect local hydrological conditions.

Spring source $\delta^{18}O_{water}$ values for Halls Spring, New Spring, Sinkhole Spring and Tessa Spring cluster around −11 to −15‰ (Fig. 5). $\delta^{18}O_{water}$ values are higher for Slope Spring (−10·5‰ in 2003, −8·3‰ in 2004) and Little Salt Spring (−0·2‰) (Fig. 5). Samples from Little Salt Spring record the highest $\delta^{18}O$ values of all the waters analysed. This high $\delta^{18}O_{water}$ value (−0·2‰) is concurrent with the high salinity of the spring (10·25 g l^{-1}), as evaporation increases both the salinity and the $\delta^{18}O$ value of the water. Agony Spring $\delta^{18}O_{water}$ values show a broad range from −15·1 to −7·7‰ (Fig. 5). Samples from deep pools found in the Agony Spring complex average −14·3‰, but samples taken from a shallow drainage pool nearby on the playa increase to −7·7‰. The deeper pools to the west are the source for the shallow drainage and the significant increase in the $\delta^{18}O_{water}$ value implies evaporative concentration.

The springs also group by location on the playa with respect to their EC values (Fig. 5). Springs with EC values less than 5 mS cm^{-1} are located in the northern part of the basin to the east of the alluvial fan (Halls Spring, Tessa Spring and New Spring) (Figs 1 and 5). Springs with EC values greater than 10 mS cm^{-1} (Agony Spring, Sinkhole Spring, Slope Spring and Little Salt Spring) group in the southern part of the basin where the alluvial fan is no longer present to the west. Thus, there appears to be a hydrologic boundary
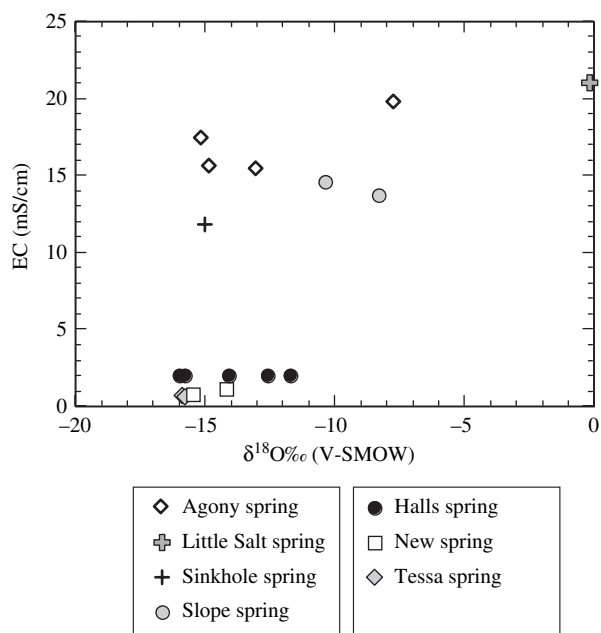
Fig. 5. $\delta^{18}O_{water}$ values (V-SMOW) and electrical conductivity measurements for water samples taken from all seven springs. Each point plotted is an average of two analyses of the $\delta^{18}O_{water}$ sample for each site. The springs in the northern part of the basin are grouped on the right-hand side of the legend, and those in the southern part of the basin are grouped on the left.

to the north of Sinkhole Spring where emergent groundwaters shift from a fresher source (the alluvial fan aquifer) in the north to a more saline, re-circulated source (the shallow brine aquifer) in the south.

If, as suggested, hydraulic head within the alluvial fan aquifer dictates the composition of the northern springs, it stands to reason that during the late summer, when hydraulic head is reduced due to decreased precipitation in the region, these springs may experience an increase in pH and/or EC due to infringement of saline waters through migration of a saline/freshwater mixing zone. Table 1 shows pH and EC values from the springs taken in May 2006 and July 2006. All springs show an increase in EC in just three months, suggesting that a reduced hydraulic head may allow for a shift in the interface between the alluvial fan aquifer and the shallow brine aquifer and validates a hydrologic control on the geochemistry of the springs.

Isotopic results for Pilot Valley carbonates

Carbon isotopes
The $\delta^{13}C_{organic}$ value of C_4 grasses range from approximately −15 to −10‰ (Cerling & Quade,
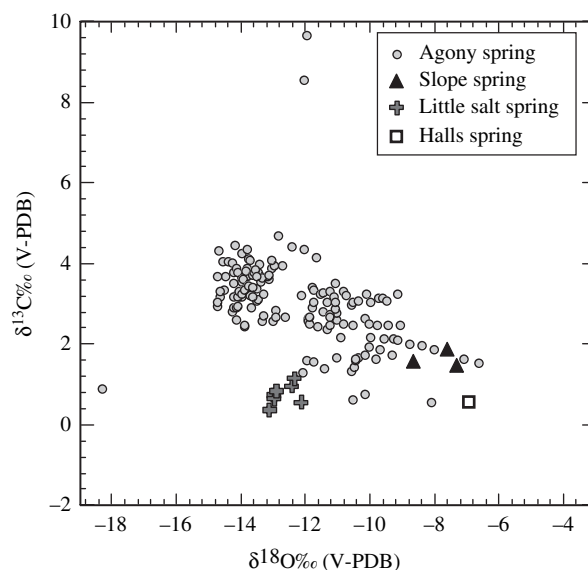
Fig. 6. $\delta^{18}O_{calcite}$ and $\delta^{13}C_{calcite}$ results for Pilot Valley rhizolith samples. All values fall within the range for precipitation in equilibrium with local (measured) aquatic conditions, indicating that the rhizoliths formed in standing water.

1993), with one instance of *Distichlis* sp. being reported at −14·4‰ (Miller *et al.*, 2005). Allowing for ∼15‰ total fractionation between plant-respired gases and calcite at 25 °C ($\alpha = 1·0044$ for diffusion of plant-respired CO_2, $\alpha \approx 1·0085$ as CO_2 goes into solution as HCO_3^- and $\alpha = 1·00197$ for temperature-dependent precipitation of calcite from solution) gives a predicted $\delta^{13}C_{calcite}$ range of 0 to 5‰ for carbonates precipitating in a C_4-dominated ecosystem (Deines *et al.*, 1974; Cerling & Quade, 1993). Measured $\delta^{13}C_{calcite}$ values from individual rhizolith samples are shown in Fig. 6. With the exception of two samples from Agony Spring, the $\delta^{13}C_{calcite}$ values range from 0·4 to 4·7‰ and are consistent with precipitation in an ecosystem dominated by C_4 grasses, such as saltgrass. Other plants in the area are CAM and C_3 plants, and their isotopic signature (as well as stem morphology) excludes them from being the host of the Pilot Valley rhizoliths. The $\delta^{13}C_{organic}$ of a C_3-dominated environment approaches an average of −27‰, and the $\delta^{13}C$ of calcite forming in such an environment should be ∼−12‰.

Oxygen isotopes
Measured $\delta^{18}O_{calcite}$ values from individual rhizolith samples are shown in Fig. 6. The total range of all rhizolith $\delta^{18}O_{calcite}$ values varies from

−18·3 to −6·7‰ and the individual $\delta^{18}O_{calcite}$ values group by their formation location on the playa (Fig. 6).

Equation 1 (Craig, 1965) can be used to calculate the temperature and/or geochemical conditions during the time of rhizolith calcite formation:

$$T(^{\circ}C) = 16\cdot9 - 4\cdot2(\delta^{18}O_{calcite} - \delta^{18}O_{water}) \\ + 0\cdot13(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2 \qquad (1)$$

where the $\delta^{18}O_{calcite}$ is expressed as V-PDB and $\delta^{18}O_{water}$ is the value of the water in which the carbonate is formed and is converted from V-SMOW to V-PDB by subtracting 0·22‰ (Coplen *et al.*, 1983). The range in $\delta^{18}O_{water}$ values reported here is consistent with $\delta^{18}O_{water}$ values of local springs, streams and snow melt. Published $\delta^{18}O_{water}$ values vary from −16‰ (V-SMOW) in the springs to −3‰ in the playa proper (Fan *et al.*, 1997); values from the present study indicate a range in $\delta^{18}O_{water}$ values for the springs from −16 to −0·2‰ (V-SMOW). Using a temperature range between 16 and 25 °C (measured, Table 1), Eq. 1 indicates that very low rhizolith $\delta^{18}O_{calcite}$ values could form in equilibrium with $\delta^{18}O_{water}$ values between −15 and −13‰ (V-SMOW). This indication is consistent with $\delta^{18}O_{water}$ values measured previously by Fan *et al.* (1997) for streams and springs sourced by snowmelt (average ∼−15‰). The higher rhizolith $\delta^{18}O$ values (∼−7‰) suggest formation in equilibrium with waters with $\delta^{18}O_{water}$ values between −5 and −7‰; this suggests that waters forming these rhizoliths are significantly more saline than those from which the rhizoliths with lower $\delta^{18}O$ values precipitated.

Using Eq. 1 and the geochemical values for Halls Spring, if rhizoliths formed in equilibrium with the source waters of the spring ($\delta^{18}O_{water}$ = −16 to −14‰ V-SMOW at 16 °C) their values should be ∼−16 to −14‰ V-PDB (in contrast to the reported value of −7‰). Conversely, the formation temperatures needed to form a rhizolith with a $\delta^{18}O_{calcite}$ value of −7‰ in equilibrium with a $\delta^{18}O_{water}$ of −16 to −14‰ (V-SMOW) (assuming no evaporative concentration) would be an implausible −6·6 to −11 °C. Therefore, it appears that the rhizoliths do not form *in* the springs proper but instead form in evaporatively concentrated warm waters on the playa that fringe the spring sources.

The data from Agony Spring provide an additional example to further test this hypothesis. Water samples from deep pools in the Agony Springs complex have an average $\delta^{18}O_{water}$ value of ∼−14·3‰ (V-SMOW), but samples taken from a shallow drainage pool nearby on the playa flat increase to −7·7‰ (V-SMOW). The deeper pools to the west source the shallow drainage and the significant increase in the $\delta^{18}O_{water}$ value implies highly evaporative conditions. The rhizoliths found around the drainage pool record $\delta^{18}O_{calcite}$ values of −11 to −12‰, indicating a formation temperature range of 31 to 36 °C (Eq. 1). The measured temperature of the water in the shallow drainage ranged from 30 to 33 °C, and is consistent with rhizolith formation in shallow water under high evaporation (Table 1). At this temperature, Rayleigh distillation indicates that 60% of the source water (initial $\delta^{18}O_{water}$ = −14·3‰ V-SMOW) would have to evaporate to yield a $\delta^{18}O_{water}$ value of ∼−7·5‰ in the adjacent shallow pool (α = 1·0089 at 30 °C); this implies extreme evaporation of the Agony Spring waters over a distance of less than 30 m.

If there was no evaporative increase in the $\delta^{18}O_{water}$, the highest rhizolith $\delta^{18}O_{calcite}$ values would require formation temperatures colder than 0 °C. Assuming a more realistic calcification temperature of 30 °C, the entire range of rhizolith $\delta^{18}O_{calcite}$ values indicate precipitation in waters with $\delta^{18}O_{water}$ values of −12 to −4‰ (V-SMOW), which is consistent with published and measured $\delta^{18}O_{water}$ values in the region. Conversely, it is unlikely that the range in isotope data is due to temperature alone, as a 5‰ range in $\delta^{18}O_{calcite}$ values implies a temperature change of ∼25 °C. The temperature fluctuation in the region does exceed 25 °C annually but, during the colder months, the playa margin is dry and the rhizoliths do not form. Certainly, both variables (temperature and $\delta^{18}O_{water}$) change, but the potential for $CaCO_3$ precipitation is enhanced with increased alkalinity and evaporation.

DISCUSSION

Hydrologic and vegetative controls on rhizolith distribution

Figure 1 indicates that upslope geomorphology may be the reason for the individual geochemistry of the springs. Immediately upslope of the springs, whose $\delta^{18}O_{water}$ values are lower than −10‰, the alluvial fan is broad and is able to collect and channel abundant surface and groundwater to the playa edge, creating a strong

hydraulic head. However, in the southern part of the basin, the alluvial fan is much thinner and/or non-existent and, therefore, the hydraulic head behind the forced convective flow in this region is significantly reduced or absent. In the southern region, this reduced hydraulic head may allow the shallow brine aquifer from the central playa to infringe on the playa margin and 'contaminate' the springs with saline, evaporatively concentrated, re-circulated brines. In fact, the highest salinity measured in the basin is from Little Salt Spring, the furthest to the south, where there is no alluvial fan upslope and, therefore, no influence from the fresher alluvial fan aquifer.

Geochemical differences in the EC and $\delta^{18}O_{water}$ data of the spring samples are explained, therefore, by upslope hydrological parameters. Springs with $\delta^{18}O_{water}$ values are near −15‰ and EC values less than 5 mS cm^{-1} probably represent springs that tap the alluvial fan aquifer and, therefore, their values remain close to the regional meteoric water value (Fig. 2). Conversely, higher $\delta^{18}O_{water}$ values (e.g. −0·2‰ at Little Salt Spring) coupled with high EC values (>10 mS cm^{-1}) may indicate a more saline source (possibly the shallow brine aquifer or re-circulated brine by free convective flow). The intermediate samples, with low $\delta^{18}O_{water}$ and high EC values, may represent brines that have significant salinity, but have not been evaporatively concentrated. Evaporation may then be the cause for the range in $\delta^{18}O_{water}$ values, such as those seen in the Agony Springs samples.

The abundance of carbonate rhizoliths near the southern, more saline springs appears, therefore, to be directly related to regional hydrology. The geochemistry of the springs (specifically, salinity) dictates the presence or absence of the host of the rhizoliths, namely saltgrass. In the northern, fresher springs, no saltgrass is found, and instead the vegetation is dominated by C$_3$ sedges (*Scirpus* sp.) and shrubs (e.g. rabbitbrush). The salinity of these springs is low (<2 mS cm^{-1}), and may not represent optimal conditions for saltgrass growth. Therefore, rhizoliths are absent. However, in the springs to the south, EC values are high (>10 mS cm^{-1}), saltgrass is abundant and rhizoliths are prolific. Therefore, salinity is a first-order control on rhizolith distribution in that high salinity is needed for saltgrass growth on the spring margins. Thus, the hydrologic divide to the south of Halls Spring may also create a vegetative boundary that predicts the distribution of rhizoliths based on saltgrass ecology.

Saltgrass can tolerate complete submergence for 24 days, and is often the first to colonize areas exposed by falling water (Ungar, 1966); so, it is typical to find saltgrass along spring margins (Fig. 4B) and in the standing water around the spring edge (Fig. 7A). The plants begin to grow shoots when daily average temperatures are above 19 °C, which, in this region of Nevada, begins in June and continues until September (Fan *et al.*, 1997).

Controls on calcite precipitation

Geochemical data on the surface and groundwater at Pilot Valley indicate that [Ca^{2+}] greatly exceeds [HCO$_3^-$] and that, for most waters, [CO$_3^{2-}$] is zero (Oliver, 1992). The carbonate ion is always present in some minor abundance (even though it is not measured) and its concentration can be calculated using the measured pH and [HCO$_3^-$]. As 2 mol of HCO$_3^-$ are needed for every 1 mol of Ca^{2+} to precipitate calcite, the inorganic carbon is the limiting factor in the precipitation of carbonate. Processes that reduce the solubility of HCO$_3^-$ in the system will, therefore, help to initiate calcite precipitation.

Bicarbonate ion solubility decreases with a concurrent decrease in pCO$_2$, an increase in evaporation and evapotranspiration and/or the addition of Ca^{2+} ions to the system (Wright & Tucker, 1991). At Pilot Valley, the supply of Ca^{2+} ions is more than sufficient, and therefore evaporation/evapotranspiration and a decrease in pCO$_2$ are more likely to be the mechanisms for lowering bicarbonate ion solubility. Evaporation/ evapotranspiration, as well as temperature, are inversely proportional to pCO$_2$ and, therefore, as evaporation and temperature increase, the pCO$_2$ decreases (Wright & Tucker, 1991). The additional exsolution of CO$_2$(aq) to CO$_2$(g) into the atmosphere (through degassing) increases the pH, which may also stimulate calcite precipitation (Drever, 1988).

An additional consideration is the effect that the saltgrass plants have on their immediate aquatic environment. Photosynthesis by aquatic plants removes CO$_2$ from the water, lowers the pCO$_2$ and creates a subsequent increase in pH (Langmuir, 1997). This effect lowers the solubility of HCO$_3^-$ and, as the pH in this system increases, the [CO$_3^{2-}$] also increases and calcite precipitation is thermodynamically more favourable (Morel & Hering, 1993). Furthermore, some plants are able to release HCO$_3^-$ at their roots from respired organic matter made in the leaves, and thereby

Fig. 7. (A) Photograph of saltgrass plants in standing water along the periphery of Agony Spring, summer 2005. Notice that the saltgrasses on drier tussocks are green and alive, and those remnants of saltgrass in standing water have no green foliage. All that remains is a short stub of the saltgrass stem, coated in salt and calcite. Foot for scale. (B) Schematic cartoon of rhizolith formation on the playa at Pilot Valley, NV. Colonization of the playa margin with saltgrass vegetation begins. Water level is high due to snowmelt, run-off and increased hydraulic head. Water temperature is cool to warm (near 20 to 25 °C), pH is neutral, and waters have not yet been evaporatively concentrated so salinity is low to moderate, depending on source waters. (C) Later in the growing season, evaporation/evapotranspiration increases, causing the water level to drop. Loss of water and an increase in temperature leads to a decrease in pCO_2. As the plants continue to photosynthesize, the pH of the system also increases. Water temperatures are warm (30 to 35 °C) and evaporative concentration causes high salinity and alkalinity, providing ideal conditions for saltgrass growth and carbonate precipitation. Calcite tubules form around plant stems in standing water. The apron denotes the base of the tube at the sediment/water interface. Once the plant dies away, the tube is filled with sediment to form a cast.
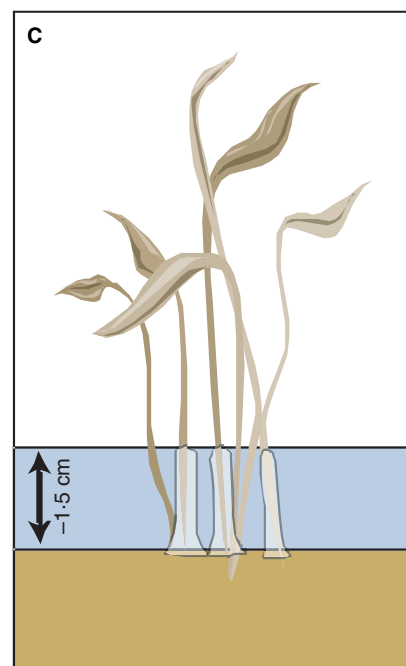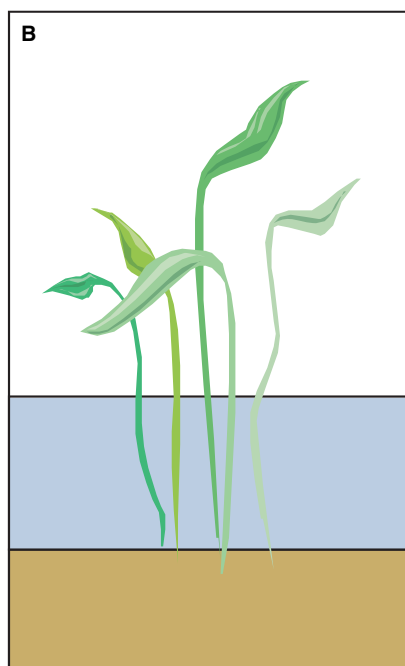
remain in electrochemical balance (Klappa, 1980); this increases the [HCO_3^-] locally, and can lead to calcification. Added to these effects is the reduction in calcite solubility with increased temperature (Langmuir, 1997). In fact, calcite solubility decreases by approximately 20% as water temperatures rise from 10 to 25 °C (Langmuir, 1997).

Each process (evaporation/evapotranspiration, high temperature and biological effects) occurs simultaneously at Pilot Valley and is equally likely as a mechanism for calcite initiation. At this time, however, it cannot be determined to what extent each process affects the initiation of the rhizolith calcite precipitation.

Rhizolith formation and timing at Pilot Valley, NV

Concentric berms were observed around the margins of the Agony Spring, suggesting that, during the spring when run-off and snowmelt are high, the springs at Pilot Valley overflow their banks. The resulting standing water on the playa around the springs provides the source waters for calcite precipitation. The saltgrass plants

colonize the playa and begin to alter their environment through photosynthesis and evapotranspiration (Fig. 7B). In addition, evaporation begins to concentrate the playa waters and further alters the geochemistry. Once conditions are right, calcite begins to form around the living saltgrass plants and creates an open, calcite tubule around the plant stem (Fig. 7C). As the ions needed for calcite precipitation are dissolved in the local waters, the height of the precipitating tubule is consistent with the water depth at the time of calcite precipitation.

As precipitation around the stem continues (in standing water), the calcite tube encounters the sediment/water interface and begins to extend laterally, presumably because it is unable to penetrate the sediment to a significant depth (Figs 3 and 7C); this creates the apron at the base of many of the Pilot Valley rhizoliths. As the plant inside the tubule dies and decays away, an open tubule is left at the sediment surface. Calcite, or micritic sediment, can then infill the tubule to create a cast. No plant material is found within the rhizoliths and, therefore, infilling of the tubule occurs after the plant host has been removed. Many rhizoliths found at Pilot Valley are upright, but reworking can occur. A geopetal structure was noted on one sample, indicating that the tube had fallen over on the sediment surface before being subsequently infilled with spongy, micritic calcite in the bottom half (possibly sediment washed into the tube) and more indurated calcite in the top half (probably precipitated from the water column).

As rhizolith distribution is dictated by saltgrass presence, the timing of rhizolith formation is concurrent with the saltgrass growing season (July to September) when daily average temperatures are suitable and a critical mass of saltgrass plants have colonized the playa and altered the geochemistry significantly. The distinctive stable isotopic signature of each spring (dictated by regional hydrology) thus provides the initial isotopic conditions for carbonate precipitating on the flooded margins of the springs. As the residence time of the water on the surface increases, evaporation and biological processes influence the geochemical composition and temperature of the waters and alter the resulting $\delta^{18}O_{calcite}$ of the rhizoliths, creating the range in values seen from each spring.

Microsampling of individual rhizoliths allows for further insight into the timing of rhizolith formation. Several samples show a steady increase in $\delta^{18}O_{calcite}$ values from the edge towards the centre. This increase suggests that the rhizolith was completely infilled with calcite during a single event. If the calcite had been diagenetically altered or precipitated during multiple years, the authors would expect to see zonation in the carbonates (and $\delta^{18}O_{calcite}$ values) indicative of multiple cycles of wetting (low $\delta^{18}O_{calcite}$ values) and subsequent evaporative concentration (high $\delta^{18}O_{calcite}$ values). Therefore, it seems evident that the rhizoliths at Pilot Valley form in one season.

Determining origin and equilibrium precipitation

Using Eq. 1, isotopic values of carbonate forming in equilibrium with ambient waters with a $\delta^{18}O_{water}$ of −16‰ at 30 °C are near −19·1‰ (Fig. 6); these represent measured conditions from Pilot Valley, and are end members for the highest temperature and the lowest $\delta^{18}O_{water}$ value. Conversely, isotopic values of carbonates forming in equilibrium with ambient waters with a $\delta^{18}O_{water}$ of −7·7‰ V-SMOW at 10 °C would be near −5·8‰, indicating the opposite end members for the coolest temperature and the highest $\delta^{18}O_{water}$ value (excluding Little Salt Spring). With the exception of the rhizoliths from Little Salt Spring, all $\delta^{18}O_{calcite}$ values of the Pilot Valley rhizoliths fall within the range of these equilibrium conditions (Fig. 6). The $\delta^{18}O_{water}$ and $\delta^{18}O_{calcite}$ values collected for Little Salt Spring do not indicate equilibrium conditions, as a $\delta^{18}O_{water}$ value of −0·2‰ would need to be lowered to ∼−10‰ to precipitate calcite with $\delta^{18}O_{calcite}$ values near −13‰ at 30 °C. At this time, it is unclear why the calcite at Little Salt Spring records disequilibrium conditions.

Even so, the bulk of the data confirm the interpretation that the rhizoliths at Pilot Valley are formed 'phreatically' under standing water conditions (Fig. 7C). Thus, the height of each rhizolith stem can be an effective proxy for water depth during their time of formation. The implications of this for the fossil record are numerous. Not only can parameters, such as pH, temperature and $\delta^{18}O_{water}$ values, be inferred by the isotopic composition of the rhizolith carbonate, but regional hydrologic parameters (e.g. water depth) can also be determined.

There is one caveat, however. As these rhizoliths are phreatic and can only form under specific ecological conditions (e.g. conditions suitable for saltgrass growth, standing water on the playa), they are only able to record a partial annual record. In fact, rhizoliths have been

located and collected on the playa surface during field visits in July and August, but have not been found at all during visits at other times of the year (November and May); this is probably due to daily average temperatures being too cold for saltgrasses and, therefore, the nucleation site for rhizolith calcite had not yet emerged. Therefore, to use fossil rhizoliths to determine aquatic conditions, the samples ought to be analysed through a variety of geochemical and microscopic methods to determine origin (phreatic or pedogenic) and, as with all rhizoliths that need a host plant around which to grow, it must be understood that the data record only a partial annual (growing season?) signal.

CONCLUSIONS

In a semi-arid region, such as the playas of the Great Salt Lake Desert, rhizoliths form in standing water around saltgrass plants when springs on the valley margin overflow. The initial geochemical conditions for the spring waters are dictated by local hydrology: freshwater springs appear in the northern region to the east of a broad alluvial fan, and more saline springs emerge to the south where the influence of the alluvial fan diminishes. The morphology of the rhizoliths and $\delta^{13}C_{calcite}$ is coincident with saltgrass (*Distichlis* sp.) being the host plant for the rhizolith carbonate. The salinity of the spring waters dictates the presence or absence of saltgrass plants on the periphery and, therefore, rhizoliths are only found around the saline, southern springs. The large range in $\delta^{18}O_{calcite}$ values indicates that the rhizoliths form as evaporation desiccates the water fringing the springs on the playa flat. The $\delta^{18}O_{calcite}$ values recorded in most of the rhizolith carbonates confirm that they form in equilibrium with ambient aquatic conditions and form, therefore, phreatically. The phreatic origin of the Pilot Valley rhizoliths makes them faithful recorders of ambient water conditions (e.g. geochemistry), as well as local hydrologic parameters (e.g. water depth), when the playa surface is flooded, but their application is restricted to a partial annual signal.

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REFERENCES

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

Andrews, J., Coletta, P., Pentecost, A., Riding, R., Dennis, S., Dennis, P. and **Spiro, B.** (2004) Equilibrium and disequilibrium stable isotope effects in modern charophyte calcites: implications for palaeoenvironmental studies. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **204**, 101–114.

Ashley, G.M. (1996) Springs, pools and adjacent wetlands, a newly recognized habitat, lowermost Bed II, Olduvai Gorge. *Geol. Soc. Am. Abst. Programs*, **28**, 28.

Botz, R., Stoffers, P., Faber, E. and **Tietze, K.** (1988) Isotope geochemistry of carbonate sediments from Lake Kivu (East-Central Africa). *Chem. Geol.*, **69**, 299–308.

Cerling, T.E. and **Hay, R.L.** (1986) An isotopic study of palaeosol carbonates from Olduvai Gorge. *Quatern. Res.*, **25**, 63–78.

Cerling, T.E. and **Quade, J.** (1993) Stable carbon and oxygen isotopes in soil carbonates. In: *Climate Change in Continental Isotope Records* (Eds P.K. Swart, K.C. Lohmann, J.A. McKenzie and S. Savin), *Am. Geophys. Union Publ.*, **78**, 217–239.

Cerling, T.E., Bowman, J.R. and **O'Neil, J.R.** (1988) An isotopic study of a fluvial-lacustrine sequence: the Plio-Pleistocene Koobi Fora sequence, East Africa. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **63**, 335–356.

Chavetz, H.S., Rush, P.F. and **Utech, N.M.** (1991) Microenvironmental controls on mineralogy and habit of $CaCO_3$ precipitates: an example from an active travertine system. *Sedimentology*, **38**, 107–126.

Coplen, T.B., Kendall, C. and **Hopple, J.** (1983) Comparison of stable isotope reference samples. *Nature*, **302**, 236–238.

Craig, H. (1965) The measurements of oxygen isotope palaeotemperatures. In: *Stable Isotopes in Oceanographic Studies and Palaeotemperatures* (Ed. E. Tongiorgi), pp. 1–24. Consiglio Nazionale delle Richerche, Rome, Italy.

Deines, P., Langmuir, D. and **Harmon, R.S.** (1974) Stable carbon isotope ratios and the existence of a gas phase in the evolution of carbonate ground waters. *Geochim. Cosmochim. Acta*, **38**, 1147–1164.

Deocampo, D.M. and **Ashley, G.M.** (1999) Siliceous islands in a carbonate sea: Modern and Pleistocene spring-fed wetlands in Ngorongoro Crater and Oldupai Gorge, Tanzania. *J. Sed. Res.*, **29**, 974–979.

Deocampo, D.M., Blumenschine, R.J. and **Ashley, G.M.** (2002) Freshwater wetland diagenesis, fossil vertebrates, and traces of early hominids in the lowermost Bed II (∼1·8 myr) playa lake-margin at Olduvai Gorge, Tanzania. *Quatern. Res.*, **57**, 271–281.

Drever, J.I. (1988) *The Geochemistry of Natural Waters*. Prentice Hall, Englewood Cliffs, NJ, 437 pp.

Duffy, C.J. and **Al-Hassan, S.** (1988) Groundwater circulation in a closed desert basin: topographic scaling and climate forcing. *Water Resour. Res.*, **24**, 1675–1688.

Fan, Y., Duffy, C.J. and **Oliver, D.S. Jr** (1997) Density-driven groundwater flow in closed desert basins: field investigations and numerical experiments. *J. Hydrol.*, **196**, 139–184.

Feibel, C.S. (2001) Archaeological sediments in lake margin environments. In: *Sediments in Archaeological Contexts* (Eds J.K. Stein and W.R. Ferrand), University of Utah Press, Salt Lake City, UT, 218 pp.

Fontes, J.C., Gasse, F. and **Gilbert, E.** (1996) Holocene environmental changes in Lake Bangong basin (Western Tibet). Part 1. Chronology and stable isotopes of carbonates of a Holocene lacustrine core. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **120**, 25–47.

Hay, R.L. (1976) *Geology of the Olduvai Gorge*. University of California Press, Berkeley, CA, 203 pp.

Hay, R.L. (1990) Olduvai Gorge: a case history in the interpretation of hominid palaeoenvironments in East Africa. In: *Establishment of a Geologic Framework for Palaeoanthropology* (Ed. L.F. Laporte), *Geol. Soc. Am. Spec. Pap.*, **242**, 23–37.

Hay, R.L. and **Kyser, T.K.** (2001) Chemical sedimentology and palaeoenvironmental history of Lake Olduvai, a Pliocene lake in northern Tanzania. *Geol. Soc. Am. Bull.*, **113**, 1505–1521.

Johnson, T.C., Halfman, J.D. and **Showers, W.J.** (1991) Palaeoclimate of the past 4000 years at Lake Turkana, Kenya, based on the isotopic composition of authigenic calcite. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **85**, 189–198.

Klappa, C.F. (1980) Rhizoliths in terrestrial carbonates: classification, recognition, genesis, and significance. *Sedimentology*, **27**, 613–629.

Koch, P.L. (1998) Isotopic reconstruction of past continental environments. *Annu. Rev. Earth Planet. Sci.*, **26**, 573–613.

Langmuir, D. (1997) *Aqueous Environmental Geochemistry*. Prentice-Hall Publishing, Upper Saddle River, NJ, 600 pp.

Levin, N.E., Quade, J., Simpson, S.W., Semaw, S. and **Rogers, M.** (2004) Isotopic evidence for Plio-Pleistocene environmental change at Gona, Ethiopia. *Earth Planet. Sci. Lett.*, **219**, 93–110.

Li, H.-C. and **Ku, T.-L.** (1997) $\delta^{13}C–\delta^{18}O$ covariance as a palaeohydrological indicator for closed-basin lakes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **133**, 69–80.

Lines, G.C. (1979) Hydrology and surface morphology of the Bonneville salt flats and Pilot Valley playa, Utah. *US Geol. Surv. Water Supply Pap.*, **2057**, 106 pp.

Liutkus, C.M., Wright, J.D., Ashley, G.M. and **Sikes, N.E.** (2005) Palaeoenvironmental interpretation of lake-margin deposits using $\delta^{13}C$ and $\delta^{18}O$ results from Pleistocene carbonate rhizoliths; Olduvai Gorge, Tanzania. *Geology*, **33**, 377–380.

Malek, I., Bingham, G.E. and **McCurdy, G.D.** (1990) Evapotranspiration from the margin and moist playa of a closed desert valley. *J. Hydrol.*, **120**, 15–34.

Manga, M. (2001) Using springs to study groundwater flow and active geologic processes. *Annu. Rev. Earth Planet. Sci.*, **29**, 201–228.

Menking, K.M., Anderson, R.Y., Brunsell, N.A., Allen, B.D., Ellwein, A.L., Loveland, T.A. and **Hostetler, S.W.** (2000) Evaporation from groundwater discharge playas, Estancia Basin, central New Mexico. *Global Planet. Change*, **25**, 133–147.

Miller, G.H., Fogel, M.L., Magee, J.W., Gagan, M.K., Clarke, S.J. and **Johnson, B.J.** (2005) Ecosystem collapse in Pleistocene Australia and a human role in megafaunal extinction. *Science*, **309**, 287–290.

Morel, F.M.M. and **Hering, J.G.** (1993) *Principles and Applications of Aquatic Chemistry*, 1st edn. John Wiley and Sons Publishing Inc., New York, NY, 588 pp.

Oliver, D.S. Jr (1992) *An Experimental Study of Groundwater Flow and Salinity Dynamics of a Playa Margin*. Unpublished MS Thesis. Utah State University, Logan, UT, 130 pp.

Pedley, H.M., Andrews, J., Ordonez, S., Garcia del Cura, M.A., Gonzales Martin, J.A. and **Taylor, D.** (1996) Does climate control the morphological fabric of freshwater carbonates? A comparative study of Holocene barrage tufas from Spain and Britain. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **121**, 239–257.

Rosen, M.R. (1994) The importance of groundwater in playas; a review of playa classifications and the sedimentology and hydrology of playas. In *Palaeoclimate and Basin Evolution of Playa Systems* (Ed. M.R. Rosen), *Geol. Soc. Am. Spec. Pap.*, **289**, 1–18.

Saez, A. and **Cabrera, L.** (2002) Sedimentological and palaeohydrological responses to tectonics and climate in a small, closed, lacustrine system: Oligocene As Pontes Basin (Spain). *Sedimentology*, **49**, 1073–1094.

Sikes, N.E., Potts, R. and **Behrensmeyer, A.K.** (1999) Early Pleistocene habitat in Member 1 Olorgesailie based on palaeosol stable isotopes. *J. Human Evol.*, **37**, 721–746.

Smith, G.A., Wang, Y., Cerling, T.E. and **Geissman, J.W.** (1993) Comparison of a palaeosol-carbonate isotope record of Pliocene-early Pleistocene climate in the western United States. *Geology*, **21**, 691–694.

Snyder, C.T. (1962) A hydrologic classification of valleys in the Great Basin, Western United States. In: *Playas and Dried Lakes: Occurrence and Development* (Ed. J.T. Neal), *Benchmark Pap. Geol.*, **20**, 113–119.

Talbot, M.R. (1990) A review of the palaeohydrological interpretation of carbon and oxygen isotope ratios in primary lacustrine carbonates. *Chem. Geol.*, **80**, 261–279.

Ungar, I. (1966) Salt tolerance of plants growing in saline areas of Kansas and Oklahoma. *Ecology*, **47**, 154–155.

Watanabe, T., Gagan, M.K., Correge, T., Scott-Gagan, H., Cowley, J. and **Hantoro, W.S.** (2003) Oxygen isotope systematics in *Diploastrea heliopora*: new coral archive of tropical palaeoclimate. *Geochim. Cosmochim. Acta*, **67**, 1349–1358.

Wright, V.P. and **Tucker, M.E.** (Eds) (1991) *Calcretes: An Introduction: Calcretes*. Blackwell Scientific Publishing, Cambridge, MA, 352 pp.

Wynn, J.G. (2000) Palaeosols, stable carbon isotopes, and palaeoenvironmental interpretation of Kanapoi, Northern Kenya. *J. Human Evol.*, **39**, 411–432.