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$\delta^{13}C$ AND $\delta^{18}O$ GEOCHEMISTRY OF PEDOGENIC CARBONATES OF MORMON MESA, SOUTHEASTERN NEVADA, USA

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INTRODUCTION

The Early Pliocene, extant paleosol at Mormon Mesa in Southeast Nevada is a rare example of advanced calcium carbonate pedogenesis, forming multiple well-indurated petrocalcic horizons and a set of morphologic features such as carbonate laminae, concretionary pisoids, and pedogenic ooids encased in a carbonate matrix (Brock and Buck, 2009). The soil represents a record of geomorphic conditions in the Mojave over approximately 4-5 million years (Bachman and Machette, 1977; Brock and Buck, 2009; Robins et al., 2012).

Most of the Mormon Mesa soil horizons are extremely calcic, with an average of 70.4% $CaCO_3$ reported from one profile (Robins et al., 2012). The remainder of the soil mineralogy is composed of detrital grains of lithic parent material, volcanic ash, and fibrous phyllosilicates interpreted as pedogenic palygorskite and sepiolite from Scanning Electron Microscopy with Energy Dispersive Spectrometry (SEM-EDS) corroborated by X-Ray Diffraction (XRD) (Brock and Buck, 2009; Robins, 2010). Formation of authigenic minerals is dependent on ratios of mineral forming components in solution within the soil, as well as on soil pH. (Brock and Buck, 2009; Robins et al., 2012; Zamanian et al., 2016). Detrital silicate grains and volcanic ash contribute Si to the soil solution with force of calcite crystallization facilitating dissolution of quartz and ash. The available silica is incorporated into authigenic fibrous magnesium silicates such as palygorskite and sepiolite (Robins et al., 2012).

Of note for paleoenvironmental interests, pedogenic calcium carbonate accumulates in arid to semi-arid, alkaline soil horizons like those at Mormon Mesa when Ca^{2+} ions from meteoric water combine with CO_2 from plant and microbial respiration, (Gile et al., 1966) and oxygen from soil water (Cerling and Quade, 1993; Zamanian et al., 2016). CO_2 is largely contributed to soil air or released into solution by microbial activity and by respiration at the plant root. At Mormon Mesa, where soil organic matter (SOM) is < 2.0 %, (Robins et al., 2012) soil CO_2 concentrations may also be impacted by the diffusion of atmospheric CO_2 into the soil profile (Cerling, 1984; Zamanian et al., 2016). Importantly, plant community compositions influence soil carbonate $\delta^{13}C$ signature. C3 plants contribute to more negative $\delta^{13}C$ values in comparison to C4 plants (Quade et al. 1989; Alonso-Zarza, 1998; Zamanian et al., 2016). Oxygen in pedogenic carbonate is sourced from meteoric water, with $\delta^{18}O$ values fractionated by regional temperature. A model describing the introduction of isotopic signatures from environmental sources is shown (Figure 1). The goal of this research project is to address the following questions: Do pedogenic carbonate $\delta^{13}C$ and $\delta^{18}O$ values vary among horizons and between features sampled at Mormon Mesa? Where do authigenic phyllosilicates occur in the micromorphology of the soil, and are they likely to record $\delta^{18}O$ values similar to those of the calcite?

METHODOLOGY

Field Methods

We identified three field sites located on the edges of Mormon Mesa and Flat Top Mesa in Clark County, Nevada. The Riverside site (MMR) is located on the southeast edge of Mormon Mesa. The Flat Top East site (FTE) and Flat Top West site (FTW) are located on the eastern and western sides, respectively, of Flat Top Mesa, which is located to the East of Mormon Mesa (Figure 2).

The Mormon Mesa soil profile overlies the Muddy Creek Formation, a variable package of fine grained sandstones, thinly bedded siltstones, and mudstones of Miocene age capped by stage II carbonate paleosol horizons. At Riverside, five distinct horizons were observed above the muddy creek unit: Muddy Creek showing stage II calcic pedogenesis, a stage III transitional horizon, stage IV laminar horizon, stage V-VI discontinuous and brecciated massive horizon (Figure 3a). The same five horizons were observed at Flat Top East and Flat Top West, with variations in thickness and morphology. For this study, one to three samples were collected at intervals (top, middle, bottom) from each horizon at each profile to create a vertical section using rock hammers, chisels, and/or a concrete cutting saw.

Stable isotope analysis

Field samples were prepared at Pomona College. For carbonate $\delta^{18}O$ and $\delta^{13}C$ analysis, samples were ground using steel rock crushers and disc mills to achieve a fine gravel/coarse sand size. For some massive horizon samples, pisoid and laminae macromorphological features were cut and isolated from the soil matrix using a diamond bladed tile saw. Pisoids, laminae, and matrix portions of each sample were kept separate for isotope analysis.

Aliquots of processed samples were analyzed in the stable isotope laboratory at the University of Massachusetts Amherst on a Finnigan Delta XL+ mass spectrometer with a Kiel III automated carbon device. Reproducibility on standards and duplicates is generally better than ± 0.2‰. $\delta^{18}O$ and $\delta^{13}C$ values are reported relative to the VPDB standard.

Micromorphology and imaging

Rectangular billets of Stage V-VI soil containing the four major macromorphological soil features observed- pisoids, laminae, and matrix- were cut to approximately 3x4x1 cm in size. For disaggregated Stage I-III samples, pieces of the soil were set in epoxy and cut into approximately 3x4x1 cm billets. At Mount Holyoke College, billets were polished and carbon sputter coated for backscatter and secondary electron imaging on a FEI Quanta 200 SEM. EDAX Genesis software was used for x-ray microanalysis.

RESULTS

Stable Isotopes $\delta^{13}C$ and $\delta^{18}O$

$\delta^{13}C$ values range between -6.01‰ and -3.33‰ across FTE, FTW, and MMR profiles and when grouped by profile (Figure 3a), all three $\delta^{13}C$ ranges overlap. However, there are generally more negative values in the FTE (median -4.92 ‰) and MMR (median -4.46‰) profiles, and higher values in FTW (median -3.87‰). One way ANOVA results support a significantly distinct range for the FTW ($p < 0.05$) $\delta^{13}C$ compared to those of FTE and MMR, but MMR and FTE values are not statistically distinct from each other.

When grouped by carbonate development stage and morphology (Figure 3b), the narrower range (-4.78‰ to -3.98‰) of the Stage II carbonate nodule samples (median $\delta^{13}C$ -4.47‰), overlaps with the broader range (-5.42‰ to -3.54‰) of the Stage III samples (median -4.38‰). Meanwhile, the Stage V-VI inset features at FTW (median -3.62‰, range -3.80‰ to -3.33‰) and rubble layer samples median -4.07; range from -4.21‰ to -3.93‰) fall at the high end of the stage III values. One way ANOVA does not support significant statistical differences between ranges.

$\delta^{18}O$ values range from -10.51‰ to -7.43‰ across the three profiles (Figure 3a) and show closer overlap among the three sites than $\delta^{13}C$, with one way ANOVA finding no significant distinction between ranges. The median value for FTE is -8.62‰. For FTW, the median is -8.16‰. For MMR, the median is 9.23‰.

For grouped stages (Figure 3b), $\delta^{18}O$ values show overlapping clusters, with $\delta^{18}O$ values for Stage III transitional horizons (median -8.98) distributed in a broad range (-10.5‰ to -8.17‰). The Stage V-VI inset features at FTW (median -7.78‰) have a narrower range (-8.14‰ to -7.78‰) and differ significantly ($p < 0.05$) from Stage II values (median -9.04‰, range -9.99‰ to -8.62‰) based on one way ANOVA.

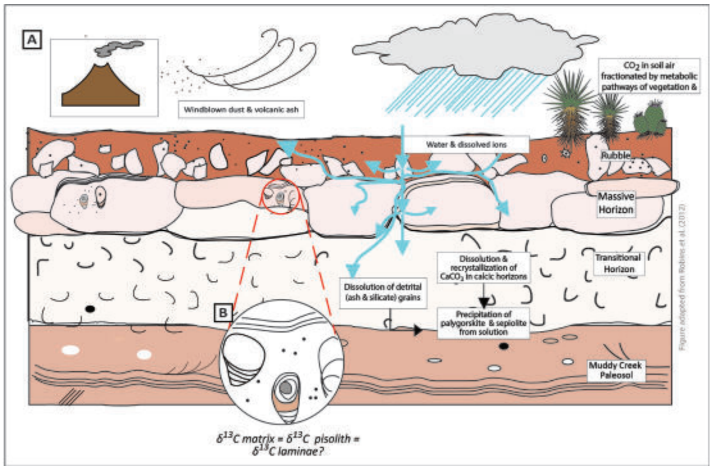

Figure 1. Illustrated model showing sources of carbon and oxygen fractionation, and of windblown parent minerals to authigenic calcite and silicates in Mormon Mesa soil. 1A shows introduction of lithogenic dust and ash, percolation of meteorically fractionated water, and metabolically fractionated CO2 at plant roots. 1B shows a detailed view of Stage IV-VI morphological features.

Rubble layer samples report intermediate values (median -8.07‰, range -8.05‰ to -8.09‰).

Micromorphology

A survey of the micromorphology and elemental composition of several thick sections of Stage V-VI pedogenic carbonate from MMR using SEM-EDS revealed a prevailing pattern to the micromorphology of the sample fabrics. Mineral identifications are supported by EDS spectra. Laminar features between 100 μm and 1 mm wide are observed in multiple samples. Laminae are defined by the alternation of lines of subangular to subrounded grains of detrital quartz in a calcium carbonate matrix with linear sections of homogenous carbonate (Figure 4a). Dissolution features in the carbonate matrix are common, especially at the contact between carbonate and detrital grains (Figure 4b). Within dissolution features, quartz grains show evidence of dissolution, with fibrous clay minerals interpreted as palygorskite and sepiolite (Robins et al., 2014) commonly filling dissolved areas between quartz grains and carbonate matrix (Figure 4a, b, c). Elemental composition of fibrous clays is shown in Figure 4d.

DISCUSSION

Values of $\delta^{13}C$ and $\delta^{18}O$ at FTE, FTW, and MMR are consistent with values for other calcic soils in similar arid to semiarid soils in southern Nevada, which range from ca. -6‰ to 0‰ for $\delta^{13}C$ and ca. -10‰ to -4‰ for $\delta^{18}O$ (Quade et al., 1989). Additionally, trends of increasingly negative isotopic values for both $\delta^{13}C$ and $\delta^{18}O$ with increasing depth below the surface are consistent with previously published data (Cerling et al., 1984; Quade et al. 1989).

$\delta^{13}C$ values ranging -6.01‰ to -3.33‰ with mean -4.45‰ suggest the presence of both C3 and C4 vegetation, with an abundance of C4 vegetation approximately 22%. This is consistent with anticipated ratios of C3 and C4 communities in arid to semiarid climates (Ehleringer, 2005) and closely reflects previously published systematic surveys of vegetation on similar soils in the region (Quade et al., 1984). Significantly higher $\delta^{13}C$ values in the FTW profile imply greater exchange with respired CO_2 from C4 vegetation in the FTW profile than in either FTE or MMR. The implication of more pervasive C4 vegetation is greater local water stress at the time and location of carbonate precipitation.

The lack of significant distinction among $\delta^{13}C$ values for pedogenic carbonate stages and morphologies implies that proportions of C3 and C4 metabolic paths do not have a substantial effect. One explanation for the non-significantly high $\delta^{13}C$ of inset Stage V-VI features in FTW is that exchange between carbonate forming solution and atmospheric CO_2 was more active in the formation of these features. Atmospheric carbon diffusion enriches $\delta^{13}C$ values up to 4.4‰ (Cerling, 1984; Zamanian et al., 2016). The shallow depth of the inset features and the possibility of dissolution-recrystallization in these features supports the plausibility CO_2 diffusion.

The lack of statistically significant distinction between $\delta^{18}O$ ranges among the three profiles suggests similar regional temperature during pedogenic carbonate precipitation. The marginally higher $\delta^{18}O$ of FTW may reflect soil solution enrichment in $\delta^{18}O$ due to evaporation before carbonate precipitation (Quade et al., 1989). This is consistent with the hypothesized local water stress at FTW inferred from statistically high $\delta^{13}C$ in FTW carbonate.

Within grouped stages, significant distinction between the $\delta^{18}O$ ranges of inset Stage V-VI features at FTW and Stage II values from all three profiles may represent precipitation under different regional temperatures. Lower $\delta^{18}O$ in Stage II carbonate indicates higher temperature at the time of carbonate precipitation compared to Stage V-VI, as the $\delta^{18}O$ value for meteoric water is decreased as evaporation increases. However, the possibility remains that relatively high $\delta^{18}O$ in FTW features is the result of evaporation of light oxygen from the carbonate-forming soil solution.

Each stage of carbonate pedogenesis has associated points of interest and challenges for interpreting paleoclimate from isotopic values. Stage II carbonate nodules represent only the earliest phase of carbonate pedogenesis, and thus do not present a full view of climate trends over time. Stage III is interpreted as forming over a very long time interval (> 1 Ma) (Brock and Buck, 2009) and varies in thickness from approximately 60 cm at FTE to over 650 cm at FTW, complicating a comparative approach between profiles. Stage V to VI features are discontinuous, varied in their morphology, and show evidence of dissolution-reprecipitation (Robins et al., 2014). Finally, the carbonate component of rubble layers are composed of fragments of one or more stage V-VII horizons. For these reasons, a more nuanced study is necessary to propose a climate history for Mormon Mesa.

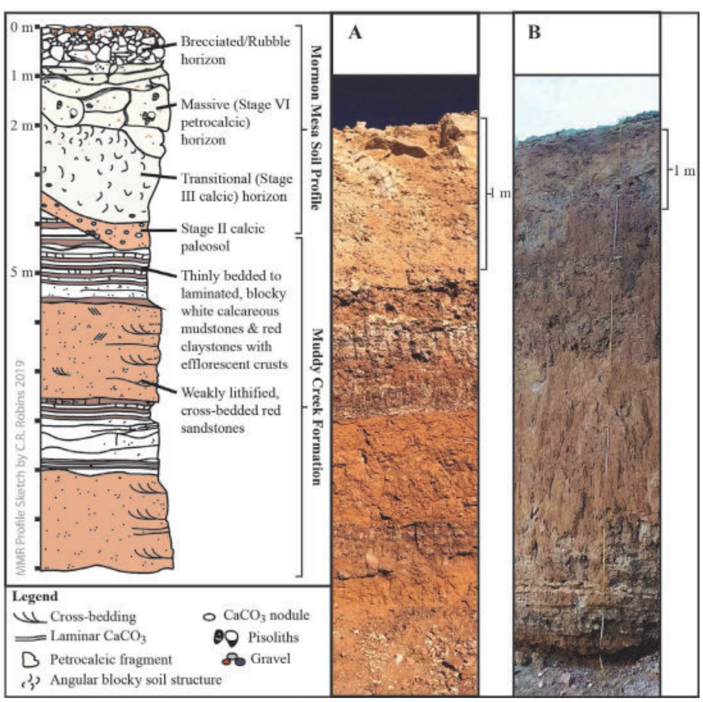

Figure 2. Sketch of MMR profile by C.R. Robins showing typical Mormon Mesa horizons. 2A field photo of FTE profile showing Muddy Creek Formation through Stage VI horizon. 2B field photo of FTW profile showing Muddy Creek Formation through Stage VI horizon.

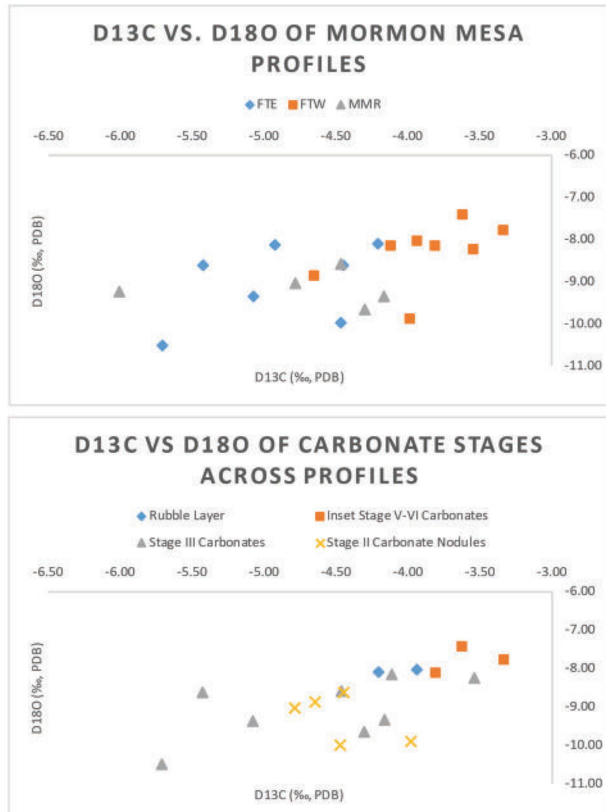

Figure 3. $\delta^{13}C$ vs. $\delta^{18}O$ stable isotope data in ‰ PDB compared between MMR, FTW, FTE profiles (top) and between carbonate stages II, III, V-VI, and rubble.

Occurrence of fibrous clay minerals interpreted as palygorskite and sepiolite from SEM-EDS secondary electron images and spectra is consistent with previously published mineralogy of Mormon Mesa soil (Robins et al., 2012; 2014). The observed morphology and spatial relationships between calcite, quartz, and phyllosilicate clay minerals supports the Robins et al. model of clay mineral authigenesis due to force of calcite crystallization. The implication of the observed morphology and indications of authigenesis is that a new set of hypotheses relating the oxygen component of Mormon Mesa soil solution and that of the pedogenic clays may be developed.

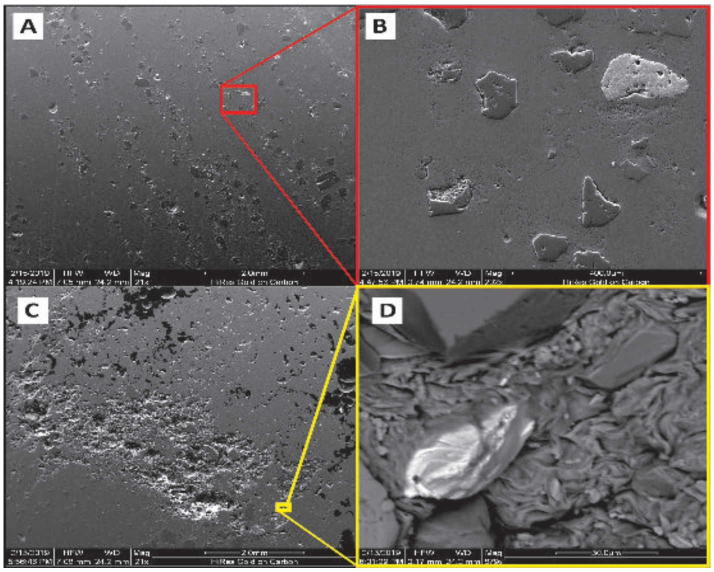

Figure 4. SEM secondary electron images showing micromorphology of sections of Stage V carbonate and clays. 4A image of laminae with bands of detrital quartz in calcite matrix. 4B enlarged view from 4A showing subangular quartz and oxide (light grain), with partial dissolution of quartz grain and precipitation of authigenic silicates. 4C image of carbonate matrix with quartz grains and dissolution features. 4D enlarged image from within dissolution feature of 4C showing fibrous authigenic phyllosilicates growing amid crystalline calcite.

CONCLUSIONS

Isotope data from pedogenic carbonate as a proxy for paleoclimate has contributed immensely to understanding of temperature and moisture regimes over recent geologic history. The use of pedogenic carbonate for regional temperature trends, however, relies on the assumption of authigenic carbonates as geochemically stable and does not account for dissolution and recrystallization of carbonate in soil. The implication of pedogenic carbonate recrystallization is an iteratively rewritten -and overwritten- climate history. Each successive phase of recrystallization captures new isotope values reflective of conditions at that moment, and ultimately contributes to time averaging of paleoclimate data. Authigenic phyllosilicate clay minerals in FTW, FTE, and MMR may be less prone to dissolution and recrystallization over the same time interval, and may as a result capture distinct signatures relevant to paleoclimate. Rather than relying on carbonate, $\delta^{18}O$ of authigenic phyllosilicates present in Mormon Mesa soil should be studied as a potential source of future paleoclimate models for this region.

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