TITLE: Inferences of Paleoenvironment from Petrographic, Chemical and Stable-Isotope Studies of Calcretes and Fracture Calcites

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INFERENCES OF PALEOENVIRONMENT FROM PETROGRAPHIC, CHEMICAL AND STABLE-ISOTOPE STUDIES OF CALCRETES AND FRACTURE CALCITES

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ABSTRACT

Past research has indicated a genetic connection between calcite formed in calcretes at the surface of Yucca Mountain, Nevada, and calcites deposited in underlying fractures of the unsaturated zone. This common genesis suggests that paleoenvironmental information, as well as the timing and pathways of past recharge episodes, might be obtained from studies of the deposits in both the calcretes and the unsaturated fractures. Chemical and isotopic modification of calcite-precipitating fluids appears to begin at the surface, largely under the influence of plant roots and their decay products. Chemical characteristics of the deeper calcites are either initiated or largely defined within the first few meters of fluid migration into the unsaturated tuffs beneath the calcretes. However, petrographic and isotopic data indicate a very unique low-$\delta^{13}$C microenvironment that is localized at the upper surfaces of the calcretes. These surfaces form an interface in the soil horizon where infiltration may pond above the underlying carbonate "plug." In order to decipher the chemistry and petrology of past recharge events, it is important to first understand microenvironments such as this that contribute to mineral precipitation/dissolution events in the pedogenic environment.

I. INTRODUCTION

Pedogenic carbonate is widely distributed at Yucca Mountain, Nevada, both at the surface in calcretes and commonly penetrating about 15 m into fractures and faults. The predominant authigenic mineral in these calcretes and shallow fillings is calcite, with somewhat lesser amounts of opal and minor local occurrences of sepiolite, other clays, and rare evaporite minerals (gypsum, halite). Several studies have linked the coarser, euhedral calcite found in deeper fractures and faults to these near-surface calcretes.\textsuperscript{1,2,3} The potential of using calcite in particular as a monitor of recharge events in unsaturated rocks has attracted attention from a number of researchers. U-series dating of calcites in fractures of the unsaturated zone at Yucca Mountain has been used to infer distinct recharge episodes at 28, 170, and 280 ka.\textsuperscript{4} Clustering of $^{14}$C ages between 33 and 45 ka has been observed, but younger occurrences may not have been sampled and the samples that were dated may appear erroneously old because of inheritance of "dead" C from dissolution of previously-formed calcites.\textsuperscript{5} The passage of carbon through such complex cycling within the calcretes is one of the points developed in this paper.

The purpose of this paper is to better define the variability in calcite petrography, chemistry, and stable-isotope compositions of the calcretes that may be genetically related to much of the deeper calcite found throughout the unsaturated zone at Yucca Mountain. Several features preserved in the calcretes provide fossil evidence of the plants and their decay products that are factors in calcrite formation. These features may have some bearing on the paleoecology (and hence paleohydrology and paleoclimatology) of the Yucca Mountain site. The samples described in this paper come from
Figure 1: Map of Yucca Mountain, showing the locations of calcite samples (sand ramps at Busted Butte; Trenches 5a, 14, 14c) and of drill cores (UZ-16, G-2, GU-3, G-4, and NRG-2) described in this paper.
localities shown in Figure 1. These include three trenches through calcrete-bearing soil profiles at Exile Hill, the calcretes and rhizoliths that have formed in eolian deposits (sand ramps) at Busted Butte, and samples from deeper fractures in several drill cores.

The calcretes at Yucca Mountain contain a wide variety of features typical of carbonate- and silica-accumulating pedogenic processes. Field, chemical, and mineralogic studies have been used to link both calcite and opal accumulation in the calcretes to the depletion of carbonate and silica from the overlying B soil horizons.\textsuperscript{6,7} Within the calcretes, accumulation of carbonate and silica may result in dense laminae containing calcite microspar (<5 \( \mu \text{m} \)) and thin deposits of botryoidal opal-A or opal-CT. These dense laminae, but in particular the more friable and porous laminae, contain various fossilized rootlets and roots. The root features, referred to collectively in this paper as rhizoliths, are often preserved as opalized root sheaths (opal-A) that may be either plugged with opal and calcite or they may form a casing in which delicate fungal microfossils formed of calcite are preserved.\textsuperscript{7} In addition to these rhizoliths, many friable or uncemented zones in the calcretes contain sand-sized (62 \( \mu \text{m} \) to 2 mm) grains of tuff detritus around which concentric rinds of calcite and opal have accumulated, forming \textit{oooids} (Figure 2A). Less common are ooids in which concentric rinds of calcite and opal have formed around nuclei of fine-grained intergrowths of these same authigenic materials with little or no tuff detritus; these are referred to as \textit{homogeneous ooids} (Figure 2B) in this paper. Another of the less common ooid-like features consists of oblate particles in which tuff detritus,
mostly silt-sized (4 to 62 μm), is cemented by calcite, opal, and smectite clay with no internal depositional structure, creating features that can be classified as pellets (Figure 2C). This paper focuses on comparisons between these features, the bulk of the associated calcrites, and one example of calcite from an overlying B soil horizon.

II. DESCRIPTION OF RESEARCH

Samples were analyzed petrographically, chemically (by instrumental neutron activation analysis, INAA), and by X-ray diffraction (XRD) and scanning electron microscopy (SEM) following methods described elsewhere. Samples of living roots were also studied by these methods, with XRD analyses performed both before and after low-temperature ashing (LTA) to remove the organic hydrocarbon constituents and concentrate the mineral residues. INAA data were collected for these mineral residues. Stable-isotope data have been collected with both bulk-sample and micro-sampling procedures. Emphasis was placed on the calcite in pedogenic calcrites at the surface of Yucca Mountain, although the transition to coarser, euhedral calcites in deeper fractures is also considered. In many cases, ooids, pellets, and rhizoliths could be separated from the encasing calcrites and analyzed individually. Variations in both C and O isotopes, when viewed in the context of calcrite textural variants, can provide specific information of paleoenvironmental significance. The importance of analyzing the calcrites lies in their role as either source material (through dissolution) for deeper calcites or as groundwater-modifying precipitates that were left behind as Ca-HCO₃ solutions passed through the soil zone on their way toward the deeper fractures in the underlying rocks. In either case, the relations between surface calcites and deep calcites must be understood before any paleohydrologic inferences are drawn from calcite analyses.

III. RESULTS

A. Chemical Compositions of Calcites

Chemical analyses of coarser calcites in deep veins of the unsaturated zone (>15 m) are readily obtained (Figure 3A). In contrast, chemical analyses of the “cleanest” calcite separates from calcrites by INAA are limited to calcite-opal intergrowths, because calcite in the calcrites is very fine-grained and not readily separable. Nevertheless, analyses of calcite intergrown with opal show that for most trace elements (with the notable exception of U) opal acts as a simple diluent. This allows direct comparison of samples in which the calcite:opal ratios are similar (e.g., Figure 3B, in which all samples have calcite:opal ratios of about 1:1).

Figure 3 illustrates some of the principal differences in calcite from calcrites, compared with calcites from deeper veins. Over 30 INAA analyses of calcrites indicate that calcite + opal intergrowths in calcrites closest to the surface do not have Ce anomalies, but negative Ce anomalies may appear in calcrite samples within 3 m of the surface. With greater depth (example at 12 m in
Figure 3B) the fine-grained intergrowths of calcite + opal acquire prominent negative Ce and Eu anomalies that strongly resemble the rare-earth-element (REE) patterns of deeper vein calcites (Figure 3A). The formation of the Ce anomaly indicates segregation of tetravalent (oxidized) Ce from the other rare earths, perhaps by Ce accumulation in Mn-oxide minerals. These variations in REE with depth are accompanied by a significant decrease in Sr content of the calcite component, from ~800-2100 μg/g Sr in calcites of the calcretes to <350 μg/g Sr in calcites of the deeper fractures.

B. Stable Isotopes in Calcites

Figure 4 illustrates the range of calcite stable-isotope compositions in samples from the three trenches at Exile Hill and from the sand ramps at Busted Butte, as well as in the unsaturated-zone calcites from four drill cores. The data shown in panels 4A to 4D include isotopic analyses for dense calcretes, for rhizoliths separated from calcretes, for ooids and pellets separated from calcretes, and for calcite at the bottom of the B soil horizon just above the calcrete in Trench 14c. Panel 4E compares the fields for these data with data points from deeper, coarse, euhedral calcites in unsaturated fractures. Within each panel of figure 4 a line is plotted representing the general trend of carbon and oxygen isotopic variations in pedogenic carbonates as a function of elevation, reflecting the present botanic environments in the Great Basin. Model soil carbonates are shown for 1160 m (present vegetation at site elevation) and for 1950 m (elevation where site vegetation of past pluvial climates is now found). These model soil carbonates are for general reference only, as there is a broad scatter in the defining data.

The stable isotopes in calcites from the calcretes in Trenches 14 and 14c (Figure 4A,B) cluster around the Great Basin soil-carbonate isotopic trend. The most prominent outlier represents calcite not from the calcretes, but from the base of the B soil horizon immediately above the calcrete in Trench 14c. On the other side of Exile Hill, in Trench 5a (Figure 4C), there is considerably more scatter in the stable-isotope data. The rhizoliths separated from this locale have light O compositions compared to the host calcrites but the most pronounced outlier is seen in the calcites of pellets (P) that are lighter in C than all other samples and heavier in O than the most closely associated calcrite. The stable-isotope data from the sand ramps at Busted Butte (Figure 4D), for both rhizoliths and host calcretes, are dispersed toward heavier C values than the calcites at Exile Hill, with a pronounced outlier of homogeneous ooids (H) that are light in C. Figure 4E shows how the patterns of stable-isotope variation in deeper fracture calcites may either fall close to or trend toward the range of calcite compositions in calcretes, but are characterized by heavier C and in some cores (G-4) or deeper portions of some cores (G-2) by lighter O. The light-C samples described above are distinctly separate.

IV. DISCUSSION

Chemical data (over 70 INAA analyses) indicate that calcites forming in calcretes at the surface of Yucca Mountain have higher Sr and generally different chondrite-normalized REE patterns than calcites deposited in underlying fractures of the unsaturated zone. The lower Sr contents of calcites further along the flowpath are not necessarily to be expected (distribution coefficients for Sr in calcite formed from dilute aqueous solutions are <1). However, the abundance of fungal needle-fiber and filament calcite found in rhizoliths within the calcrete suggests that processes other than equilibrium, inorganic precipitation are important. The highest Sr/Ca ratios yet found in these locales are within the mineral matter of living roots (with Sr/Ca ratios of 0.006-0.020) where the C and Ca are held in part within amorphous residues but are mostly contained in the mineral whewellite (CaC₂O₄·H₂O), rather than in calcite. Recycling of these constituents through inorganic dissolution or fungal activity may lead to precipitation of calcites with lower Sr/Ca ratios in the ranges observed in the calcretes (Sr/Ca of calcite calcites = 0.002-0.005). Kinetic effects in precipitating these very fine-grained (<5 μm) calcites can be an important factor, for rapid crystallization of calcite will significantly enhance the incorporation of Sr over equilibrium Sr/Ca partitioning. Subsequent slow, near-equilibrium precipitation of coarse euhedral calcite in deeper fractures could lead to the lower Sr/Ca ratios (<0.001) observed in these crystals.

It has been suggested that the stable-isotope data indicate a genetic relationship between the calcites of surface calcretes and the calcites within underlying unsaturated-zone fractures. The nature of this relationship appears to vary....
Circled crosses represent model Yucca Mountain soil carbonate forming at present (under current vegetation at 1160 m elevation) and in the past when vegetation was similar to that now found at ~1950 m.
from core to core (Figure 4E): one core (G-2) has systematically lighter O and heavier C with depth; another (GU-3) contains calcites that deviate little from the surface calcretes; others (G-4; NRG-2) have widely varying δ13C but less variation in δ18O. The bulk of the calcrete data summarized in Figure 4E are consistent with these various relationships between calcretes and deeper calcites, but there are several outliers with light C compositions that appear to represent unique features within the calcretes. The largest deviations in stable-isotope composition within the soils appear to be in homogeneous ooids ("H" in Figure 4D), in pellets ("P" in Figure 4C), and in the analysis of carbonate from the lowest portion of a B soil horizon ("B" in Figure 4B). In these features or locales, δ13C is as light as -8.8 to -10.5. Regional Basin and Range studies9 indicate that soil δ13C does become lighter with depth, but the lightest values only approach -9 at extreme elevations (2500 m); even under past pluvial conditions, the δ13C in soil carbonates of the localities considered here should have model values10 no lighter than -8. The anomalously light C of the homogeneous ooids, pellets, and B-horizon soils needs another explanation.

It is possible that the conditions that lead to anomalous light C values require processes other than enhanced soil respiration and complete dominance of C3 vegetation.9 These other processes could be related to the occurrence of the anomalous light-C values in locations at the very tops of the calcretes, where soil water is prone to accumulate. Kinetic isotopic effects in root-zone respiration, favoring lighter stable-isotope compositions, may be one factor.13 Another factor could be the influence of biogenic processes other than botanical. The occurrence of smectite along with calcite andopal as a cementing agent in the light-δ13C pellets in Trench 5a is an indication that these pellets formed in a locally unique environment. The characteristic oblate form of these pellets and their fabric, in which silt-sized constituents are cemented by calcite without concentric or radial structure (Figure 2C), suggest that these may be fecal pellets.14 although their authigenic calcite-opal-smectite mineralogy is a carbonate-enriched variant of local B-horizon soils that may not require organic processes for formation. Whether or not organic processes are involved, the restricted interval of light-C samples at the uppermost surfaces of the calcretes in Trench 14c, Trench 5a, and Busted Butte appears to represent a unique microenvironment.

V. CONCLUSIONS

Chemical, petrographic, and isotopic data are consistent with models suggesting that calcites in deep veins of the unsaturated zone at Yucca Mountain were precipitated from surface-derived waters.1,3,5 However, the data also indicate: that calcites at depth formed in a variety of environments, and from fluids significantly different from those that precipitate calcite in calcretes at the surface. Chemical and isotopic modification of calcite-precipitating fluids begins at the surface, locally under the influence of biologically-mediated environments (viz. roots and their decay products). Chemical characteristics of the deeper calcites are at least partially defined within the first few meters of fluid migration into the unsaturated zone. Possibly overprinted on this record of fluid change with depth, however, are potential kinetic effects, either abiogenic kinetic effects (e.g., enhanced incorporation of Sr into calcite with rapid evaporation-driven precipitation in calcretes) or biogenic kinetic effects leading to lighter isotopic compositions in zones where root growth is particularly concentrated.13 The complexity of various pathways of chemical and isotopic modification (incongruent dissolution of tuff detritus, whewellite formation within plant roots, fungal and perhaps bacterial cycling of whewellite into calcite, and subsequent calcite dissolution and reprecipitation) may be discernible in the chemical and isotopic data. The isotopic data in particular point to a unique low-δ13C microenvironment that is localized at the upper surfaces of the calcretes. This may be a special plane in the soil horizon, where infiltration ponds above the underlying carbonate "plug." If paleoenvironments are to be examined on the basis of the calcrete record, it is important to gain a better understanding of microenvironments such as this that contribute to calcrete formation.

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