9 M.Y. RECORD OF SOUTHERN NEVADA CLIMATE FROM YUCCA MOUNTAIN SECONDARY MINERALS

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I. INTRODUCTION

Yucca Mountain, Nevada, is presently the object of intense study as a potential permanent repository for the Nation's high-level radioactive wastes. The mountain consists of a thick sequence of volcanic tuffs within which the depth to water table ranges from 500 to 700 meters below the land surface. This thick unsaturated zone (UZ), which would host the projected repository, coupled with the present day arid to semi-arid climate, is considered a favorable attribute of the site. Evaluation of the site includes defining the relation between climate variability, as the input function or driver of site- and regional-scale ground-water flow, and the possible future transport and release of radionuclides to the accessible environment.

Secondary calcite and opal have been deposited in the UZ by meteoric waters that infiltrated through overlying soils and percolated through the tuffs. The oxygen isotopic composition ($\delta^{18}O$ values[a]) of these minerals reflect contemporaneous meteoric waters and the $\delta^{13}C$ values reflect soil organic matter, and hence the resident plant community, at the time of infiltration.[1] Recent U/Pb age determinations of opal in these occurrences,[2] coupled with the $\delta^{13}C$ values of associated calcite, allow broadbrush reconstructions of climate patterns during the past 9 M.y.

[a] Stable isotope compositions are reported as the per mil (‰) deviations of the samples from the International standards VPDB (for C) and VSMOW (for O). Calcite CO_2 was extracted by routine methods derived from McCrea[4] and $\delta^{13}C$ values measured by mass spectrometry at the Isotope Geology Branch of the USGS in Denver. Calcite $\delta^{13}C$ values reported here are routinely reproducible to ±0.1‰.

MINERALIZATION SETTINGS

The UZ tuff sequence consists of two thick, generally welded tuffs, the Tiva Canyon and Topopah Spring Tuffs, separated by a thin interval of bedded, poorly welded tuffs of the Paintbrush Group. The welded tuffs are relatively impermeable but fracture readily, providing open pathways for percolation fluxes, whereas the bedded tuffs are much less fractured but are porous and permeable and support matrix flow of percolating waters. Most secondary mineralization in the UZ is found as drusy coatings on the footwalls of fractures or the floors of lithophysal cavities, although matrix cements of calcite and (or) opal occur locally within the bedded units.

Secondary mineralization sequences in the UZ may be sorted into early, middle, and late stages. A sparsely distributed early stage consists of silica phases (typically chalcedony with or without euhedral quartz druses) locally associated with sparry, but often corroded, calcite. Main stage mineralization contains blocky to thick-bladed calcite ± opal, frequently with dusty growth zones marked by abundant semi-opaque inclusions. Late stage calcite, again locally with opal, occurs as euhedral, clear, thin-bladed, spade- or fan-shaped crystals and as overgrowths on older calcite. Qualitatively, secondary mineral occurrences in the Tiva Canyon Tuff appear similar to those in the Topopah Spring Tuff, but are thinner, have lower calcite:silica ratios, and contain little early stage calcite.

CONTROLS ON UZ CALCITE $\delta^{13}C$ VALUES

The carbonate chemistry of UZ infiltration is characterized by the general reaction

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$$CaCO_3 + CO_2 + H_2O \longleftrightarrow 2HCO_3^- + Ca^{2+}, \qquad (1).$$

where the carbon component is more or less equally contributed by the oxidation of decaying plant matter within the soils and the dissolution of preexisting carbonate. Plant matter $\delta^{13}C$ values range from less than -30‰ to about -9‰.[3] Variability in the makeup of the resident plant assemblage will, therefore, cause large variations in the $\delta^{13}C$ of the bicarbonate that enters, and potentially mineralizes, the UZ.

Plants follow one of two photosynthetic pathways, designated as C3 and C4, in producing plant organic matter with $\delta^{13}C$ ranges of -27±5‰ and -13±4‰, respectively.[3] Plants following the C4 pathway evolved during the Cenozoic and can withstand high temperatures and drought better than C3 plants. Hot, dry lowlands favor C4 plants (largely grasses), whereas wetter and cooler uplands favor C3 plants.

Cerling[5], in modeling soil C isotope chemistry and pedogenic calcite formation, demonstrated that predominantly C3 plant assemblages result in pedogenic calcite with $\delta^{13}C$ less than -8‰ whereas predominantly C4 environments could result in calcite with $\delta^{13}C$ values as large as +3‰. Isotopic evidence of C4 plants was first recorded in the southwestern US between 6 and 7 Ma.[6] By inference, it may be concluded that all pedogenic and UZ calcite with $\delta^{13}C$ values greater than about -8‰ are younger than ~7 My.

Secondary calcite $\delta^{13}C$ values in the UZ range from nearly -10 to nearly +10‰ and generally decrease with time (Figs. 1 and 2). Within this range, virtually all values greater than +2‰ are from the early calcite stage[b], main stage calcite ranges from about -9 to +2‰, and late stage ranges from about -9 to -5‰.

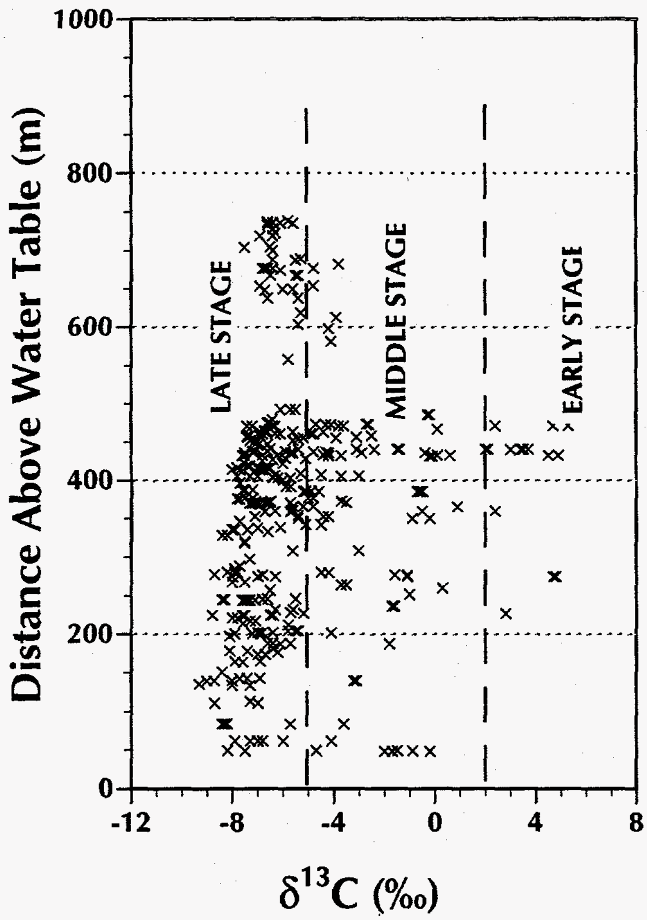

Figure 1. Unsaturated-zone secondary calcite $\delta^{13}C$ values from Yucca Mountain drill core occurrences. Ranges of Early, Middle and Late Stages are bounded by dashed lines.

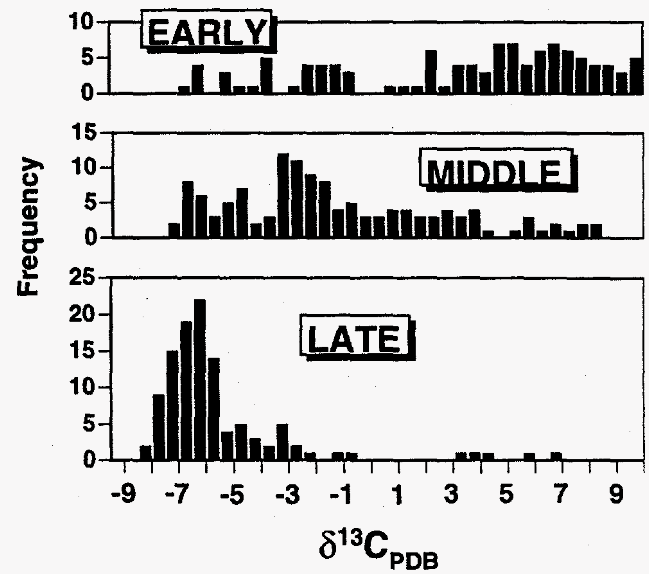

Figure 2. Histograms of the $\delta^{13}C$ values of microsamples of calcite from Exploratory Studies Facility occurrences. Early, Middle and Late refer to the relative paragenetic position of each calcite sample.

[b] According to soil geochemical models,[5] $\delta^{13}C$ values greater than +4‰ are incompatible with derivation from soil organic matter. Exchange with a reduced-carbon compound, such as methane (CH_4), is the most likely means of producing significant amounts of ^{13}C-enriched calcite. Because the carbonate-CH_4 carbon isotope fractionation is very large and positive, this would increase the carbonate $\delta^{13}C$ values. In nature this equilibration may happen organically, via methanogenic bacteria which metabolize CO_2 and produce CH_4 and water, or inorganically, by direct isotopic exchange between carbonate species and CH_4.

AGE VS. CALCITE $\delta^{13}C$ VARIATIONS

Three geochronometers have been applied to timing the formation of UZ secondary minerals: ^{14}C, $^{230}Th/U$, and U/Pb. Radiocarbon and $^{230}Th/U$ have useful ranges back to ~40 ka and ~400 ka, respectively, and were used in efforts to relate UZ hydrology to regional climate variations during the past several hundreds of thousands of years.[7] Recent U/Pb age determinations have greatly extended secondary mineral geochronology of the UZ.

Uranium-lead age determinations indicate that secondary calcite, opal, chalcedony, and quartz have been forming in the tuffs for at least the past 9 My.[2,7] Figure 3 is a plot of the U/Pb or, for younger occurrences, $^{230}Th/U$ ages of opal vs. the $\delta^{13}C$ values of associated calcite from samples collected from the Topopah Spring Tuff in the Exploratory Studies Facility underground workings. Occurrences where calcite and the dated material were physically coincident are plotted as points. Where calcite was bracketed by dated levels within an occurrence, the approximate age of the calcite was interpolated and plotted as a point with two arrows. Where the calcite preceded dated material, which therefore provided only a minimum calcite age, the calcite was plotted at that age with an arrow extending to the right on the plot.

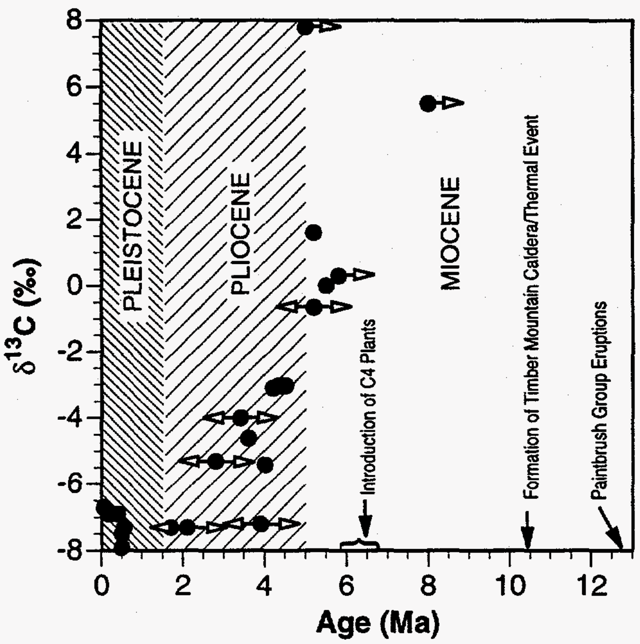

Figure 3. Secondary calcite $\delta^{13}C$ values plotted against ages (My) determined by U/Pb of $^{230}Th/U$ techniques[2,7]. Data from calcite samples bracketed by dated material are marked by double arrows and calcite samples underlying dated material (i.e., having a minimum age) are marked by single arrows to the right.

Secondary calcite of Pleistocene age (0 to 1.6 Ma on figure 3) has $\delta^{13}C$ values that range from -4.5 to -7.5‰ and which are similar to the values of late stage calcite. Figure 3 shows that between 2 and 4 Ma, $\delta^{13}C$ values begin to increase, and by 5 to 6 Ma, have risen to values of 0 to +2‰. Preliminary $\delta^{13}C$ values from an occurrence within the Tiva Canyon Tuff whose depositional geochronology is reported by Neymark et al.[2] (their Fig. 3a in this volume) bracket this shift from late to middle stage $\delta^{13}C$ values more precisely, at between 3.0 and 3.5 Ma. The three oldest calcite occurrences, with minimum ages of approximately 5, 8, and 9 Ma, have $\delta^{13}C$ values between 6 and 8‰, in accord with the early stage of mineralization.

COMPARISON WITH OTHER REGIONAL CLIMATE RECORDS

Soil calcite $\delta^{13}C$ values decrease with increasing elevation in southern Nevada.[8] Based on this relation, Pleistocene climates at Yucca Mountain have ranged between a modern southern Nevada microclimate found at an elevation of around 1400m, with a plant community comparable to the present day southern end of Yucca Crest (and $\delta^{13}C$ of about -4.5‰), and a modern southern Nevada microclimate found at elevations of around 1800 m, with a pinyon-juniper-sagebrush plant community like that found on Shoshone Mountain or the flanks of Rainier and Pahute Mesas (and $\delta^{13}C$ of about -7.5‰).

Thompson[9] inferred that western US climates probably were milder, wetter, and less seasonal prior to about 2 Ma from studies of paleosol carbonate,[10] Searles Lake salinity,[11] and Lake Tecopa water depths,[12] all indicating a significant shift in regional climate sometime prior to 1-2 Ma. Winograd at al.[13] also argued for a climate shift at about 1 Ma and suggested that it might be related to uplift of the Sierra Nevada mountains.

Main stage calcite $\delta^{13}C$ values of -5 to +2‰ support a significantly different climate prior to about 3 Ma, with more abundant, at times even dominant, C4 vegetation. Modern climates forming soil carbonate of -5 to +2‰ include prairie settings from Kansas to Minnesota and tropical savannas and wooded grasslands of Africa.[14] Such grasslands likely were widespread in southern Nevada during the middle and late Pliocene.

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