

Stable Isotopic Evidence for a Pedogenic Origin of Carbonates in Trench 14 near Yucca Mountain, Nevada

JAY QUADE AND THURE E. CERLING

Layered carbonate and silica encrust fault fractures exposed in Trench 14 near Yucca Mountain, site of the proposed high-level nuclear waste repository in southern Nevada. Comparison of the stable carbon and oxygen isotopic compositions of the fracture carbonates with those of modern soil carbonates in the area shows that the fracture carbonates are pedogenic in origin and that they likely formed in the presence of vegetation and rainfall typical of a glacial climate. Their isotopic composition differs markedly from that of carbonate associated with nearby springs. The regional water table therefore remained below the level of Trench 14 during the time that the carbonates and silica precipitated, a period probably covering parts of at least the last 300,000 years.

ONE OF THE CHIEF ASSUMPTIONS used to justify locating a high-level nuclear waste repository at Yucca Mountain is that the buried waste will remain well within the unsaturated zone for the next several hundreds of thousands of years, regardless of even large changes in water-table elevation in response to climate change. A serious challenge to the validity of this assumption was the discovery of a complex network of carbonate and silica fillings in the fractures associated with several faults bordering Yucca Mountain. The best known and the most controversial of these fracture fillings are located in Trench 14, which crosses the Bow Ridge fault (Fig. 1). The thick, well-layered, and well-indurated nature of the fillings caused immediate concern because of similarity in these respects to vein cements and travertines associated with springs (1) and because of the apparent Quaternary age of some of the carbonate (2). A spring origin would imply that there was a rise in the regional water table, presumably during glacial maxima, to at least the level of Trench 14. Trench 14 is about 150 m above the level of the proposed repository and 400 m above the water table. A return to glacial hydrologic conditions might then result in ground-water flooding of the repository and rapid transport of radionuclides to nearby discharge points, such as Trench 14.

There has been a substantial effort at

establishing the origin of the fracture cements in Trench 14 (1). An alternate hypothesis to a spring origin is that the carbonates and silica formed in soils in the vadose zone for hundreds of thousands of years (2). In this case, meteoric water infiltrating through the fractures deposited carbonate and silica as a normal part of desert soil formation.

To test these two hypotheses, we compared the carbon and oxygen isotopic data from Trench 14 to those in modern desert soils. We sampled soils in settings where the water table has remained tens to hundreds of meters below the surface during pedogenesis and therefore where ground water has played no role in carbonate formation. We took special care to sample soils younger than 7000 years old in order to establish the relation between the isotopic composition in soil carbonate and modern vegetation and rainfall (3). Pack-rat midden and pollen evidence shows that the distribution of vegetation has not greatly changed in the region during that span (4). We sampled soils displaying weak Stage I morphology (5), a degree of development consistent with a mid-to-late Holocene age. Five accelerator dates on thin carbonate coatings from three representative soils yielded ages between 3820 and 820 years (Table 1) (6).

The $\delta^{13}\text{C}$ content of modern soil carbonate varies substantially with elevation (Fig. 2) because of variations in (i) the isotopic composition of desert plants and (ii) the proportion of atmospheric CO_2 in the des-

ert soil atmosphere (3). Plants fractionate C along three differing metabolic pathways: C₃, C₄, and CAM. The C₃ plants, including conifers, mountain shrubs, and some grasses, make up virtually all of the biomass at higher elevations in the southern Great Basin. The $\delta^{13}\text{C}$ of these plants average -24 to -25 per mil at high-elevation sites, and coexisting soil carbonate has a $\delta^{13}\text{C}$ higher than in this biomass by 14 to 16 per mil (7). At lower elevations, C₄ and CAM (8) plants, as well as many C₃ shrubs and herbs, are present; here, C₄ plants are the most abundant, and they have an average $\delta^{13}\text{C}$ of -13 per mil. A larger proportion of atmospheric CO₂, with an average $\delta^{13}\text{C}$ of -6 per mil, is present deep in soils at low elevations because of lower plant respiration rates. This C reservoir further increases the $\delta^{13}\text{C}$ of soil CO₂—and therefore also of soil carbonate—that is derived from the mix of C₃ and C₄ plants. Holocene-age soil carbonates from each of the major vegetation zones therefore display a distinct $\delta^{13}\text{C}$ signature (Fig. 2). For example, the $\delta^{13}\text{C}$ of soil carbonates average -9 per mil in the ponderosa pine zone (>2400 m) and -7.4 ± 0.8 per mil (15 samples) in the pinyon-juniper-sage zone (1800 and 2300 m). Near sea level in Death Valley, the $\delta^{13}\text{C}$ of soil carbonates is -2 to $+2$ per mil, reflecting the contribution of C₃ creosote and C₄ desert holly shrubs, as well as some mixing of atmospheric CO₂ deep in the soil (3). The $\delta^{18}\text{O}$



Fig. 1. The fracture system filled with layered calcite and silica, exposed on the south wall, east end of Trench 14. The trench wall is about 3.5 m high.

Table 1. The ^{14}C dates (in ^{14}C years before present) by accelerator mass spectrometry on pedogenic carbonate from three (SM-2, 3, 4) soils in the Spring Mountains, 100 km south of Yucca Mountain (6). For each sample, we scraped 50 to 100 mg of material from clast undersides, taking care not to include any carbonate from the host clast or from older cements. Further details on soil sites, designated by these field numbers, is in (3).

Lab no.	Field no.	Age	Soil depth (cm)
AA-3697	SM-3(B)	1210 \pm 50	15
AA-3698	SM-2A	1900 \pm 60	Surface
AA-3699	SM-2B	3820 \pm 55	10 to 15
AA-3700	SM-2C	1785 \pm 65	30 to 40
AA-3701	SM-4	820 \pm 50	50 to 60

composition of soil carbonate also decreases with elevation (Fig. 3), irrespective of parent material, primarily because the $\delta^{18}\text{O}$ composition of rainfall also decreases with increasing elevation. Evaporation or differing penetration of meteoric water seasonally also may influence the $\delta^{18}\text{O}$ of pedogenic carbonates (3).

We sampled five Holocene-age soils in the vicinity of Trench 14. The local vegetation is dominated by C₃ shrubs such as black bush (*Coleogyne ramosissima*) and Nevada joint fir (*Ephedra nevadensis*); creosote (*Larrea divaricata*), burrobush (*Ambrosia dumosa*), and twin fruit (*Menodora spinescens*) are less abundant. Shadscale (*Atriplex confertifolia*), a C₄ shrub, is also common. All the herbs, and some of the grasses (mainly *Stipa* sp. and *Oryzopsis hymenoides*), are C₃ plants. Fluffgrass (*erioneuron pulchellum*), a C₄ grass, grows in the early summer. This mix of C₃ and C₄ plants, and moderate plant respiration rates, produces $\delta^{13}\text{C}$ values in soil carbonate of -4.2 to -7.1 per mil (14 samples) below a depth of 50 cm. The $\delta^{18}\text{O}$ (PDB) of the same carbonates nearly all fall between -7 and -10.6 per mil.

We analyzed 22 samples from most of the major veins exposed in Trench 14. The $\delta^{13}\text{C}$ of all but one of samples ranges from -6.3 to -7.7 per mil (average -7.0 ± 0.4 per mil, Fig. 2). The Trench 14 carbonates have low $\delta^{13}\text{C}$ values compared to those in nearby Holocene-age soil carbonate; these low values indicate that the Trench 14 carbonates did not form in equilibrium with the modern vegetation in the area. However, the C isotope data do overlap with values from modern soils about 750 m above the site, where cover is dominated by pinyon (*Pinus monophylla*), juniper (*Juniperus osteosperma*), and sagebrush (*Artemisia tridentata*). Samples from this vegetation zone yielded a $\delta^{13}\text{C}$ average of -7.4 ± 0.8 per mil. A single sample from Trench 14 yielded a result of -4.6 per mil, a value that is

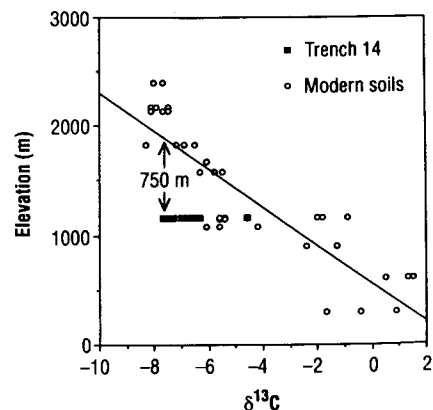


Fig. 2. The $\delta^{13}\text{C}$ (PDB) of pedogenic carbonate in modern soils developed on volcanic parent materials along elevation transects in the southern Great Basin. The linear regression (shown) for 39 soil analyses is: elevation (in meters) = $(554.4 \pm 103.8) - (174.98 \pm 18.3)z$, where z is the $\delta^{13}\text{C}$ (PDB) of soil carbonate. The $\delta^{13}\text{C}$ compositions of all but one sample from Trench 14 are lower than that for carbonate in Holocene-age soils in the vicinity but overlap with the $\delta^{13}\text{C}$ range of soil carbonate ~ 750 m higher on the transects.

observed in modern soils nearby. The other 21 samples from Trench 14 display a narrow range of $\delta^{18}\text{O}$ (PDB), between -10.5 and -11.8 per mil (average of -11.3 ± 0.3 , Fig. 3). Again, this is close to the values for modern soil carbonate in the pinyon-juniper-sage zone (average -11.5 ± 1.4 per mil) and is unlike nearby modern soils at -9.8 ± 1.2 per mil (9).

Evidence from fossil pack-rat middens indicates that vegetation zones were displaced about 1,000 m downward during the last full-glacial period (16,000 to 19,000 years ago) (4). Juniper, sagebrush, and pinyon then dominated the vegetation at Yucca Mountain. Our evidence indicates that the Trench 14 carbonates, if formed in soils, would have precipitated in equilibrium with this plant assemblage during the glacial maxima. The $\delta^{18}\text{O}$ of ground water in the region during glacial times was 1.5 to 2.0 per mil less than that of modern ground water (10, 11); this is close to the 1.5-per-mil average difference we observe between carbonates in Trench 14 and nearby modern soils.

A further test of a soil versus spring origin comes in comparing the C isotopic composition of coexisting carbonate and occluded organic matter. The difference should be 14 to 16 per mil in soils with relatively high respiration rates, including those found under pinyon-juniper-sage cover (7). The Trench 14 carbonates contain 0.12 to 0.18% organic C (Table 2). The average difference between carbonates and occluded organic matter was found to be 14.6 ± 0.2 per mil (3 samples), which supports a pe-

Table 2. The $\delta^{13}\text{C}$ (PDB) of coexisting carbonate and occluded organic (org.) matter from Trench 14. Roughly 30-g samples of carbonate were pyrolyzed at 650°C for 1 hour in covered crucibles, thus converting organic matter to pure carbon. Carbon was then concentrated by hydrolysis of the carbonate with 3N HCl.

Sample	Org. C (per-cent*)	$\delta^{13}\text{C}$ car-bonate (per mil)	$\delta^{13}\text{C}$ org. matter (per mil)	Differ-ence (per mil)
YM-14-8B	0.18	-6.3	-21.2	14.9
YM-14-11B	0.13	-7.0	-21.6	14.6
YM-14-12B	0.12	-7.3	-21.7	14.4

*By weight.

ogenic origin for the vein fillings in Trench 14. The spring carbonates we collected from veins at Ash Meadows (see below) did not contain sufficient occluded organic matter for analysis.

Uranium-trend dates and other geologic evidence (2, 12) suggest that carbonate in several fractures exposed in Trench 14 accumulated during the last 300,000 years, but that other fractures were filled earlier. As glacial periods have occurred about every 100,000 years (10), cementation events in the fractures could have occurred in one or more of many glacial periods during the latter half of the Pleistocene, and possibly earlier.

How do the isotope results on carbonates from Trench 14 compare to those expected for carbonates of unequivocal spring origin? To answer this question we considered two situations that account for the different types

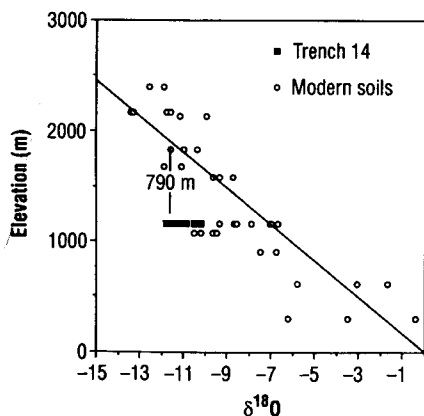


Fig. 3. The $\delta^{18}\text{O}$ (PDB) of pedogenic carbonate in modern soils developed on volcanic parent materials along elevation transects in the southern Great Basin. The linear regression (shown) for 39 soil analyses is: elevation (in meters) = $(-149.0 \pm 207.7) - (173.7 \pm 18.5)z$, where z is the $\delta^{18}\text{O}$ (PDB) of soil carbonate. On average, Trench 14 carbonates have $\delta^{18}\text{O}$ values consistent with soil carbonate now ~790 m above the site in the lower pinyon-juniper-sagebrush zone, the same setting indicated by the C isotopes in Trench 14.

of spring conditions found in the region: (i) spring discharge from the regional water table in fractured, transmissive bedrock; and (ii) cool spring discharge fed by local perched water.

Vein carbonate associated with springs that discharge from the regional water table have been analyzed in the Ash Meadows area south of Yucca Mountain (10, 13). Carbonates there and at Trench 14 fill major extensional fractures within a few meters of the surface, from which, in the case of Ash Meadows, ground water discharges directly from a major aquifer. Although different ground-water systems underlie the two areas, the age, temperature, and most aspects of the isotope chemistry of the two systems are alike. The $\delta^{18}\text{O}$ (SMOW) of ground water at Ash Meadows is nearly identical to that of the ground water underlying Trench 14, at -13 to -13.5 per mil (10, 11, 14). However, the $\delta^{13}\text{C}$ of dissolved inorganic carbon in Ash Meadows ground water is greater by 3 to 4 per mil in comparison to ground water under Trench 14, probably because of exchange with Paleozoic carbonate rocks along the flow path.

The $\delta^{18}\text{O}$ of spring carbonates from Devil's Hole, located near to Ash Meadows, is about -14.5 and -16.5 per mil (PDB) for interglacial and glacial climates, respectively (10) (Fig. 4). These values are appreciably lower than values for Trench 14 carbonates because of the low $\delta^{18}\text{O}$ ratios of the ground waters and high temperatures of the springs. The $\delta^{18}\text{O}$ values of carbonates in Trench 14 require temperatures of formation of $\leq 15^\circ\text{C}$ (15), if the inferred $\delta^{18}\text{O}$ range of ground water during the last 250,000 years (10, 11) is correct. Spring discharge from the regional aquifer at such low temperatures is highly unlikely at Trench 14 in view of the geologic setting. Temperatures in springs at Ash Meadows-Devil's Hole and in ground water under Trench 14 (14) generally exceed 28°C because of deep circulation of ground water, and these temperatures are unaffected by short-term (<300,000 year) climate fluctuations (10). Temperatures as low as 20°C are known from minor springs fed by deeply circulated water at Ash Meadows. But in these springs, water passes slowly to the surface through aquitards composed of fine-grained Pliocene basin-fill, probably after leakage from the more transmissive carbonate aquifer below. The slow circulation apparently causes spring water to partially or wholly equilibrate with near-surface temperatures (16). No fine-grained strata have been observed in the Trench 14 area. The transmissive nature of the fractured volcanic rocks and fault system at Trench 14 would have led to rapid ascent of ground water, as in the examples from Ash Meadows, where

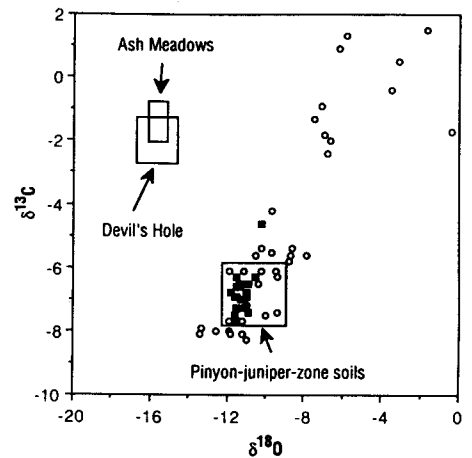


Fig. 4. The $\delta^{18}\text{O}$ (PDB) versus $\delta^{13}\text{C}$ (PDB) of carbonates from Holocene soils (○)/(■), Trench 14, and springs. In all, 21 of the 22 analyses from Trench 14 fall within the isotopic field for Holocene-age soil carbonate found in the pinyon-juniper-sagebrush zone on volcanic parent material. A single result lies in the field defined by modern soils in the vicinity. Spring carbonates from Ash Meadows (13) and Devil's Hole (10) plot completely outside the observed range for carbonates in modern soils and in Trench 14.

springs flowing from bedrock have temperatures $\geq 28^\circ\text{C}$ irrespective of discharge rate (16).

The $\delta^{13}\text{C}$ of spring carbonate at Ash Meadows and Devil's Hole ranges from -1.5 to -2.9 per mil (17) (Fig. 4). This carbonate precipitated in isotopic equilibrium with HCO_3^- in ground water that had a $\delta^{13}\text{C}$ of -4 to -5 per mil. The HCO_3^- in ground water under Yucca Mountain is much more variable, ranging between -11 and -2 per mil (14). If such a broad range of spring water compositions did produce over a long period the narrow range of $\delta^{13}\text{C}$ values observed in Trench 14 carbonates, it would be highly fortuitous.

The overriding difficulty with the second situation described above, spring discharge of local perched water, is that the hydrogeologic setting is generally wrong. Springs in perched water systems normally display a large upgradient catchment area and an aquitard unit that crops out at the point of discharge. Perched water in the region is typically found above and discharges from strata with a low permeability, such as zeolitized air-fall tuffs (16). In contrast, the rocks at Trench 14 are highly fractured ash-flow tuff and permeable alluvium; the nearest thin ash-fall aquitards are several hundred meters below Trench 14. However, the possibility of a perched water setting cannot be refuted by our isotopic results. The water in perched zones could have originated locally as precipitation and therefore had a similar oxygen isotopic composition to soil water. The HCO_3^- in perched

water may also be in equilibrium with locally derived plant CO₂, as HCO₃⁻ is in soil water.

Other evidence also supports a pedogenic origin for the Trench 14 carbonates. The morphology (2) and petrography of the carbonates and silica fillings are consistent with a soil origin, as is micromorphological, clay mineralogical, trace element (18), and isotope tracer (19) evidence. Oxygen isotopes from the silica cements indicate that the temperatures of formation were ~15°C, consistent with that in a pedogenic environment (2).

REFERENCES AND NOTES

1. P. S. Justus and N. K. Stablein, *Geotimes* 34, 14 (1989); papers presented at the DOE/NRC meeting on the calcite and opaline silica peer review, 25 to 27 May 1987, Las Vegas, NV; D. T. Vaniman, D. L. Bish, S. Chipera, *Los Alamos Natl. Lab. Rep. LA-11289-MS (UC-70)* (1988).
2. E. M. Taylor, *U.S. Geol. Surv. Bull.*, in press.
3. J. Quade, T. E. Cerling, J. R. Bowman, *Geol. Soc. Am. Bull.* 101, 464 (1989).
4. W. G. Spaulding, *U.S. Geol. Surv. Prof. Pap.* 1329 (1985). Spaulding mainly sampled middens from all around the adjacent Nevada Test Site and Amargosa Desert, within ~100 km of Trench 14, and from the Sheep Range near Las Vegas.
5. L. H. Gile, F. F. Peterson, R. B. Grossman, *Soil Sci.* 101, 347 (1966). Weak Stage I refers to pedogenic carbonate only as coatings on clast undersides.
6. J. Quade, *Quat. Res.* 26, 340 (1986); E. M. Taylor, thesis, University of Colorado, Boulder (1986); S. G. Wells, L. D. McFadden, J. C. Dohrenwend *Quat. Res.* 27, 130 (1987). Soil carbonate development is dependent on time and other factors, such as parent material, dust flux, and so forth. However, weak stage I morphology is observed to be associated with surfaces younger than late Pleistocene, irrespective of parent material. Carbonate coatings of our samples were discontinuous patches on clast undersides and were ≤1 mm in thickness. Clasts were occasionally encrusted with older cements, and these were avoided. The patterns displayed by stable C isotopes in these soils (3) indicate that there has been negligible detrital contamination or inheritance from dissolution of parent material. As such, these dates represent a composite age of all the layers of carbonate present. Because of the very young ages we obtained, it is unlikely that any pre-Holocene component to the carbonate is present.
7. T. E. Cerling, J. Quade, Y. Wang, J. R. Bowman, *Nature* 341, 138 (1989). Complete isotopic equilibrium between C species is obtained before the precipitation of soil carbonate, and this accounts for 10 to 11 per mil of the enrichment. Diffusion effects on soil CO₂ account for about 4.4 per mil further enrichment in the carbonates. Parent material has no influence on the outcome (3). All stable isotope analyses on carbonates are reported relative to PDB (Pec Dee Belemnite) using standard notation, where $\delta^{13}\text{C}(\text{PDB})$ or $\delta^{18}\text{O}(\text{PDB}) = \left(\frac{R_{\text{sample}}/R_{\text{standard}}}{1} - 1 \right) \times 1000$ and $R = \frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{standard}}}$ or $\frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}}$ respectively. The isotopic composition of water is reported relative to SMOW (standard mean ocean water).
3. CAM plants, which include cactus and most yucca, are present at lower elevations but don't exceed 10% of the biomass at any site. They average -18 per mil in $\delta^{13}\text{C}$.
9. We observed that the $\delta^{13}\text{C}$ (PDB) and the $\delta^{18}\text{O}$ (PDB) of carbonates appear to be constant below about 40-cm depth in modern soils at this general elevation (3). Above 40 cm, mixing with the atmospheric CO₂ causes progressive enrichment up to the soil surface. All the Trench 14 samples come from 0.9 to 3.4 m below the surface, and display no systematic trends with depth. All our modern soil carbonates that we used to fingerprint isotopically each of the vegetation zones come from 0.5 to 2.2 m depth.
10. I. J. Winograd, B. J. Szabo, T. B. Coplen, A. C. Riggs, *Science* 242, 1275 (1988).
11. H. C. Claassen, *Chem. Geol. (Isot. Geosci. Sect.)* 58, 311 (1986); L. Benson and H. Klieforth, in *Aspects of Climate Variability in the Pacific and Western Americas*, D. H. Peterson, Ed. (*Monogr.* 55, American Geophysical Union, Washington, DC, 1989), pp. 41-59.
12. J. N. Rosholt et al., *U.S. Geol. Surv. Open-File Rep.* 85-540 (1985). At least three episodes of faulting and subsequent fracture filling are evident from cross-cutting relations in the south wall of Trench 14 (2). The age of the last event is currently assessed at no older than 300,000 years ago and is likely around 150,000 years ago. This estimate is based on the estimated age of the Stage IV petrocalcic horizon [see (5) for this terminology] cut by the youngest fissures and the presence in one fissure of a basaltic ash thought to be 150,000 years old. The two earlier faulting episodes do not cut the Stage IV carbonates or deposits dated by U-trend methods at about 450,000 years ago. This method, however, remains experimental. The few published U-series dates on the veins are problematic because they contain excess ²³²Th, and therefore do not exhibit closed-system behavior. More dates, particularly by the U-series and ¹⁴C methods, are clearly warranted.
13. R. L. Hay, R. E. Pexton, T. T. Teague, T. K. Kyser, *Geol. Soc. Am. Bull.* 97, 1488 (1986).
14. L. V. Benson and P. W. McKinley, *U.S. Geol. Surv. Open-File Rep.* 85-484 (1985).
15. To calculate the maximum possible temperatures of carbonate formation, we used -11.5 per mil (SMOW) for ground water (interglacial water) and the most depleted carbonates from Trench 14, -11.5 per mil (PDB). This gives a temperature of 15.4°C. Waters showing a typical glacial-age composition [-13.5 per mil (SMOW)] give a temperature of 7.3°C.
16. I. J. Winograd and W. Thordarson, *U.S. Geol. Surv. Prof. Pap.* 712-C (1975).
17. P. D. Coplen and I. J. Winograd, in preparation.
18. D. T. Vaniman, D. L. Bish, S. Chipera, *Los Alamos Natl. Lab. Rep.* LA-11289-MS (UC-70) (1988).
19. D. R. Muhs, J. W. Whitney, R. R. Shroba, E. M. Taylor, C. A. Bush, *Proceedings of the International High-level Nuclear Waste Management Conference*, Las Vegas, NV, 8 to 12 April, (American Society of Civil Engineers, New York, 1990).
20. We thank M. Mifflin, I. Winograd, and L. Benson for their useful discussions and help, and R. J. Johnson for his logistical assistance. Analyses were performed at the University of Utah and Yale University. This work was supported primarily by the Nevada Nuclear Waste Project Office, and by National Science Foundation grant BNS-8703304.

25 June 1990; accepted 3 October 1990