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U and Sr Isotopes in Ground Water and Calcite, Yucca Mountain, Nevada: Evidence Against Upwelling Water

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Hydrogenic calcite and opaline silica deposits in fault zones at Yucca Mountain, Nevada, have created considerable public and scientific controversy because of the possible development of a high-level nuclear waste repository at this location. Strontium and uranium isotopic compositions of hydrogenic materials were used to test whether the veins could have formed by upwelling of deep-seated waters. The vein deposits are isotopically distinct from ground water in the two aquifers that underlie Yucca Mountain, indicating that the calcite could not have precipitated from ground water. The data are consistent with a surficial origin for the hydrogenic deposits.

YUCCA MOUNTAIN, NEVADA, HAS been selected for geologic evaluation as a potential site for a high-level nuclear waste repository (*1*). Faults and fractures cutting the volcanic rocks at Yucca Mountain are commonly filled with low-temperature secondary carbonates, oxides, and silicates (hydrogenic deposits) that precipitated from aqueous solutions. Because these deposits mark the pathways of past fluid migration, an understanding of their origins is critically important in evaluating the site and predicting whether flooding of the repository is likely in the future.

In the vicinity of Yucca Mountain, trenches have been excavated across faults as part of the investigation of Quaternary tectonic activity (*2*). Trench 14, excavated across the Bow Ridge fault on the eastern side of Yucca Mountain (Fig. 1), exposes a vein-like deposit of calcium carbonate and subordinate opaline silica (Fig. 2) much wider and more complex than mineralogically similar deposits in other trenches. The origin of these veins and those at Busted Butte (Fig. 1) has been the focus of considerable controversy (*3*).

Four main origins have been proposed for the hydrogenic deposits (*4*): (i) deposition associated with pedogenic (soil-forming) processes whereby descending meteoric waters interact with surficial materials and precipitate minerals along fractures and faults; (ii) deposition from cold springs due to movement of regional or perched ground water along faults; (iii) deposition from hot water (temperature ≫ 30°C) along faults; and (iv) deposition through seismic upwelling of hot or cold water along faults as a direct result of strain release during faulting. Proponents of models that would result in flooding of the repository predict doomsday scenarios (*3*).

Early field and mineralogic studies of deposits exposed at Trench 14 and other sites suggested that the hydrogenic deposits formed by processes related to pedogenesis (*5*). Stable isotope studies showed that $\delta^{18}O$ and $\delta^{13}C$ of the vein deposits have values and relations similar to those in the local soils (*6*). Furthermore, the ground waters currently beneath Yucca Mountain would have to be greatly cooled and perhaps isotopically modified to precipitate the observed calcites (7).

We describe Sr and U isotopic compositions of the deposits and of possible source waters. Neither Sr nor U fractionate isotopically during precipitation of hydrogenic deposits. Isotopic identity between hydrogenic deposits and possible source waters would be permissive evidence for a genetic link, whereas isotopic disparity would preclude any direct genetic relationship (*8, 9*).

Sr is an excellent tracer in the hydrologic cycle because it is relatively abundant in water and because its isotopic composition, reported as $^{87}Sr/^{86}Sr$, can be measured with great precision and accuracy (± 0.00005 or better). Ground water attains its Sr isotopic signal at recharge and along its flow path by dissolution of or exchange with minerals in the aquifer (*8*). Differences between the isotopic composition of the ground water and that of the bulk aquifer can result from preferential dissolution of minerals with different $^{87}Sr/^{86}Sr$ values. Commonly, in rocks that are old enough to have an accumulated radiogenic Sr from the decay of ^{87}Rb, a phase with a low Rb/Sr value (for example, plagioclase) is preferentially attacked, and water is less radiogenic (lower $^{87}Sr/^{86}Sr$ value) than its host rock (*9*). However, disequilibrium between solid and liquid during mineral precipitation does not occur (*10*), and the isotopic composition of a solid and of the water from which the solid precipitated will be identical.

The Sr isotopic compositions of ground waters in the Tertiary aquifer beneath Yucca Mountain and of vein carbonates at Trench 14 and Busted Butte do not overlap significantly (Fig. 3). The 15 samples of ground water from the Tertiary aquifer have a mean $^{87}Sr/^{86}Sr$ value of 0.71092 ± 0.00074 (standard deviation), and the 28 samples of vein carbonate have a mean $^{87}Sr/^{86}Sr$ value of 0.71241 ± 0.00022 A t test shows that the mean values are significantly different ($P < 0.05$). The two water samples from the Yucca Mountain area with the largest $^{87}Sr/$

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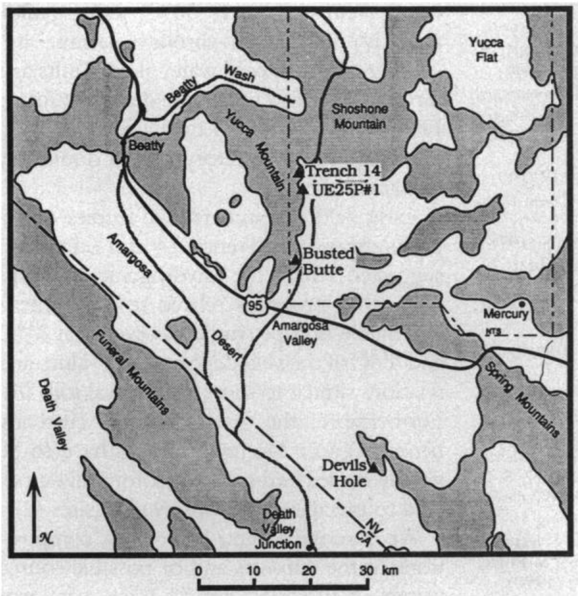

Fig. 1. Map showing the location of Trench 14, the Busted Butte sampling site, the Paleozoic aquifer drill hole, UE-25p#1, and Devils Hole.

^{86}Sr values were taken from drill holes in the unsaturated zone; the five samples with smaller $^{87}Sr/^{86}Sr$ values are from the saturated zone. The least radiogenic sample ($^{87}Sr/^{86}Sr = 0.70925$) was obtained from a well in Beatty Wash just north of Yucca Mountain (Fig. 1). A single bailed sample from deep within the Paleozoic aquifer (drill hole UE-25p#1, Fig. 1) has a significantly lower $^{87}Sr/^{86}Sr$ value than carbonate vein samples (Fig. 3). Thus, the Sr data clearly preclude precipitation of the carbonate deposits in Trench 14 and at Busted Butte from present-day ground water in the Tertiary aquifer beneath Yucca Mountain, and, if the bailed sample is representative of the dissolved Sr in the Paleozoic aquifer at Yucca Mountain, that source can also be excluded. However, more samples obtained by pumping from the Paleozoic aquifer are needed to confirm this conclusion on the basis of Sr data alone.

Ground water currently beneath Yucca Mountain is much younger than the bulk of the carbonate deposits at Trench 14. The analyzed ground waters have apparent ^{14}C ages of 4 to 30 thousand years (ka) (*11*), whereas the vertical veins in Trench 14 have U-series ages of 228 to >400 ka (*2, 12*). Possible long-term temporal isotopic variations in the ground water systems beneath Yucca Mountain cannot be constrained directly. However, a long-term isotopic record of a major flow system east of Yucca Mountain is contained in carbonate deposits at Devils Hole, an open fracture in Cambrian limestone at the discharge of the Ash Meadows flow system (*13, 14*). The Ash Meadows flow system extends east and north of the Nevada Test Site and is apparently separated from Yucca Mountain by a potentiometric high located near the eastern edge of Fig. 1 (*15*). It discharges at a spring line about 50 km south-southeast of Trench 14 and at an altitude approximately 430 m lower than Trench 14. Calcium carbonate was deposited continuously for nearly the last 600,000 years at Devils Hole. The presence of these deposits demonstrates the long-term stability of the flow systems in the region, and the successive layers of calcite preserve a long-term record of the isotopic composition of ground water. The $^{87}Sr/^{86}Sr$ values of six carbonate samples and present-day water vary beyond experimental error (0.71232 to 0.71282), but the isotopic composition has not changed greatly during the last 600,000 years (*16*). A similarly limited range in $^{87}Sr/^{86}Sr$ values can reasonably be inferred for ground water of the Tertiary aquifer in the Yucca Mountain area because both systems are within the same geologic province and any geologic changes affecting one would have affected the other as well. Thus, by analogy with the isotopic stability of the Ash Meadows flow system, we conclude that the ground water beneath Yucca Mountain for the past 600 ka is not likely to have had $^{87}Sr/^{86}Sr$ values high enough to have been a source for the Sr in the vertical vein deposits.

Fig. 2. Photograph of the south wall of Trench 14 showing the large vein deposits of calcite and opaline silica.

Might the ground water have acquired radiogenic Sr during ascent? The saturated part of test well WT-4 is entirely within the Calico Hills tuff, which has an average rock $^{87}Sr/^{86}Sr$ value of 0.7133 (*18*), but the water has a $^{87}Sr/^{86}Sr$ value of 0.71002 (*19*). The saturated part of test well WT-7 is entirely within the Topopah Springs Member of the Paintbrush Tuff, which has an average rock $^{87}Sr/^{86}Sr$ value of 0.7160 (*18*), but the water has $^{87}Sr/^{86}Sr$ value of 0.71027 (*19*). In neither case is the water as radiogenic as its host [which has been noted for other water–silicic rock pairs (*9*)], and, in both cases, even prolonged contact with a host rock that is much more radiogenic than the vein carbonates has not increased the $^{87}Sr/^{86}Sr$ value in the water enough to permit a genetic relation between the ground water and the hydrogenic deposits.

The similarity of $^{87}Sr/^{86}Sr$ values for vein carbonates and ground water in the Ash Meadows flow system with those of the carbonates at Trench 14 and Busted Butte is fortuitous because this flow system does not extend beneath Yucca Mountain. Furthermore, the system probably has not discharged at altitudes higher than the mouth of Devils Hole during the past several hundred thousand years, and water table elevations have not been more than 4 to 9 m higher in the past 100,000 years (*13*). The Sr isotope budget of the Ash Meadows system is a complex integration of values acquired in the recharge areas and along the flow paths (*17*). The mean $^{87}Sr/^{86}Sr$ value

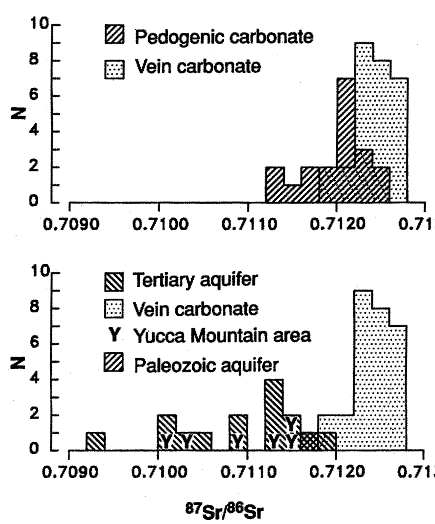

Fig. 3. Histograms showing the distribution of Sr isotopic compositions for the vein carbonates, pedogenic carbonates, and water from the Tertiary-Quaternary aquifer (*19*). Also shown are results for one water sample from the Paleozoic aquifer obtained from drill hole UE-25p#1.

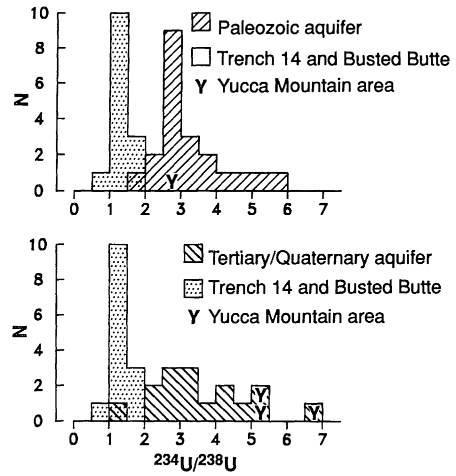

Fig. 4. Histograms showing the current isotopic composition of U in water from Tertiary/Quaternary and Paleozoic aquifers and that of hydrogenic carbonates from Trench 14 and Busted Butte at the time of crystallization. The carbonate samples include three vein samples, four calcrete samples (all from Trench 14), and seven rhyzoliths (from calcic horizons at Busted Butte) (*12, 13, 25*). Where two or more analyses exist for a single site, results have been averaged. In cases where there are significant disagreement between analyses (>0.1), the most recent results have been used.

($\pm 1\sigma$) for the larger springs at Ash Meadows, which account for 83% of the discharge, is 0.71250 ± 14. Three small springs at the southeastern end of the spring line carry Sr with much higher $^{87}Sr/^{86}Sr$ values (between 0.71703 and 0.71909), possibly reflecting a more local effect. Water entering the system through Paleozoic limestones in the Spring Mountains acquires Sr with a $^{87}Sr/^{86}Sr$ value between 0.7084 and 0.7088. Sr with higher $^{87}Sr/^{86}Sr$ values (up to 0.7155) is added to the system from far to the northeast in the vicinity of Pahranagat and Emigrant valleys. The integration of these disparate Sr isotope values to yield relatively uniform values centered at 0.71250 for the larger springs at Ash Meadows develops within the final 30 to 40 km of the flow system. Thus, ground water both in the Ash Meadows flow system ($^{87}Sr/^{86}Sr$ values of 0.7084 to 0.7191) and in the Tertiary aquifer in the vicinity of Yucca Mountain ($^{87}Sr/^{86}Sr$ values of 0.7093 to 0.7119) shows substantial regional isotopic variability. If carbonate veins, which are distributed over several tens of square kilometers, were deposited from either system at various localities along the flow paths, they would also show this regional variability in $^{87}Sr/^{86}Sr$, a variability not observed in the vein carbonates at Yucca Mountain and vicinity (Fig. 3).

The $^{87}Sr/^{86}Sr$ values in the vein and pedogenic carbonates are very similar, but the vein materials are, on the average, slightly more radiogenic (Fig. 3). The isotopic composition of the vein carbonate has been influenced by entrained silicates and, possibly, by the host rock. For example, the two least radiogenic vein carbonate samples at Trench 14 ($^{87}Sr/^{86}Sr$ values of 0.71190 and 0.71187) have acquired unradiogenic Sr from an adjacent lens of Sr-rich basaltic ash ($^{87}Sr/^{86}Sr$ values of 0.70888); other parts of the same vein yielded values of 0.71246 to 0.71261 (*19*). The volcanic wall rock for the veins contains Sr with higher $^{87}Sr/^{86}Sr$ values (0.7120 to 0.7202) than that of the vein carbonate (*19*). A small component of Sr derived from the host volcanic rocks by long-term weathering could account for the slight separation between vein and pedogenic carbonate. On a more regional scale, including a number of samples from Crater Flat, $^{87}Sr/^{86}Sr$ values ($\pm 1\sigma$) for the pedogenic carbonates and vein carbonates are indistinguishable at 0.71233 ± 28 (n = 37) and 0.71238 ± 26 (n = 39) (*20*). Pb isotopic data generally support the same conclusions as Sr and clearly show the effects of admixed volcanic detritus on the isotopic composition of the carbonate veins (*21*).

Disequilibrium between ^{234}U and its parent isotope ^{238}U can develop in ground water over time by alpha recoil and related processes (*22*). The degree of disequilibrium is expressed by the activity ratio $^{234}U/^{238}U$, which is generally precise to ±0.04 (1σ) and which at equilibrium conditions is unity.

The $^{234}U/^{238}U$ for ground water in southern Nevada is typically greater than 2.0 (that is, more than a 100% excess of ^{234}U) (*22*). The disequilibrium is even more pronounced in the vicinity of Yucca Mountain, where three samples from the Tertiary-Quaternary aquifer have $^{234}U/^{238}U$ values greater than 5.0, and one sample from the Paleozoic aquifer has a $^{234}U/^{238}U$ value of 2.71 ± 0.09 (Fig. 4). In contrast, vein carbonates and horizontal laminar carbonates were deposited by waters with a $^{234}U/^{238}U$ value of 1.6 or less (Fig. 4), and the four analyzed vein samples from Trench 14 had $^{234}U/^{238}U$ values of less than 1.4 at the time of deposition (*12*). Thus the regional aquifers and veins cannot be genetically related. The $^{234}U/^{238}U$ for soils of the Yucca Mountain area is less than 2.00 and generally less than 1.40 (*12, 23*). These values agree well with those observed for the carbonate veins and horizontal laminar carbonates (Fig. 4) and, therefore, suggest that the U in both types of carbonates was derived from water percolating through the overlying soils.

The initial activity ratio in 21 samples from Devils Hole representing ages of 60 to 300 ka ranged from 2.65 to 2.82 (*24*). If a similarly narrow range existed in ground water beneath Yucca Mountain, which is highly probable, the veins at Busted Butte and Trench 14 cannot have been precipitated from any of the regional aquifers.

$^{87}Sr/^{86}Sr$ and $^{234}U/^{238}U$ data preclude precipitation of vein and other carbonates exposed in Trench 14, Busted Butte, and Crater Flat from ascending waters like those currently in aquifers beneath Yucca Mountain. Isotopes in these systems do not fractionate during chemical reactions or phase changes, and, therefore, the large differences observed between isotopic compositions of ground water (or old hydrogenic deposits formed from ground water) and isotopic compositions of vein carbonate at Trench 14 and Busted Butte preclude a genetic relation between the two. This conclusion is further supported by the isotopic compositions for C and O in the vein carbonates and ground water samples (*6, 7*). Thus, all modes of origin that require bringing water from depth to form the vertical vein deposits can be ruled out.

The Sr, U, Pb, C, and O isotope systems all show a good correspondence between pedogenic and vein carbonates. Thus, carbonate veins, such as those exposed at Trench 14 and Busted Butte, must have formed by descending rather than ascending water as follows (*25*): Meteoric water dissolves or washes dust high in carbonate into permeable zones, such as fractures and porous soils. In addition, some soil CO_2 combines with Ca from the bedrock or soil; this too dissolves in the vadose water. Next, evaporation and transpiration remove water from the vadose zone, thereby increasing concentrations of dissolved species sufficiently that calcite and opaline silica precipitate. The force of crystallization pushes blocks apart on a microscopic scale such that over time, blocks are left separated from one another with pedogenically precipitated minerals forming bands that are concentric to the blocks or parallel to vein walls, as shown on Fig. 2.

REFERENCES AND NOTES

1. Series of articles by the Department of Energy, Nuclear Regulatory Commission, State of Nevada, and U.S. Geological Survey [*Geotimes* **34**, 17 (1989)].
2. W. C. Swadley, D. L. Hoover, J. N. Rosholt, *U.S. Geol. Surv. Open-File Rep. 84-788* (1984).
3. "A mountain of trouble," *New York Times Magazine*, 18 November 1990, p. 36; *Raleigh News and Observer*, 25 November 1990; "A mountain of nuclear trouble," *Boulder Daily Camera*, 25 November 1990, p. 1B; "Yucca mountain: Safe haven or future calamity," *Las Vegas Sun*, 23 November 1990, p. 10B.
4. G. N. Hanson, V. R. Baker, P. M. Bethke, P. J. Hudleston, G. R. Roquemore, "Report of the peer-review panel on the proposed program of studies of the calcite and opaline silica deposits in the Yucca Mountain area, Nevada" (Department of Energy, Las Vegas, NV, 1987).
5. E. M. Taylor and H. E. Huckins, *Geol. Soc. Am. Abstr. Programs* **18**, 418 (1986); D. T. Vaniman, D.

L. Bish, S. Chipera, *Los Alamos Nat. Lab. Rep. LA-11289-MS* (1988).
6. J. Quade and T. E. Cerling, *Science* **250**, 1549 (1990).
7. J. F. Whelan and J. S. Stuckless, *Proceedings of the American Nuclear Society International Meeting on High-Level Radioactive Waste Management*, Las Vegas, NV, 8 to 12 April 1990 (American Nuclear Society, La Grange Park, IL, 1990), p. 930; J. F. Whelan and J. S. Stuckless, unpublished manuscript.
8. J. S. Stuckless and Z. E. Peterman, unpublished manuscript; J. L. Banner, G. J. Wasserburg, P. F. Dobson, A. B. Carpenter, C. H. Moore, *Geochim. Cosmochim. Acta* **53**, 383 (1989); N. Clauer and Y. Tardy, *C. R. Acad. Sci. Ser. D* **273**, 2191 (1971); K. D. Collerson, W. J. Ullman, T. Torgersen, *Geology* **16**, 59 (1988); A. Starinsky, M. Bielski, A. Ecker, G. Steinitz, *Isot. Geosci.* **1**, 257 (1983).
9. R. H. McNutt, S. K. Frape, P. Fritz, M. G. Jones, I. M. MacDonald, *Geochim. Cosmochim. Acta* **54**, 205 (1990); P. C. Smalley, R. Blomqvist, A. Raheim, *Geology* **16**, 354 (1988).
10. P. J. Patchett, *Earth Planet. Sci. Lett.* **50**, 181 (1980).
11. L. V. Benson and P. W. McKinley, *U.S. Geol. Surv. Open-File Rep. 85-484* (1985).
12. D. R. Muhs *et al.*, unpublished manuscript; D. R. Muhs, unpublished data.
13. B. J. Szabo and I. J. Winograd, unpublished manuscript.
14. I. J. Winograd, B. J. Szabo, T. B. Coplen, A. C. Riggs, *Science* **242**, 1275 (1988).
15. I. J. Winograd and W. Thordarson, *U.S. Geol. Surv. Prof. Paper 712-C* (1975).
16. D. B. Marshall *et al.*, *Proceedings of the American Nuclear Society International Meeting on High-Level Radioactive Waste Management*, Las Vegas, NV, 8 to 12 April 1990 (American Nuclear Society, La Grange Park, IL, 1990), p. 921.
17. R. W. Spengler and Z. E. Peterman, *Proceedings of the American Nuclear Society Meeting on High-Level Radioactive Waste Management*, Las Vegas, NV, 28 April to 3 May 1991 (American Nuclear Society, La Grange Park, IL, 1991), p. 1416.
18. B. D. Marshall, Z. E. Peterman, J. S. Stuckless, K. Futa, S. A. Mahan, unpublished manuscript.
19. Z. E. Peterman, J. S. Stuckless, J. S. Downey, E. D. Gutentag, *Geol. Soc. Am. Abs. Programs* **22**, A295 (1990); U.S. Geol. Surv., unpublished data.
20. B. D. Marshall, Z. E. Peterman, K. Futa, J. S. Stuckless, *Proceedings American Nuclear Society International Meeting on High-Level Radioactive Waste Management*, Las Vegas, NV, 28 April to 3 May 1991 (American Nuclear Society, La Grange Park, IL, 1991), p. 1423.
21. R. E. Zartman and L. M. Kwak, unpublished manuscript.
22. J. K. Osmond and J. B. Cowart, in *Uranium Series Disequilibrium—Applications to Environmental Problems*, M. Ivanovich and R. S. Harmon, Eds. (Clarendon, Oxford, England, 1982), p. 202.
23. J. N. Rosholt *et al.*, *U.S. Geol. Surv. Open-File Rep. 85-540* (1985).
24. K. R. Ludwig, K. R. Simmons, B. J. Szabo, A. C. Riggs, I. J. Winograd, *Geol. Soc. Am. Abstr. Programs* **22**, A310 (1990).
25. Environmental Protection Agency, *U.S. Environ. Prot. Agency Rep. EMSL-LV-539-4* (1976); R. A. Zielinski and J. N. Rosholt, *U.S. Geol. Surv. J. Res.* **6**, 489 (1978); J. K. Osmond and J. B. Cowart, unpublished data from B. J. Szabo, personal communication.
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