^{238}U-^{234}U-^{230}Th ages of secondary deposits and evidence on the rate of recent radionuclide migration at the Nopal I natural analog

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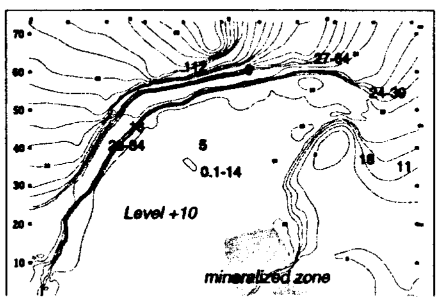
INTRODUCTION

The Nopal I uranium ore deposit of the Peña Blanca mining district, Chihuahua, Mexico (Figure 1), has proven useful as a natural analog for the proposed repository for high-level nuclear waste at Yucca Mountain, Nevada (e.g., Pearcy et al., 1994; CRWMS M&O, 2000a). Observations of uranium (U), thorium, radium, and protactinium distributions in the deposit and surrounding rocks may serve as an analog for release and migration of radionuclides from a repository. Tuffs and fractures containing iron-oxyhydroxide minerals in and near the ore body indicate that U has been mobilized out of the ore body, preferentially along fractures, during the last few hundred thousand years (Prikryl et al., 1997; Pickett & Murphy, 2001). Secondary deposits of caliche and opal around the deposit also indicate U migration. This work (i) documents the extent to which uranium has been mobilized, (ii) obtains ^{230}Th-^{234}U-^{238}U dates on these materials, (iii) calculates limits on release rates on the basis of secondary mineral mass and age information, and (iv) considers constraints these estimated release rates may place on performance assessment models for the proposed Yucca Mountain repository.

Figure 1. View from the northeast of the Nopal I uranium deposit. Dashed blue line is approximate outline of the zone of visible uranium ore on both Levels +00 m and +10 m. The pink arrow points to a road cut containing some of the caliche samples.

Figure 2. Caliche coating near-vertical fractures from area indicated on Figure 1.



SAMPLES

crystalline calcite:
- fills fractures and coats free surfaces with euhedral crystals up to 1 cm wide.

caliche:
- occurs along tuff fracture faces, from just below to two meters below the pre-mine surface (Figure 1).
- layers typically range from 1 to 10 mm thick and occur in masses up to 15 cm thick (Figure 2).
- XRD: calcite with and without quartz and sanidine.

opal:
- coats tuff or tuff breccia in limited portions of the Nopal I exposure.
- occasionally occurs with uranophane that precedes and postdates opal deposition.

URANIUM CONTENTS

crystalline calcite:
- 0.1 to 30 ppm
-Average 10 ppm, using perched water data from site, yields D(U/Ca) of 0.5, consistent with experimental coprecipitation data [Pickett et al., 2000; D(U/Ca) is the ratio of U/Ca in calcite to that in water]

caliche:

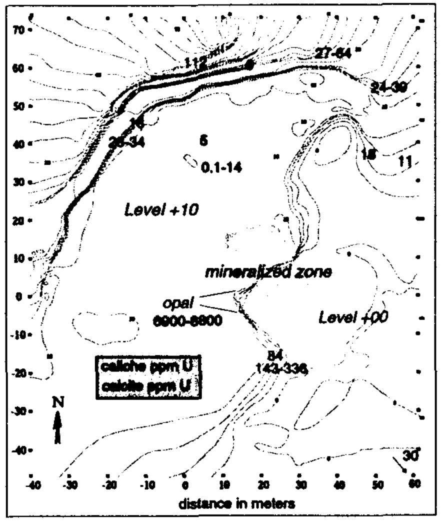


Figure 3. Map of Nopal I deposit with U concentrations indicated. Contour interval is 2 m.

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caliche:

- 24 to 335 ppm
- Calculated carbonate contents (firing) are 0.5 to 98 %, typically 60 to 80 %. From preliminary experiments, 12 to 100 % of U is leachable, typically 10 to 50 %. Estimated U concentrations in 1 M HNO_3-leachable solid range up to around 100 ppm.
- Highest concentrations are found in location that was downhill from the ore body prior to excavation (Figure 3).
- Caliches appear to be recorders of U migration from the ore body along near-surface fractures.

opal:

- 6900 to 8800 ppm in clear greenish samples.
- Opal with strong yellow color has 12 percent U; suggestive of included U minerals.

^{230}Th-^{234}U-^{238}U DATES

TIMS analyses by Larry Mack, University of Texas at Austin. Discussed here are "model ages" on total rock dissolutions, with no corrections to activity ratios. See Figures 4 and 5.

crystalline calcite:

- 213 ka and older.
- Due to their relatively low U and old ages, calcites will not be discussed further. Our interest in radionuclide migration focuses on the most recent events.

caliche:

- 18 to 136 ka, with one at secular equilibrium.
- New data and a previously reported isochron age (54 ka; Pearcy et al., 1994) are shown with U concentration in Figure 6. There appears to be an episode of deposition of high-U materials around 50 ka, supported by a previously measured 54 ka high-U opal age. The caliches in this episode are from the same road cut, but they are from distinct layers and/or fractures.

opal:

- One previously measured age at 54 ka.
- Others are at or near secular equilibrium.

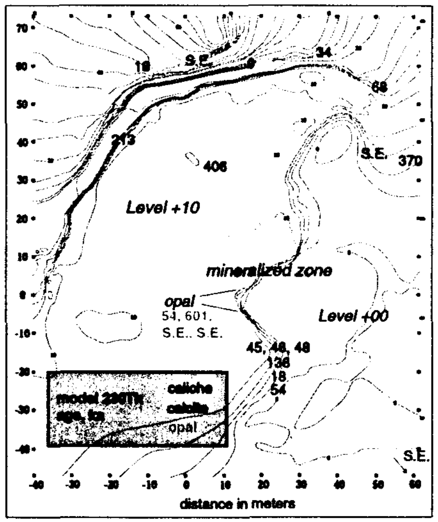

Figure 4. Map of Nopal I uranium deposit with ^{230}Th-^{234}U-^{238}U model ages in thousands of years. "S.E." indicates secular equilibrium within uncertainty.

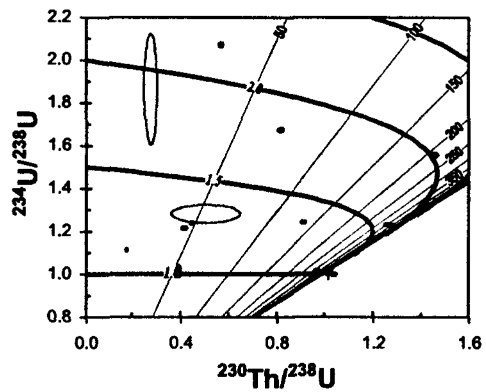

Figure 5. ^{230}Th-^{234}U-^{238}U evolution plot of Nopal I samples; values are activity ratios. Green = caliche; red = calcite; blue = opal. Black lines show ^{230}Th ages in ka. Blue curves are calculated initial $^{234}U/^{238}U$. Open symbols are previous alpha spectrometry data.

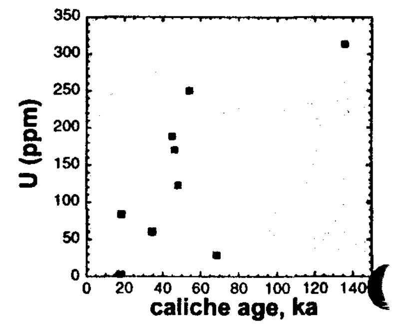

Figure 6. Caliche U concentrations through time.

Are the caliche ages real?

Initial $^{230}Th/^{232}Th$ can be high and variable in this high-U system, so ^{230}Th ages may need to be corrected. In addition, preliminary 1 M HNO_3 caliche leaching tests show that substantial amounts of U exist in more than one component.

The isotopic system may be tested through plots of total-dissolution and leaching analyses (e.g., Bischoff & Fitzpatrick, 1991; Luo & Ku, 1991; Kaufman, 1993). A leachate-total dissolution pair was analyzed for one of the caliches (Figure 7). The 0.1 M HNO_3 leachate contained 66 percent of the total-rock U, suggesting substantial contributions from at least two components. That the leachate and total rock have similar ages (Figure 7) while both have large proportions of the uranium budget lends confidence to the ages within a few thousand years. The significance of the "isochron" values is questionable.

It is considered unlikely that continuous deposition over many thousands of years, with the measured date merely reflecting an average, is important for the caliches. If long-term continuous deposition were important for the one leached sample, the two components would not be expected to yield similar ages. In addition, two of the samples falling in the ca. 50 ka period were from adjacent 6 mm-thick layers and yielded similar ages of 45 and 48 ka, inconsistent with long-term continuous deposition.

Leaching on other caliches is underway. In lieu of that information, the total-rock dates are interpreted as valid ages.

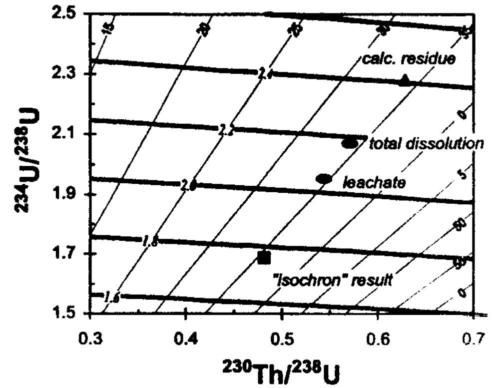

Figure 7. Activity ratios from a caliche from 40 m north of the ore body (64 ppm U). Black ^{230}Th age curves are labeled in ka. Blue curves = calculated initial $^{234}U/^{238}U$. Red error ellipses show measured total rock and leachate, yielding 34.3 and 34.6 ka. Blue square is a ^{230}Th-^{232}Th-^{234}U-^{238}U "isochron" fit through the two measured points (method of Ludwig & Titterington, 1[illegible]). Blue triangle is calculated for the leach residue using mass balance.

EPISODICITY OF RELEASE

An episode of elevated U release and migration is indicated by the apparent age clustering of high-U deposits at around 50 ka. Radionuclide release models for the proposed repository at Yucca Mountain do not include episodes of enhanced release (NRC, 2001; CRWMS M&O, 2000b). Rather, release is treated as continuous, with climate change addressed by stepwise changes in infiltration rates.

A lower limit on the rate of episodic U release at Nopal I can be calculated from the ca. 50 ka caliche deposition data. The following assumptions are made:

- 10,000 year episode duration (estimated from Figure 6)
- 100 ppm in caliche (all ca. 50 ka caliches in Figure 6 have > 100 ppm U)
- caliche volume of 1000 m^3 (10 cm-thick caliche covering 10,000 m^2; masses reach up to about 15 cm thick)

The calculated rate of U deposition is 30 g/y. This estimate is highly uncertain, because it depends on extrapolations of field and laboratory observations.

Because much more U is transported than is actually captured in the caliches, this deposition rate provides a lower limit on release rate. The degree to which release rate exceeds deposition rate should far exceed any uncertainty in the calculated deposition rate. An upper limit on the long-term U release rate for the site based on solubility-limited U concentration and constant, modern-day water flux is also 30 g/y (Murphy and Pearcy, 1992). Consistency between the independently estimated upper limit on the long-term release rate and lower limit on the episodic deposition rate lends credibility to the magnitude of these estimates. Furthermore, as noted above, that the U episodic release rate likely greatly exceeds the calculated deposition rate suggests that the episodic release rate is much greater than the long-term maximum estimate. Rapid episodic release could most simply be explained as resulting from greater water flux (compared to present) related to climate episodes. These rates can be used to evaluate rates used in performance assessments of the proposed repository.

DISCUSSION

1. Recent U migration is reflected in the U content of deposits of caliche, opal, and—to a lesser extent—calcite.

2. Caliche deposits record the most recent mobilization, within the past 100 ka, presumably under conditions generally similar to the present. Significant U moblization on this time scale is consistent with previous U-series studies (Prikryl et al., 1997; Pickett & Murphy, 2001).

3. The U-Th isotopic systematics in the caliches do not simply reflect carbonate-detritus mixing. Rather, U has been deposited in both carbonate and siliceous authigenic phases. Leaching tests or total-dissolution "isochrons" are needed because application of simple detritus corrections would be inappropriate, particularly in light of expected wide variations in detrital $^{230}Th/^{232}Th$.

4. Leachate results on one sample strongly suggest that the different authigenic components are similar in age. Until leaching analyses are completed, this observation lends confidence to interpretation of the U-Th model ages as accurate.

5. Deposition of high-U caliches and opal at around 50 ka suggests an episode of elevated U migration at rates greater than long-term estimates (which are based in part on present climate).

6. Because of analogous hydrologic and chemical conditions at Yucca Mountain, models of radionuclide release at the proposed repository based on variations in infiltration rate should consider the possibility of episodic enhancement. Current models employing stepwise changes in infiltration rate may address this possibility, but should be assessed in light of the natural analog information. A transient episode of enhanced release preceded and followed by lower release may affect dose differently than a long-term series of stepwise changes.

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