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U.S. Nuclear Regulatory Commission
ATTN: Dr. John W. Bradbury
Division of Waste Management
Two White Flint North, Mail Stop TD-13
Washington, DC 20555

Subject: Transmittal of the deliverable "Radiometric Dating of Minerals from the Nopal I Deposit–Journal Paper" (Intermediate Milestone 5708-871-720).

Dear Dr. Bradbury:

The enclosed paper is specified as IM 5708-871-720 in the CNWRA Operations Plans for the closeout of the Key Technical Issue (KTI) on Radionuclide Transport. The publication title for this paper is "Isotopic Constraints on Radionuclide Transport at Peña Blanca." The paper will be submitted for publication in the proceedings of the 7th European Commission Natural Analogue Working Group Meeting.

If you have any questions regarding this submittal, please contact me (210) 522-5540 or Dr. David Pickett (210) 522-5582

Sincerely,

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Isotopic Constraints on Radionuclide Transport at Peña Blanca

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ABSTRACT

^{238}U-series and U/Pb isotopic systematics have been interpreted at the Nopal I natural analog, Peña Blanca, Mexico, in terms of U mineral history and the nature and timing of U transport. The analog consists of a vertical, roughly cylindrical uranium deposit, hosted by fractured, silicic tuff, with U contained chiefly in uranyl phases. Three samples of uranophane, the most abundant uranyl phase in the deposit, yield ^{238}U/^{206}Pb and ^{235}U/^{207}Pb internal and external isochron ages of 3.4 and 3.2 Ma, respectively. These ages represent an episode of oxidation of uraninite. Activity data on uranium-series nuclides ^{230}Th, ^{234}U, and ^{238}U from rocks surrounding the deposit indicate a relatively recent, episodic history of U mobilization. ^{234}U and ^{230}Th excesses point to a multistage, and in some cases shifting, history dominated by early mobilization of U out of the primary uranium deposit and deposition outside, followed by episodic partial U depletion from rocks outside the deposit. The data indicate that these processes acted over the past few hundred thousand years to the present. Uranium transport in percolating, oxidizing meteoric waters is the preferred dominant process, consistent with isotopic data on present-day perched and seep waters collected at the site. The isotopic and chemical data reveal a history of (i) uraninite deposition several million years ago, (ii) deposition of uranyl silicates during a single period around 3 Ma, and (iii) complex episodic U mobilization and remobilization in the past few hundred thousand years. Because of the strong analogy between conditions at Peña Blanca and Yucca Mountain, the demonstrated timing, episodicity, and complexity of transport at Peña Blanca suggest that such conditions can be expected at Yucca Mountain and are likely to be important to radionuclide transport at the proposed repository.

INTRODUCTION

The natural analog at the Nopal I uranium deposit, Peña Blanca district, Chihuahua, Mexico, has been studied for years due to features that are remarkably analogous to the proposed US site for disposal of high-level nuclear waste at Yucca Mountain, Nevada (Murphy and Pearcy, 1992; Pearcy et al., 1994; Pearcy et al., 1995; Pickett et al., 1997). A summary of this work is included in an article in this volume by Murphy et al. This article presents a summary of uranium-series and U/Pb isotopic data, which have helped in interpreting the history of uranium transport at the site, and a discussion of implications for radionuclide transport at Yucca Mountain.

The rationales for studying Nopal I as a natural analog, the geologic setting, and studies of mineralogy, fracture geometry, transport, and geochemistry have been reported previously (Murphy and Pearcy, 1992; Pearcy et al., 1994; Pearcy et al., 1995; Murphy et al., 1997; Pickett et al., 1997). The isotopic data discussed here are reported in detail by Prikryl et al. (1997) and Pickett et al. (1997). The vertical, roughly cylindrical uranium deposit is characterized chiefly by U-bearing phases uranophane, soddyite, and schoepite. Previous studies (Pearcy et al., 1995; Prikryl et al., 1997) reported evidence that aqueous transport of U away from the deposit occurred chiefly along meso-scale fractures. The host rock at the level of investigation is fractured silicic tuff. Uranium-series data were obtained by alpha and gamma spectrometry on rock samples from both the uranium deposit and the surrounding tuff, and by mass spectrometry on water samples from the vicinity. Locations of U-series sampling traverses are shown in Figure 1; the sampled surfaces had been exposed during exploratory mining. In addition, U/Pb isotopic data were obtained by mass spectrometry on uranophane (Figure 1) in order to determine the timing of oxidation of uraninite, and the stability of this potentially solubility-limiting uranyl mineral in an oxidizing, unsaturated setting.

URANOPHANE U/Pb DATA

Three samples of uranophane-bearing rock were collected from Level +10 (numbers 494 and 102; Figure 1) and from the wall adjoining Level +00 (291), and uranophane-rich material was removed by scraping from fractures and voids. Uranophane from these textural settings grew late in the uraninite oxidation petrogenetic sequence (Pearcy et al., 1994). One sample (494) was checked by X-ray diffraction and treated by heavy liquid separation and mild leaching; five fractions of apparently varying uranophane purity were produced by hand-picking. Two other samples were subjected only to hand- picking for uranophane. U/Pb analysis was performed by L. Mack, University of Texas, by thermal-ionization mass spectrometry. All but one of the samples have U concentrations within 5 percent of the stoichiometric mass value of 56 percent [nominal formula $Ca(UO_2)_2Si_2O_7{\cdot}6H_2O$]; this agreement is excellent considering weighing uncertainties on these very small samples. The five sample 494 fractions define U/Pb isochrons (Figure 2) yielding ^{206}Pb-^{238}U and ^{207}Pb-^{235}U ages of 3.4 and 3.2 Ma, respectively. The other two samples also plot on the 494 isochrons.

The range of U/Pb ratios in the uranophane fractions indicates mixing between uranophane and other minerals due to the impurity of the separates. This is supported by the nature of the two samples plotting closest to the $^{238}U/^{204}Pb = 0$ and $^{235}U/^{204}Pb = 0$ axes in Figure 2: the low-U/Pb 494 separate received no hand-picking after gravity and leaching treatments, and sample 291 uranophane was contained in an amorphous mass with no visible coarse crystals, necessitating hand-picking by yellow color alone. Because of the prevalence of near-stoichiometric U contents, some contaminants must be Pb-rich in order to lower U/Pb ratios appreciably; candidates include Fe oxides and perhaps kaolinite. The effect of mixing obscures the true initial Pb isotope ratios of the uranophane and affects the slopes of the isochrons, from which ages are calculated. In the case of the 494 separates, the "isochron"

spread is due to mixing between uranophane with high Pb isotope and U/Pb ratios, and a low-U/Pb component with Pb isotope ratios close to the calculated initial values. The linearity of the plots suggests that the pure uranophane end-member varied little in its U/Pb and Pb isotope ratios. Because of the high U/Pb ratios, initial $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios *lower* than the calculated values would affect the slopes of the mixing lines negligibly. However, if uranophane initial Pb isotope ratios were *higher*, the true ages would be *less* than the calculated values of around 3 Ma. Two lines of evidence suggest this is not the case. First, sample 102 lies on the isochron; it would be fortuitous for this separate sample to do so given the possible ranges of initial Pb isotope and U/Pb ratios among different hand samples (291 lies too near the intercept to provide a strong constraint). Second, and more importantly, differences in Pb isotope ratios between uranophane and the other phases requires that contaminant phases be closed to Pb exchange during uranophane formation. The most Pb-rich phases were probably Fe oxides and oxyhydroxides, which were also initially formed during the oxidation of U phases (Pearcy et al., 1994; Prikryl et al., 1997). It is difficult to envision a major oxidizing event which would not cause Pb mobilization and Pb isotope homogenization at the hand-sample scale.

For these reasons, the isochron ages are interpreted to represent a single event of uranophane formation at around 3 Ma. Areal coverage is insufficient to conclude that all uranyl phases are this age, but consistency among three samples from a deposit only 30 m across is strongly suggestive. A similar age of 3.6±0.4 (2σ) Ma on the secondary phase jarosite from another U deposit in the district [P. Goodell, written communication] suggests that this may have been a regional event.) Pearcy et al. (1994) reported a chemical U/Pb age on precursor uraninite of 8±5 Ma, consistent with a probably younger age for uranophane generated by oxidation of uraninite.

URANIUM-SERIES DISEQUILIBRIUM DATA

Uranium-series disequilibrium data on samples from both inside and outside the uranium deposit are useful for discerning the history of U mobility subsequent to uranophane formation. Infilling materials along major fracture sets from traverses B and E (Figure 1) are dominated by goethite, amorphous Fe-oxyhydroxides, hematite, jarosite, kaolinite, and quartz, and contain no detectable U minerals (Prikryl et al., 1997). In the other traverses, bulk rocks were sampled consisting of generally fractured silicic tuff with an alteration assemblage dominated by kaolinite and Fe oxides. Uranium concentration data in horizontal traverses demonstrate U transport at least tens of meters from the deposit (Pickett et al., 1997); the vertical component of transport was not studied, but may have been greater. Mesofractures have accommodated more distal U transport. Microprobe data from one of the fractures (traverse B in Figure 1) demonstrate that U was incorporated in the fracture infilling minerals during their growth by adsorption and/or coprecipitation, accommodating U contents of up to thousands of ppm (Prikryl et al., 1997). It is also apparent that more highly fractured tuff accommodated more U transport than less fractured rock. Pearcy et al. (1995) showed data indicating that there is little transport of U from fractures into tuff; therefore, matrix diffusion has apparently been unimportant in the studied portion of the system.

Figure 3 shows profiles of uranium-series radionuclide activity ratios along the Level +10 traverses. Most fracture and matrix rocks from outside the deposit exhibit ^{230}Th-^{234}U-^{238}U disequilibrium relationships, i.e., activity ratios not equal to one. Inside the deposit, bulk rocks have equilibrium activity ratios and fracture materials show disequilibrium. The observation of uranium-series disequilibrium requires open system U transport within the last few hundred thousand years. $^{234}U/^{238}U$ ratios greater than unity (Figure 3a) indicate addition of water-mobilized U during this period. However, $^{230}Th/^{234}U$ ratios significantly greater than unity (Figure 3b) require a subsequent U removal event. A general model is shown in the $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ plot in Figure 4. Initial secular equilibrium is assumed, followed by (i) addition of U mobilized from the deposit (with a $^{234}U/^{238}U$ ratio of 2 for illustrative purposes), (ii) elapse of at least 20 ,000 years with evolution back toward secular equilibrium, and (iii) partial U removal with or without ^{234}U-^{238}U fractionation. Points in the "forbidden zone" require multiple stages of U mobilization (Osmond and Ivanovich, 1992; Scott et al., 1992). Samples plotting near or above the upper bound of this zone can be explained without resorting to later U depletion. Initial U addition is likely to have occurred in a more complex, rather than single-event, manner, requiring longer times than shown (Scott et al., 1992).

The most notable activity ratio trends with distance (Figure 3) are decreasing $^{234}U/^{238}U$ (traverses B and E) and increasing $^{230}Th/^{238}U$ (E). The simplest explanations for these trends are that (i) there has been multistage and differential U deposition along the fractures (e.g., less frequent and older U deposition at greater distance), and (ii) greater fractional U depletion is possible in lower-U rocks. The general picture is one of wide spatial variation in the timing and episodicity of U transport.

Sequential extraction results on Fe oxide-rich fracture infillings reveal distinct histories for different phases/sites within the rocks (Pickett et al., 1997). Most notably, uranium-series distributions demonstrate that U sequestered in secondary phases - chiefly Fe oxides and oxyhydroxides - is incorporated in the minerals, through either coprecipitation or dissolution/reprecipitation. Crystalline Fe oxides contain a majority of the U budget of the rocks, and amorphous Fe phases and adsorbed U account for 10-20 percent each. Currently accessible surface sites do not contain a large proportion of the U budget.

U/Th isotopic data on unsaturated zone waters from Nopal I are consistent with the U transport model. Two waters collected from a perched water zone in 10 meter-deep BH-12 (Figure 1) have $^{234}U/^{238}U$ of 2.2, and seep waters collected in the adit 8 m below Level +10 gave values of 5.1 and 2.8. Transported U in the oxidizing unsaturated zone at Nopal I therefore has the high ^{234}U enrichments implied by the high ratios in rocks and fracture infillings outside the U deposit.

In summary, uranium-series data imply a complex, episodic history of U mobility, with periods of both U deposition and U removal over the last few hundred thousand years. Uranium transport in percolating, oxidizing, meteoric waters is the preferred dominant process, owing chiefly to the association between U mobilization and Fe oxide precipitation

resulting from oxidation of reduced Fe species such as pyrite (Pearcy et al., 1994; Prikryl et al., 1997). This regime is also consistent with the heterogeneity of transport histories over a small area and the isotopic data from present-day water. The multistage nature of transport implies shifts in geochemical and/or hydrologic conditions since the initial mobilization of U from the deposit. These shifts could be related to geologic (e.g., uplift) and/or climatologic changes (Pickett et al., 1997).

An event of possible significance in the late-stage history occurred at 54 ka; that age has been determined from ^{230}Th-^{234}U-^{238}U analyses of U-rich opal (B. Leslie, personal communication) and caliche (Pearcy et al., 1994) that precipitated on and adjacent to the uranium deposit. Although the nature of the event is unknown, it was clearly marked by water movement and U mobilization in a weathering environment. Because the initial U enrichment in the studied rocks from outside the deposit is constrained by U-series activity ratios to have occurred at least a few hundred thousand years ago, the 54 ka event may represent U removal from the altered tuffs and fracture assemblages.

SYNTHESIS

The isotopic and chemical data reveal a history of (i) uraninite deposition several million years ago, (ii) deposition of uranyl silicates during a single period around 3 Ma, and (iii) complex episodic U mobilization and remobilization persisting through the past few hundred thousand years. These isotopic data constrain interpretation of transport at Nopal I in three important ways. First, the uranophane age demonstrates the long-term stability of uranyl phases in limiting release of U. Second, the U-series data constrain the timing of U transport in the host rock. Finally, the U-series systematics reveal multiple episodes of U mobilization and remobilization. The episodicity of recent U transport is likely related to environmental factors affecting groundwater flux, with climate variation likely to have had a strong influence (Pickett et al., 1997).

Because of the strong analogy between conditions at Peña Blanca and Yucca Mountain, the demonstrated timing, episodicity, and complexity of transport at Peña Blanca suggest that such conditions can be expected at Yucca Mountain and are likely to be important to radionuclide transport at the proposed repository.

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Division of Waste Management. This paper is an independent product of the CNWRA and does not necessarily reflect the views or regulatory position of the NRC.

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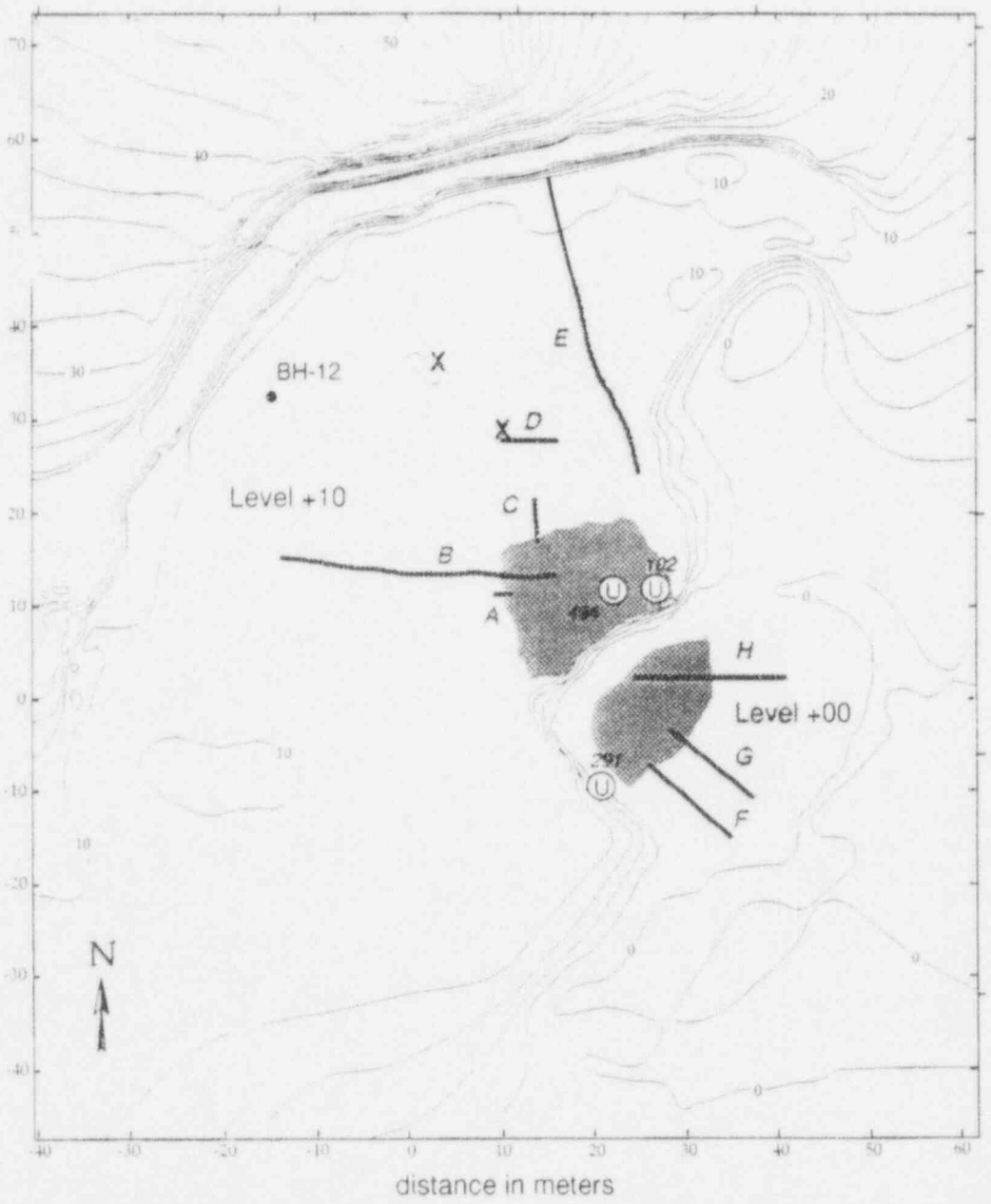
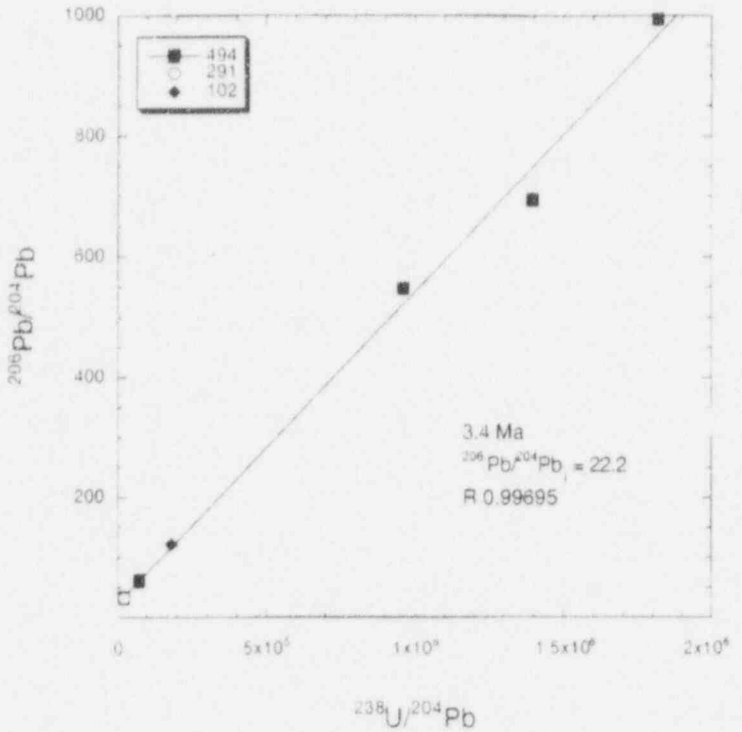


Figure 1 - Map of the Level +00 and Level +10 exposures at Nopal I, showing sampling traverses (heavy lines A-H). Water was collected at Borehole 12 and in the Level +00 adit at projected locations marked by X's. The circled U's denote numbered uranophane samples. Light gray denotes the area cleared of debris for detailed study, and the dark gray area is the zone of visible uranium mineralization, or uranium deposit. Contour interval is 2 m, referenced to zero at Level +00; axes (in meters) correspond to a NS-EW field grid.



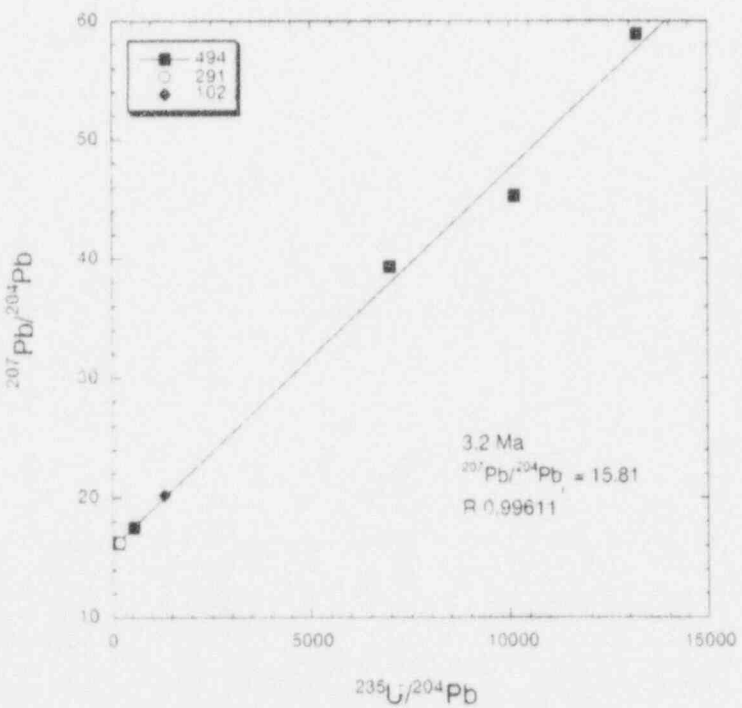


Figure 2 - ^{206}Pb-^{238}U and ^{207}Pb-^{235}U plots for Nopal I uranophane, with calculated ages and initial Pb isotope ratios based on linear fits to the five 494 data points.

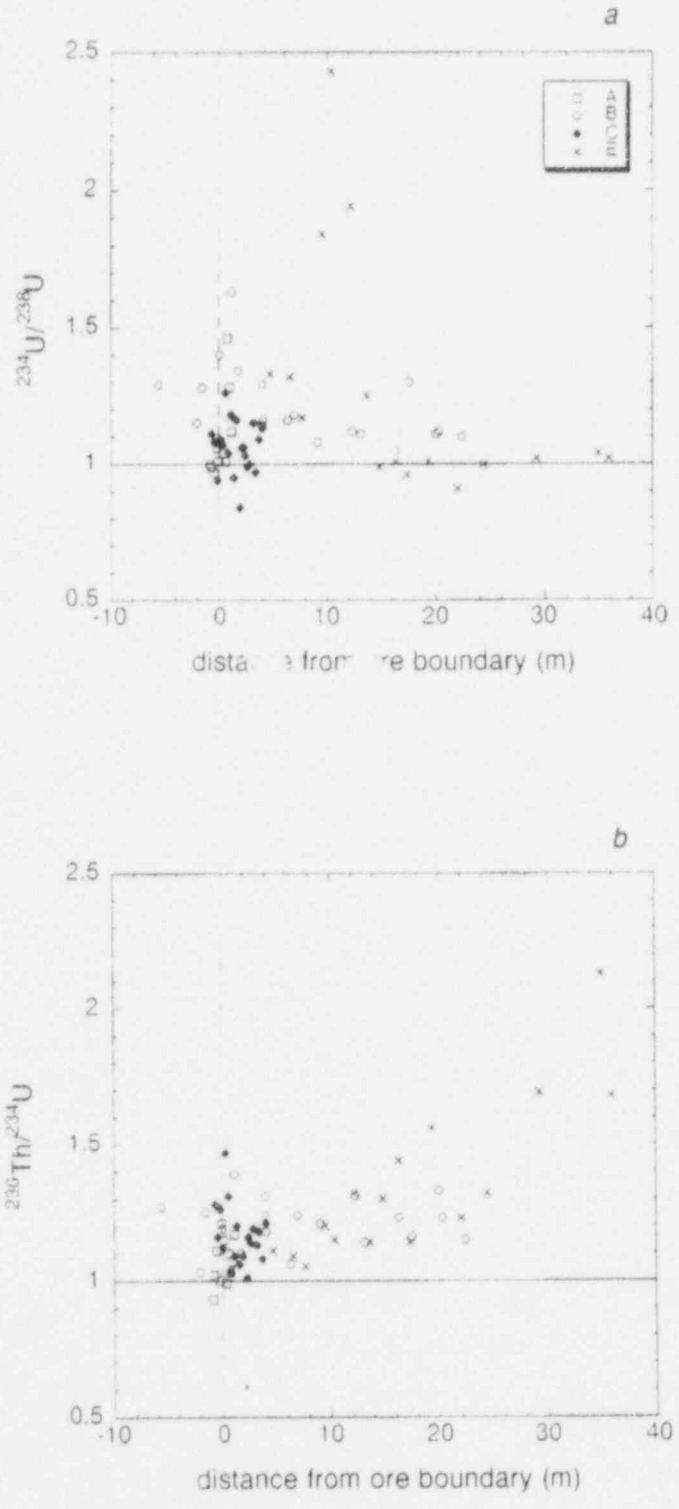


Figure 3 - Uranium-series activity ratios (a) $^{234}U/^{238}U$ and (b) $^{230}Th/^{234}U$ along the Level +10 traverses.

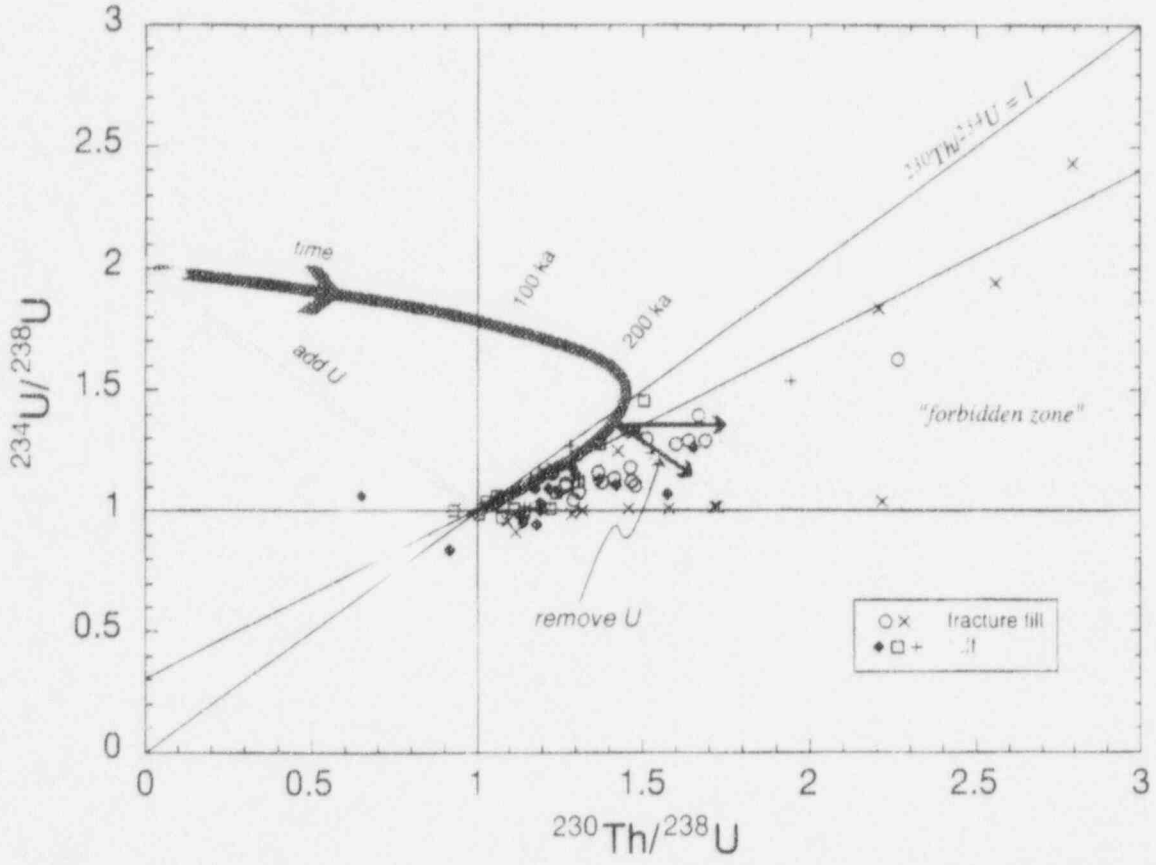


Figure 4 - $^{234}U/^{238}U$ versus $^{230}Th/^{238}U$ plot of Nopal I traverse bulk rock samples, with model for evolution. Symbols as in Figure 3, with the addition of crosses for traverse D. Note the different axis scales. The model assumes an initial rock at or near secular equilibrium (i.e., both ratios equal to one) to which high-$^{234}U/^{238}U$ U is added from an aqueous phase, followed by significant time evolution (note time labels on curve), and finally by partial U removal with or without U isotope fractionation. Not all rocks would have followed the same path, and U addition and removal likely occurred in a more continuous or episodic manner. Thus, the times involved could have been much longer than those shown. The "forbidden zone" reflects combinations of the two activity ratios which require multistage histories.