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U-Series Disequilibria in Soils, Peña Blanca Natural Analog, Chihuahua, Mexico.

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ABSTRACT- The Nopal I uranium deposit located in the Sierra Peña Blanca, Mexico. The deposit was mined in the early 1980s, and ore was stockpiled close by. This stockpile area was cleared and is now referred to as the Prior High Grade Stockpile (PHGS). Some of the high-grade boulders from the site rolled downhill when it was cleared in the 1990s. For this study soil samples were collected from the alluvium surrounding and underlying one of these boulders. A bulk sample of the boulder was also collected. Because the Prior High Grade Stockpile had no ore prior to the 1980s a maximum residence time for the boulder is about 25 years, this also means that the soil was at background as well. The purpose of this study is to characterize the transport of uranium series radionuclides from ore to the soil.

Transport is characterized by determining the activities of individual radionuclides and daughter to parent ratios. Isotopes of the uranium series decay chain detected include ^{210}Pb, ^{234}U, ^{230}Th, ^{226}Ra, ^{214}Pb, and ^{214}Bi. Peak areas for each isotope are determined using gamma-ray spectroscopy with a Canberra Ge (Li) detector and GENIE 2000 software.

The boulder sample is close to secular equilibrium when compared to the standard BL-5 (Beaver Lodge Uraninite from Canada). Results for the soils, however, indicate that some daughter/parent pairs are in secular disequilibrium. These daughter/parent (D/P) ratios include ^{230}Th/^{234}U, which is greater than unity, ^{226}Ra/^{230}Th, which is also greater than unity, and ^{210}Pb/^{214}Bi, which is less than unity. The gamma-ray spectrum for organic material lacks ^{230}Th peaks, but contains ^{234}U and ^{226}Ra, indicating that plants preferentially incorporate ^{226}Ra. Our results, combined with previous studies require multistage history of mobilization of the uranium series radionuclides. Earlier studies at the ore zone could limit the time span for mobilization only to a few thousand years. The contribution of this study is that the short residence time of the ore at the Prior High Grade Stockpile requires a time span for mobilization of 20-30 years.

I. INTRODUCTION

The Peña Blanca natural analog is located in the Sierra Peña Blanca, approximately 50 miles north of Chihuahua City, Mexico. The Peña Blanca site is considered a natural analog to the proposed Yucca Mountain nuclear waste repository because they share similar characteristics of structure, volcanic lithology, tectonic activity, and hydrologic regime.

One of the uranium-mineralized zones, the Nopal I deposit, is a brecciated zone that lies mostly in the Tertiary Nopal formation, which is silicic ash flow tuff. The uranium bearing mine is part of a large breccia pipe in Tertiary ignimbrites dated to be 44 Ma [1]. Previous studies focused on the brecciated zone and the surrounding area of the mine. Most samples that were analyzed for these studies were infillings from several fractures that make up an E-W fracture zone that runs from the middle of the breccia zone to the non-brecciated country rock (Fig.1).

The focus of this study is the mobility of radionuclides from high-grade ore boulders of the Prior High Grade Stockpile into local soils. The Prior High Grade Stockpile is located approximately 250 meters west of the Nopal 1 mine. High-grade boulders from the mine were stockpiled here in the 1980s, while the area was being mined and later moved to another location in the 1990s. The advantage of this is a short, well constrained residence period. Some of the boulders rolled down slope from the site, and one of these boulders is the focus of our study. In order to analyze the mobility of the radionuclides from this boulder into the soil, soil samples were collected under, around, and into the subsurface near the boulder.

The soil samples were then analyzed using gamma ray spectroscopy. This method was used because individual radionuclide peaks from the uranium decay series could be produced and relative activities determined. Then, these peaks could be used to form ratios using daughter/parent pairs to determine equilibrium or disequilibrium for that pair. By knowing the characteristics of each radionuclide and this ratio, a deficiency or excess could be determined for either the daughter or parent.

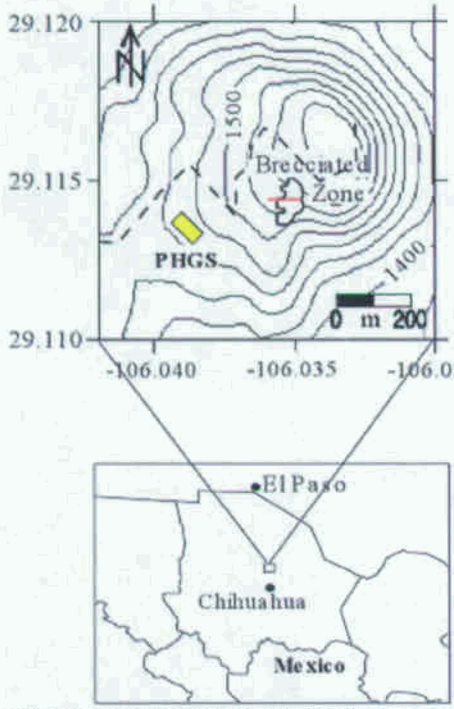

Fig. 1: Site map of the Nopal 1 Mine (brecciated zone) and PHGS. Red line represents the E-W fracture zone. Contour interval is 20 m.

II. PREVIOUS STUDIES IN RADIONUCLIDE MOBILITY AT NOPAL I

Radionuclide mobility at the Nopal 1 deposit has been studied in the past. Southwest Research Institute (SWRI) did some of the first work in the 1990s [2, 3, 4]. Their main goal was to describe the petrology of the brecciated zone and uranium source and to monitor migration of uranium radionuclides in the E-W fracture zone. In these studies, gamma-ray spectroscopy was employed. They discovered secular disequilibrium in the fracture infillings. They found ratios greater than unity when comparing ^{234}U/ ^{238}U, ^{230}Th/ ^{234}U, and ^{226}Ra/^{230}Th inside and outside the brecciated zone of the Nopal 1 deposit. They determined that there were excesses of ^{234}U, ^{230}Th, and ^{226}Ra in the fracture infillings outside the brecciated zone. They interpreted multistage mobilization that requires ^{230}Th>^{234}U>^{238}U. Based on the half-life of ^{234}U they placed mobilization of the radionuclides within the last million years.

Wong and others conducted a similar study in 1999 [5]. Again gamma-ray spectroscopy was employed, and the fracture infillings and ore were analyzed. They found secular disequilibrium between ^{230}Th and ^{234}U and also between ^{226}Ra and ^{230}Th similar to SWRI. Inside the brecciated zone, daughter/parent (D/P) ratios of ^{230}Th/ ^{234}U and ^{226}Ra/ ^{230}Th are greater than unity. The most pronounced mobility was in veins and fractures with oxidized alteration minerals, e.g. hematite. Contrary to the studies at SWRI, they thought that mobility had been within the last 8 ka based on the mobility of ^{226}Ra.

A recent study of the Nopal 1 deposit was conducted by Murrell and others in 2002 [6]. Thermal Ion Mass Spectrometry (TIMS) was used to analyze samples from the E-W fracture zone of the Nopal 1 deposit. Disequilibrium between ^{226}Ra / ^{230}Th was seen. This ratio was found to be greater than unity, similar to earlier studies, though they did not observe disequilibrium within ^{230}Th/^{234}U. The time line proposed for radionuclide mobility was within the last 50,000 years based on the half-lives of the radionuclides analyzed.

Leslie and others [7] conducted a study of radium activity of the Phacelia robusta, growing among the ore on the Prior High Grade Stockpile. Using photonegative paper they were able to see the tracks of alpha particles produced as the radionuclides in the plants cells decayed. The plant was powdered and analyzed. Samples contained large excesses of ^{226}Ra, indicating that the plants were fixing radium into their cellular structure.

III. FIELD METHODOLOGY

Soil samples were collected from the surface and subsurface, under and around a point source. The point source is a boulder that rolled downhill from where it was originally deposited sometime between the placement of the Prior High Grade Stockpile in the 1980s and the removal of the uranium ore boulders in the early 1990s.

The point source was identified in an initial field trip to the site and designated Potential Scientific Target (PST) #110. Field scintillometer readings from the boulder yielded approximately 100,000 counts per minute.

After the site around the boulder was roped off, an estimated drip line was outlined using string and anchored to the surface. The drip line is approximately where water fell from the boulder onto the soil surface during rain events. After the drip line was marked, the boulder was rolled about three meters up slope from the sample site. Three reference points were placed around the site with rebar and cement. These reference points made it possible for 'x' and 'y' coordinates to be measured once a grid was set up. A laser level was used to create a datum line above the surface so than a 'z' coordinate could be measured.

Prior to sampling, a surface gamma survey was conducted using a scintillometer. Fifty readings were taken around the sample site, with the head of the scintillometer facing down, to obtain an idea of how the boulder had affected the soil surface around it. Special care was taken to avoid readings close to where the boulder sat after being rolled away. The gamma survey is shown in Figure 2 and is described in the results section below. The gamma survey map was created using Surfer7 software.

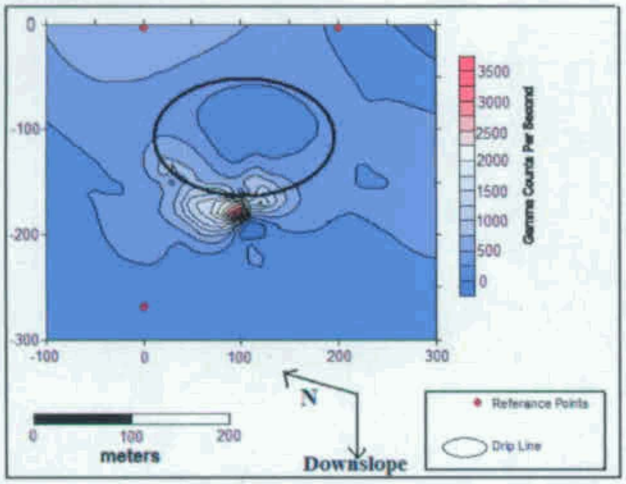

Fig. 2: Surface Radiometric survey of PST 110.

After the survey, seven 30 cm by 30 cm squares of rigid plastic cardboard were set on the surface to mark where samples would be taken (Fig. 3). Each square was labeled with a "B" for "block" and a number. This designator was put on each sample to indicate where it came from. Three squares were placed in a line down slope from the boulder and one where the boulder sat prior to being moved. The other three were placed to the sides of the boulder position.

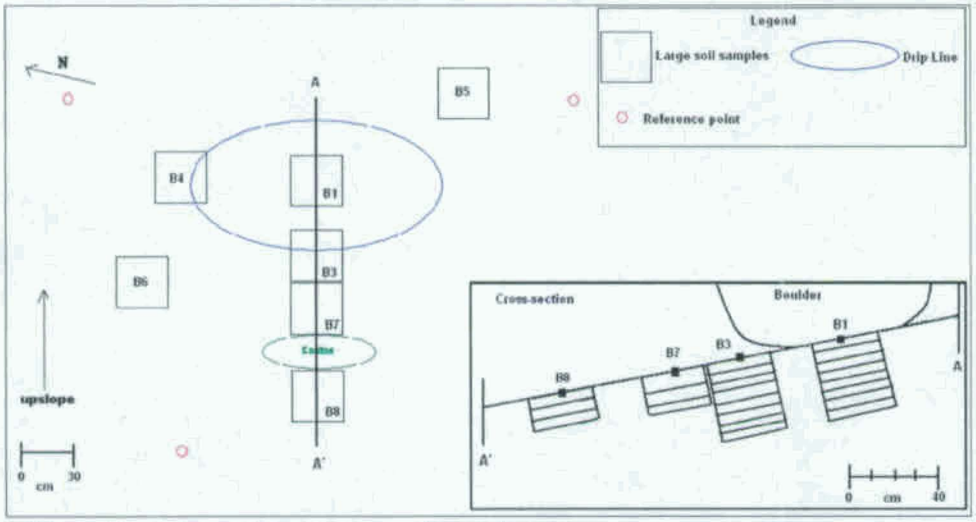

Fig. 3: Plan view and cross-section of sample area.

The samples were taken in horizontal layers into the subsurface. A metal frame was used to keep the soil in place while the samples were collected to prevent mixing. The cemented rebar reference points were used to assign 'x' and 'y' coordinates for each sample. A laser level was used to create a datum line so that a 'z' coordinates for each sample could be measured. The samples were put into 700ml plastic containers with a lid and given a DOE designator and a name with PST number, square number, and layer number (e.g. 110-B3-2). Each sample weighs approximately 1kg. This large amount of sample was needed to insure that each sample had a sufficient radionuclide content to be detectable. Altogether, 31 samples were collected.

IV. ANALYTICAL PROCEDURES

The samples were analyzed in the laboratory at the University of Texas at El Paso using gamma-ray spectroscopy. The instrument used was a Canberra lithium-drifted geranium (Ge (Li)) detector. Gamma-ray spectroscopy is an efficient method to analyze a large number of large samples in a short amount of time with minimum sample preparation. Each sample was counted in its original container for between three days to a week and a half depending on its activity.

Three types of samples were analyzed for the study: bulk soil samples, crushed boulder, and an organic fraction. Twelve of the 31 bulk soil samples have been counted: the first three layers from B1, B3, B7, and B4 (Fig. 3). A boulder sample was also counted for comparison. The boulder sample (PointE) was chipped off PST #110, crushed in the lab, and put into a container like that of the bulk soil samples to keep a consistent geometry. The organic fraction consists of roots handpicked from sample 110-B3-3 with tweezers and put into a similar container.

The spectra were produced and analyzed with GENIE 2000 software. The software was used to generate peak areas or relative activities for each isotope in the sample and calculate the error for each peak. These isotope peaks then were turned into daughter/ parent (D/P) ratios of the uranium decay chain.

In order to determine if the D/P pairs for the samples were in equilibrium or disequilibrium, a standard, BL-5, was used for comparison. BL-5 is uraninite from the Beaver Lodge deposit, obtained from Canada Centre for Mines and Technology and certified to be in secular equilibrium. BL-5 was cast in a resin disk by Wong in 1995 and used in that form for this study. BL-5 was counted in the gamma-ray detector in the same fashion as the soil and boulder samples and produced the same peaks. D/P ratios were calculated for BL-5 and all samples were normalized to BL-5.

Before the data were normalized, a self-attenuation correction was completed. The National Institute of Standards and Technology (NIST) SRN 4275c standard was used to perform the attenuation correction. The standard was placed on top of three bulk samples-110-B3-1, 110-B1-3, and 110-B7-3, and on top of an empty container. 4275c was also counted on top of BL-5, an empty resin disk, and the boulder sample as well. Each was counted for five days, and twelve peaks were used for analysis. The following algorithm was used to produce the attenuation curve and for interpolation for all unknowns [8].

$$\mathbf{A/O=Ln\ (T/I)/(T/I)-1}$$

I= unattenuated counts per second (empty container)
T=attenuation counts per second (full sample container)
A/O=attenuation correction as dependent on energy (keV)

A graph was generated with A/O on the y-axis and energy (keV) on the x-axis. The coordinates were exported into SigmaPlot 2000, and a polynomial regression was done to fit a line to the data. The program produces the equation, and interpolation can be completed for all unknowns. The A/O for each of the unknown's energies was divided through the peaks areas for every bulk sample.

V. RESULTS

Figure 2 shows the result of the field gamma survey. This map shows an area of high counts where a large concentration of radionuclides resides in the soil, coincident with the drip line of the boulder. Dripping moisture, therefore, is probably the main cause of mobilization of the radionuclides via mechanical and chemical weathering. A few lobes of intensity surround this hot spot, indicating other surface transport processes, such as wind, but it is noteworthy that the radioactivity drops off over a very short distance away from the boulder. Nuclide transport occurs only a limited distance from the place of origin, i.e. the boulder. The field gamma survey records only total intensities of radionuclides, while the gamma counting done in the lab yields activities of the individual radionuclides (Figs. 4-7). For these figures, the samples are normalized to BL-5, as discussed above. Non-unity ratios imply secular disequilibrium.

Figure 4 shows that ^{214}Pb/ ^{226}Ra and ^{214}Bi/^{214}Pb are in secular equilibrium. ^{214}Bi and ^{214}Pb have half-lives of 27 min. and 20 min., respectively, and therefore these ratios should be in secular equilibrium given our counting protocols. The ratios for these isotopes were used as a control to monitor the precisions and accuracy of the isotope pairs that did exhibit disequilibrium. Figures 5 through 7 show the disequilibrium daughter/parent pairs. Values greater than unity were observed for most samples for ^{230}Th/ ^{234}U and ^{226}Ra/^{230}Th. The disequilibrium for the pair ^{230}Th/ ^{234}U indicates a deficiency of ^{234}U. The disequilibrium between ^{226}Ra/^{230}Th indicates an excess of ^{226}Ra. The last pair that was found to be in disequilibrium was the ^{210}Pb/ ^{214}Bi, which exhibits a ^{210}Pb deficiency.

Figures 5 through 7 show both lateral and vertical trends for the soil samples. In the disequilibrium pair ^{230}Th/ ^{234}U (Fig. 5) there is a similar trend for samples in B1, B3, and B4: the deepest layers analyzed thus far of B1, B3, and B4 (i.e. 110-B1-3, 110-B3-3, and 110-B4-3) are the furthest from equilibrium. The first two layers of B1 are close to equilibrium (110-B1-1, 2), along with the boulder sample (PointE), while the first two layers on B3 and B4 show some disequilibrium (110-B3-1, 2; 110-B4-1, 2). For B7, the samples in the vertical profile (110-B7-1, 2, 3) show similar disequilibrium within error. These trends may be caused by the proximity of B1, B3, and B4 to the drip line, whereas B7 is farther a field (Fig. 3).

The plot of ^{226}Ra/^{230}Th exhibits another pattern (Fig.6). The trend is almost the opposite of Figure 5. The boulder is very close to equilibrium (PointE). The sample that is farthest from equilibrium is the topmost layer from B1 (110-B1-1), the directly underneath the boulder. The two layers below it (110-B1-2, 3) begin to approach the same degree of disequilibrium as the remainder of the samples. Samples from B3, B7, and B4 have similar patterns of disequilibrium. The ratio of ^{210}Pb/ ^{214}Bi (Fig.7) does not exhibit trends with respect to either depth or distance from the boulder.

The ^{226}Ra excesses were investigated in the organic material from one of the soil samples. The organics were counted for two weeks to obtain the best resolution. A large ^{226}Ra peak was observed, whereas a ^{230}Th peak was not observed at all. This is similar to the results obtained by Leslie et al. [4] from plants growing on the Prior High Grade Stockpile.

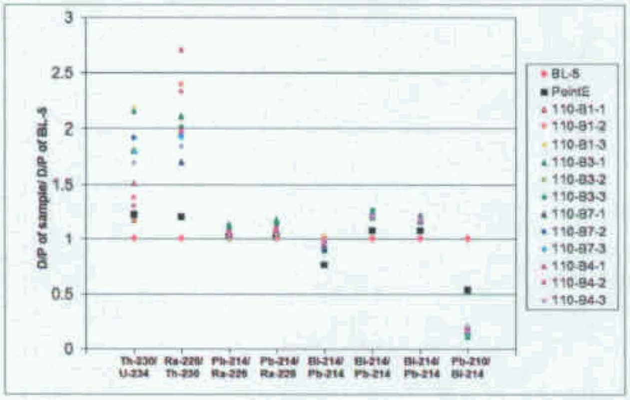

Fig. 4: All bulk samples normalized to BL-5 to identify secular equilibrium/disequilibrium. Color-coding is as follows: B1 samples are in oranges, B3 samples are in greens, B7 samples are in blues, and B4 samples are in purples. Samples for each block are listed in order of increasing depth.

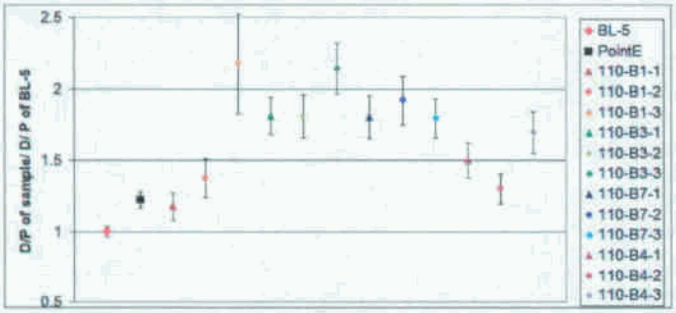

Fig. 5: Th^{230}/U^{234} for samples from the Prior High Grade Stockpile. Color-coding as in Fig. 4.

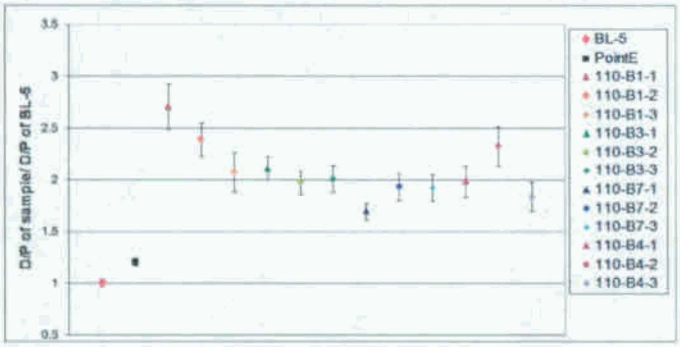

Fig. 6: Ra^{226}/Th^{230} for samples from the Prior High Grade Stockpile. Color-coding as in Fig. 4.

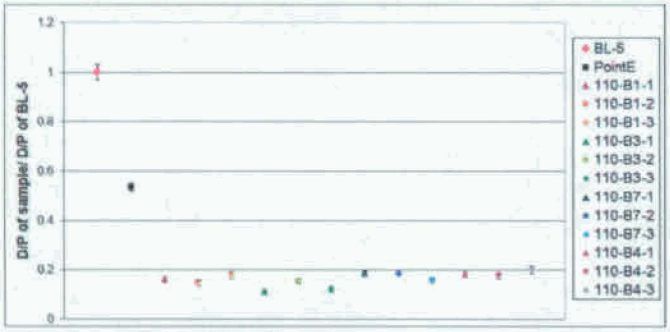

Fig. 7: Pb^{210}/Bi^{214} for samples from the Prior High Grade Stockpile. Color-coding as in Fig. 4.

VI. DISCUSSION

These results indicate that mechanical weathering is not the only mechanism by which radionuclides are being transported on the surface and subsurface in this region. The relative activities and disequilibrium shown in Figures 4 through 7 indicate that the radionuclides have traveled vertically as much as 5 to 6cm into the soil. Our hypothesis is that those layers are deeper than mechanical transport would penetrate, thus requiring chemical weathering, i.e. leaching. As water fell on the boulder, the radionuclides were leached and percolated into the soil. The maximum residence time of 25 years for this boulder indicates that mobilization was quick, but the results also show that the radionuclides have not traveled far from the original location of the boulder.

We conclude from this study that mobilization of the uranium radionuclides has happened within the last 20-30 years. This differs from previous studies by SWRI [2, 3, 4] that places mobilization sometime within the last 1 million years. Murrell et al. [6] placed mobilization within the last 50,000 years, and Wong et al. [5] that placed mobilization within the last 8,000 years. All of these studies used the half-lives of radionuclides to develop their time constraints. The importance of this study is that patterns of mobility similar to those of previous studies were found, but given the residence time of the boulder; the time scale could be narrowed down considerably.

The relative abundance of radionuclides in the soil indicates that multistage mobilization has occurred. The deficiencies of ^{234}U relative to ^{230}Th imply that ^{230}Th is being sorbed and retained in the soils, while ^{234}U is moving through. The excesses of ^{226}Ra can be accounted for by the fact that ^{226}Ra is soluble and may be fixed by plants as documented by Leslie et al. [7].

These observations have been documented in several other studies in the area [4]. The studies by Wong et al. and SWRI in which gamma ray counting was also used found similar results concerning the disequilibrium between ^{230}Th/^{234}U and ^{226}Ra/^{230}Th [2,3,4,5]. These studies both found deficiencies of ^{234}U and large excesses of ^{226}Ra in the large E-W fracture system. These results are very similar to what has been found in the soils of Prior High Grade Stockpile. Our results are comparable to previous studies because the boulders from the Prior High Grade Stockpile were once part of the in-situ uranium deposit; so it appears that the radionuclides are behaving the same, only in different location. Water transport has played a large role in mobilization in both systems.

The study done by Murrell and others [6] showed different results using Thermal Ion Mass Spectrometry (TIMS). Instead of finding excesses of ^{226}Ra, they found deficiencies and they also reported equilibrium between U and Th pairs. The discrepancies may be because they used a different technique to analyze their samples, or because of their sample preparation method.

Other D/P pairs that are out of equilibrium in our study and have not been documented by previous studies are ^{210}Pb and ^{214}Bi, with a deficiency of ^{210}Pb. ^{210}Pb was depleted in the soils, presumably because radon was escaping into the atmosphere and decaying into ^{210}Pb. This deficiency of ^{210}Pb has been seen in waters collected from local water wells (unpublished data). These observations are explained by the high mobility of ^{210}Pb, which has most likely been leached out of the soil by water. The ^{210}Pb deficiency may be a function of both water chemistry and radon loss to the atmosphere. The fact that ^{214}Pb is in equilibrium in the encapsulated samples shows that radon is now being retained in the sample containers.

VII. CONCLUSIONS

This study of the samples in this desert system indicates that environment plays a large role in how radionuclides are mobilized. The disequilibrium that exists between some of the D/P pairs shows that the soil is an open system in which radionuclides move freely. Multistage mobilization is prominent since radionuclides were found in soil and organic samples, and disequilibrium was found between D/P pairs. These conclusions agree with several previous studies. Water is a dominant factor in radionuclide mobilization because the most radioactive samples were found closest to the drip line, while radioactivity decreased in samples that were farther from the drip line. The idea of water being the dominant mode for movement is supported by the surface gamma survey.

The ^{226}Ra excesses found in all the soil samples and organic material are indicative of ^{226}Ra fixation by plants as described by Leslie et al. [4]. The ^{234}U deficiencies described in this study and in others can be attributed to uranium solubility and the relatively quick movement of uranium in soils. Overall, the mobilization was quick, with a time span of 25 years, but the radionuclides have not traveled far from the original source boulder.

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