Project Title: **Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria**

Laboratory Investigators: Robert Roback, Mike Murrell (505-667-4845, mmurrell@lanl.gov), and Steve Goldstein; Chemical Science and Technology Division Los Alamos National Laboratory

Campus Investigators: Teh Lung Ku (213-740-5826, rku@usc.edu) and Shangde Luo; Department of Earth Sciences University of Southern California

Goals Of Project:

The research is directed toward a quantitative assessment of contaminant transport rates in fracture-rock systems using uranium-series radionuclides. Naturally occurring uranium- and thorium-series radioactive disequilibria will provide information on the rates of adsorption-desorption and transport of radioactive contaminants as well as on fluid transport and rock dissolution in a natural setting. This study will also provide an improved characterization of preferential flow and contaminant transport at the Idaho Environmental and Engineering Laboratory (INEEL) site. To a lesser extent, the study will include rocks in the unsaturated zone. We will produce a realistic model of radionuclide migration under unsaturated and saturated field conditions at the INEEL site, taking into account the retardation processes involved in the rock/water interaction. The major tasks are to (1) determine the natural distribution of U, Th, Pa and Ra isotopes in rock minerals. sorbed phases on the rocks, and in fluids from both saturated and unsaturated zones at the site, and (2) study rock/water interaction processes using U/Th series disequilibrium and a statistical analysis-based model for the calculation of in-situ retardation factors of radionuclides and rock/water interaction timescales.

Geologic heterogeneity plays an important role in transporting contaminants in fractured rocks. Preferential flow paths in the fractured rocks act as a major pathway for transport of radioactive contaminants in groundwaters. The weathering/dissolution of rock by groundwater also influences contaminant mobility. Thus. it is important to understand the hydrogeologic features of the site and their impact on the migration of radioactive contaminants. In this regard, quantification of the rock weathering/dissolution rate and fluid residence time from the observed decay-series disequilibria will be valuable. By mapping the spatial distribution of the residence time of groundwater in fractured rocks, the subsurface preferential flow paths (with high rock permeability and short fluid residence time) can be determined.

Technical Description of Work:

The uranium and thorium decay series can be applied to the study of transport because they contain several isotopes of the same elements with different decay half lives. This allows simultaneous solutions to the mass-balance model equations for all isotopes of an element which in turn provides information on parameters such as residence time of fluid in the fractured rock, surface area and permeability, and dissolution rate of the rocks. By using decay-series disequilibria as a natural analog to contaminant transport, the combined effect of variable speciation associated with formation of colloids and organic compounds are taken into account, and the sorption capacity and retardation factors determined by this approach are site-dependent. Because the U- and Th-decay series exhibit elements with a range of chemical properties, one may use the

analog approach to simultaneously assess the migration of different radioactive wastes containing transuranic, as well as alkali-, alkali earth, and lanthanide elements, in groundwater systems.

This research will provide improved characterization of preferential flow and contaminant transport by providing the following information:

1. Fluid residence time (transport rates) in the basalt aquifers at various locations. This information is useful for characterizing the preferential flow path or field in the fractured rock system.

2. The in-situ adsorption and desorption rate constants, as well as the retardation factors, of various radionuclide wastes. The retardation factor is fundamental to the characterization of contaminant transport since it describes the transport rate of radionuclides relative to that of fluids.

3. Rock dissolution rate and its relation to preferential flow and contaminant transport in the fractured rocks.

Accomplishments to Date:

Work on this project began at Los Alamos National Laboratory (LANL) in the Fall of 1996. Due to a delay in funding to the University of Southern California (USC), work was not able to begin at the campus until May 1, 1997. Initial work at LANL began with literature searches and evaluation of existing data regarding the hydrogeology and radionuclide transport at INEEL. Coordination planning with scientists at INEEL, the Lawrence Berkeley National Laboratory (LBNL) and the University of Illinois (UI) was also begun. Uranium and thorium analyses on a set of water samples obtained from Dr. Tom Johnson (UI) were initiated. At USC, Dr. Shangde Luo began analyses of the short-lived U- and Th-series daughters concentrated on filters obtained from INEEL water sampling.

On the basis of published information and preliminary analysis, it soon became apparent that large-volume samples (10 to 500 liters) would be needed for much of our work. Collection of such samples is beyond the scope of routine water sampling currently underway at INEEL by the USGS. In order to maximize scientific communication and facilitate the necessary collection of large water samples, Drs. Roback and Luo visited INEEL over April 7 - 11. A one-day meeting was attended by Drs. Roback and Luo along with USGS, INEEL and Idaho State University scientists and resulted in valuable exchange of scientific information regarding the Snake River Plain aquifer. Importantly, the logistics for follow-on sampling this summer were agreed upon. During the remainder of the trip Roback and Luo collected four surface and groundwater samples in and around the INEEL utilizing a MnO_2 filtration system. This sampling method proved to be viable and will be employed during a more extensive sampling trip this summer. Preliminary results are discussed below. Roback also collected 14 solid core segments from two drill cores that penetrate the aquifer at INEEL. These samples were collected from the saturated and unsaturated zones and include “fresh” and oxidized basalt, sediment interbeds and precipitates. These samples will be analyzed as whole-rock and leached fractions for the full suite of uranium- and thorium-series nuclides. We anticipate that the sample suite will provide an excellent data set, which, in conjunction with our groundwater data will be used to evaluate water-rock interaction.

We have collected ourselves, or obtained

through USGS routine sampling 47, 0.5 to 1.5 liter ground- and surface-water samples either on site or nearby INEEL. Twelve of these samples have been analyzed for U concentration and isotopic composition. Data are presented in Table 1, sample locations are shown in the Appendix. Uranium concentrations from ground waters range from 0.3 to 2.5 ppb. Isotopic results for the samples indicate that all samples have natural $^{235}U/^{238}U$ ratios, contain no ^{236}U, and have a range of $^{234}U/^{238}U$ activity ratios between 1.6 and 3.0. These are important results which suggest that anthropogenic effects at INEEL should not influence our results for the naturally occurring U- and Th-series daughters.

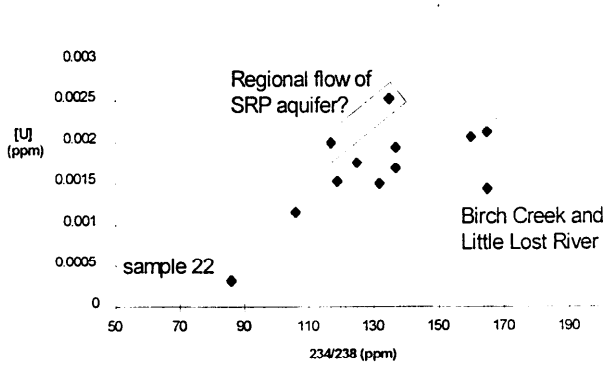
Table 1. U concentration and isotopic composition of groundwater from INEEL

Sample	U (ppm)	(+/-)* (%)	34/23 (ppm)	(+/-) (%)	234 ctivity
USGS 89A (INEEL1)	1.155E-03	0.27	105.5	0.30	1.92
AREA 2A (2)	1.938E-03	0.16	136.6	0.17	2.49
ANP 6A (3)	2.121E-03	0.13	165.4	0.18	3.01
USGS 6A (4)	1.748E-03	0.13	124.7	0.18	2.27
USGS site 9A (5)	1.717E-03	0.19	137.4	0.17	2.50
USGS site 17A (6)	1.427E-03	0.10	165.3	0.14	3.01
USGS 18A (7)	2.059E-03	0.31	159.8	0.12	2.91
USGS 22A (8)	3.314E-04	0.27	84.9	0.86	1.55
USGS 32P (9)	2.529E-03	0.16	134.7	0.19	2.45
USGS 32P (9, duplicate)	2.524E-03	0.11			
USGS 29A (10)	1.997E-03	0.21	117.2	0.24	2.13
USGS 103A (11)	1.489E-03	0.11	132.5	0.18	2.41
USGS 104A (12)	1.518E-03	0.12	118.9	0.20	2.16

*
uncertainties are reported at the 2 sigma level
(234U/238U) sample/(234U/238U) sec. eq.; where $^{234}U/^{238}U$sec. eq atom ratio = 54.93

Uranium concentrations positively correlate with $^{234}U/^{238}U$ ratios (Figure l), suggesting that mixing is important in controlling the U isotopic composition of groundwater at INEEL. Groundwater nearest the Birch Creek and Little Lost River recharge areas (samples 18, ANP-6 and site 17) have the highest $^{234}U/^{238}U$ ratios. Samples from wells 29 and 32 most likely represent water dominated by the regional Snake River Plain Aquifer flow and show lower $^{234}U/^{238}U$ ratios. Sample 22 has the lowest $^{234}U/^{238}U$ and uranium concentration. The uranium values for the remainder of the samples can be derived by mixing of these three "end-members". Analysis of additional samples will better define end-members and allow quantitative evaluation of groundwater mixing at INEEL.

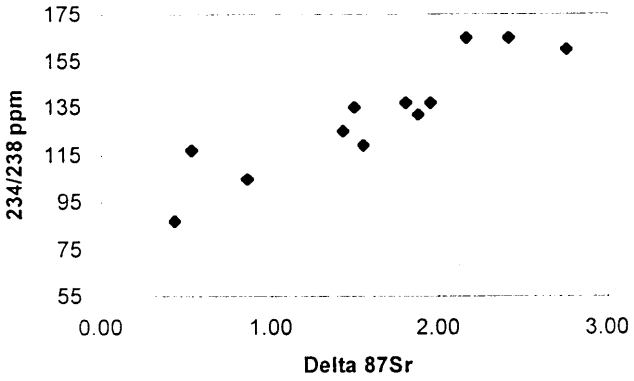
Figure 1. U concentration vs. $^{234}U/^{238}U$



$^{234}U/^{238}U$ activity ratios are highest nearest the minor recharge areas of Birch Creek and Little Lost River and decrease in the inferred direction of groundwater flow. This is not the trend expected if alpha recoil and selective leaching of ^{234}U from radioactively-damaged sites were the dominant factors in influencing $^{234}U/^{238}U$ values. Instead, the observed pattern suggests that water/rock interaction in the aquifer is modifying the uranium isotopic composition of the groundwater toward that of the host basalt through bulk dissolution. This would move the $^{234}U/^{238}U$ activity ratio towards unity (55 ppm). This hypothesis can be tested by comparing the uranium isotopic data with Sr isotopic data because Sr isotopics are not influenced by processes of alpha recoil or selective leaching. Also shown in the appendix are contours of $^{87}Sr/^{86}Sr$ (T.

Johnson, written commun.) for the same samples. Figure 2 shows a plot of delta 87 (difference in parts per mil between $^{87}Sr/^{86}Sr$ sample and seawater). The positive correlation between $^{234}U/^{238}U$ activity ratios and strontium isotopic ratios strengthens the above hypothesis. Thus, dissolution of basalt appears to be dominant over alpha recoil or selective leaching processes in controlling the uranium isotopic composition of the groundwater at INEEL. This may be due to the abundance of unstable and readily dissolvable volcanic glass in the basalt.

Figure 2. $^{234}U/^{238}U$ vs. Delta ^{87}Sr



Precipitation may also be important in controlling the uranium concentration and isotopic composition of INEEL groundwaters. Calcite and clays are common precipitates in the basalt aquifer at INEEL. Precipitates from cores were collected to evaluate their role in controlling the groundwater isotopic composition at INEEL

Preliminary data for thorium concentrations for INEEL waters are at the level of 0.2 to 0.4 ppt. Larger samples will be collected and processed to obtain Th concentration and isotopic data. These samples will be collected this summer.

We have demonstrated that uranium isotopics are useful to track flow patterns, and groundwater mixing at INEEL and can be used to constrain factors controlling goundwater isotopic composition. This initial data set will be used to select wells for collection of large-volume samples from which we will determine a full suite of uranium- and thorium-series isotopics.

Major efforts at USC involved the development of a MnO_2-fiber filtration system for collecting large-volume groundwater samples for analyses of a suite of short-lived uranium and thorium-series isotopes by radioactivity-counting techniques. The system was tested in the field during April and was used to collect four large-volume water samples: three from streams that represent the local recharging source waters and one from a USGS monitoring well in the area. We are in the process of measuring isotopes of Ra (^{226}Ra, ^{228}Ra and ^{224}Ra), Th (^{232}Th, ^{230}Th, ^{234}Th and ^{228}Th), Pb (^{210}Pb) and Po (^{210}Po) in the samples. The activities of ^{210}Pb appear to be too low for y-counting; we plan to measure them by a-counting of its daughter ^{210}Po after about one year of ingrowth. We anticipate to report and discuss the results in our next report.

Projections:

We are on schedule for 1997 projections in most aspects of the study. These include (1) uranium analyses and preliminary interpretations, (2) establishing natural levels of U- and Th-series daughters at INEEL. (3) obtaining additional rock and water samples. (4) coordinating future sampling, and (5) establishing communication and collaborations. These efforts have yielded valuable information and contributed to attaining the stated goals of the project.

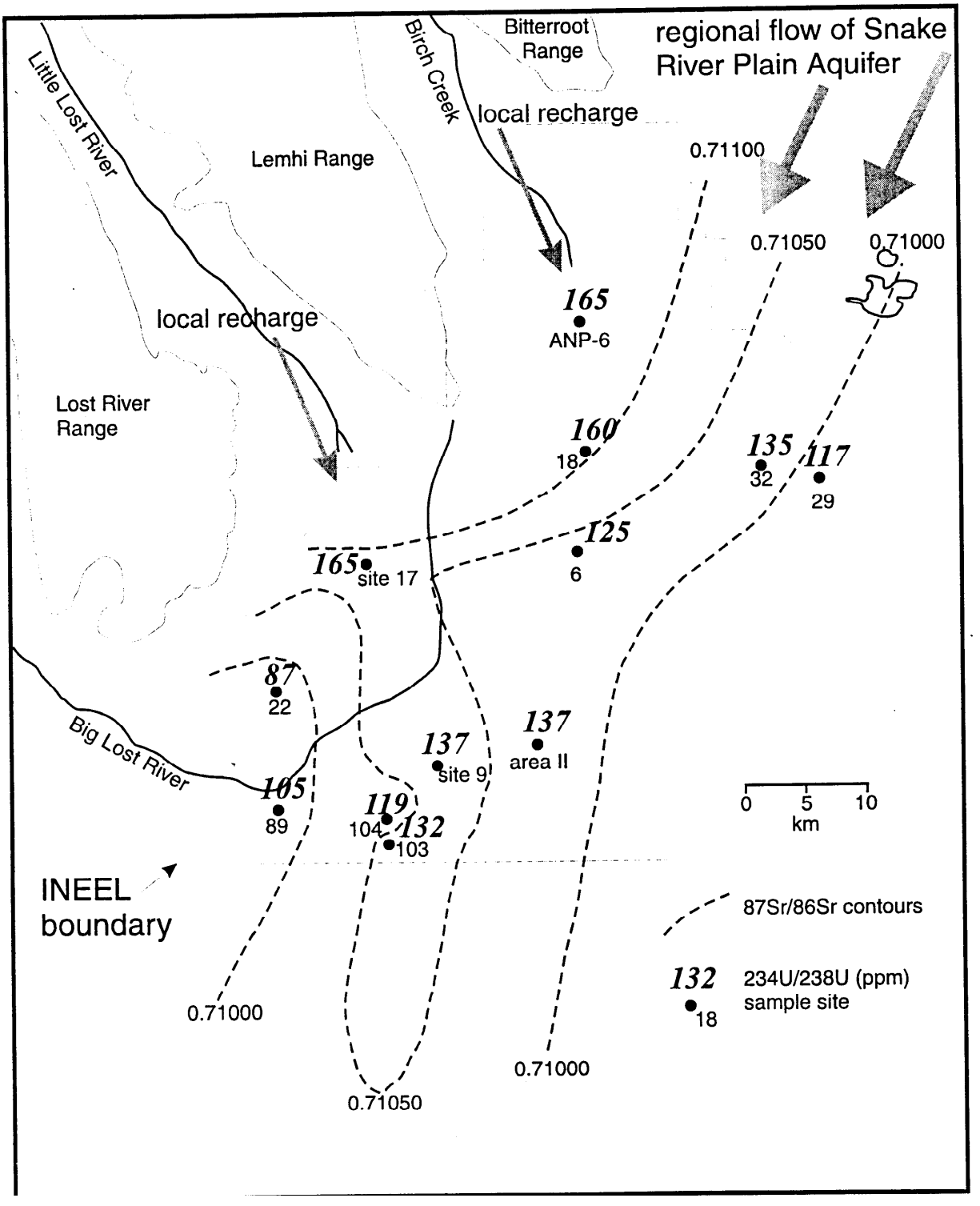
The need for large-volume samples has required that we organize a sampling trip dedicated solely for the collection of our large samples. This trip has been tentatively scheduled for August of 1997. Data obtained thus far will help to guide future sample site selection and collection of samples. By the end of the August sampling trip, we expect to have most of the samples needed to address the goals of the project. Tasks for the remainder of the year will include additional uranium analyses, collection of large-volume samples and initial analysis of these samples for the proposed suite of uranium- and thorium-series nuclides (^{234}Th, ^{228}Th, ^{230}Th, ^{232}Th, ^{226}Ra, ^{228}Ra, ^{224}Ra, ^{210}Pb, and ^{210}Po), and preparation and initial analysis of whole rock samples collected in April. Much of this current work will carry over into the 1998 fiscal year, with detailed modeling to follow. We will report initial results at the Geological Society of America annual meeting in Salt Lake City this October.

Funding:

Spending levels for the LANL portion of the project are on target. The May 1 starting date in funding the USC portion of this project has delayed their participation in the project.

Issues/Problems:

Because of the delay in funding the USC portion of the project, the details of collecting large samples were effectively put on hold until May 1, 1997. In spite of this delay, we succeeded in obtaining many solid and water samples and in getting a number of high quality uranium measurements. USC now has received funding and we can now move on together with all portions of the project.



Appendix 1. Map showing locations of groundwater samples and 234U/238U ratios. Also shown are contours of 87Sr/86Sr (T. Johnson, written communication).