LBL-29867

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

Presented at the Fall Meeting of the Materials Research Society, Symposium P, Boston, MA, November 26–29, 1990, and to be published in the Proceedings

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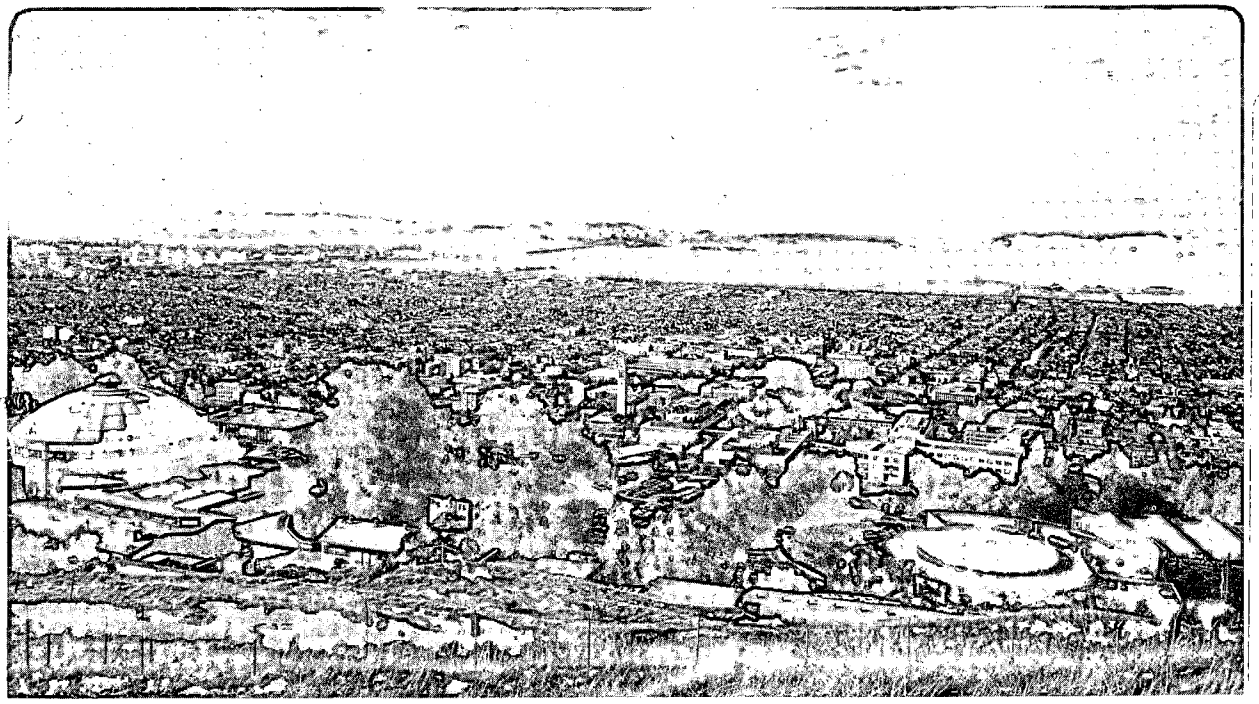

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This work was supported by the Director, Office of Civilian Radioactive Waste Management, Office of Facilities Siting and Development, Siting and Facilities Technology Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

RADIONUCLIDES IN HYDROTHERMAL SYSTEMS AS INDICATORS OF REPOSITORY CONDITIONS

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ABSTRACT

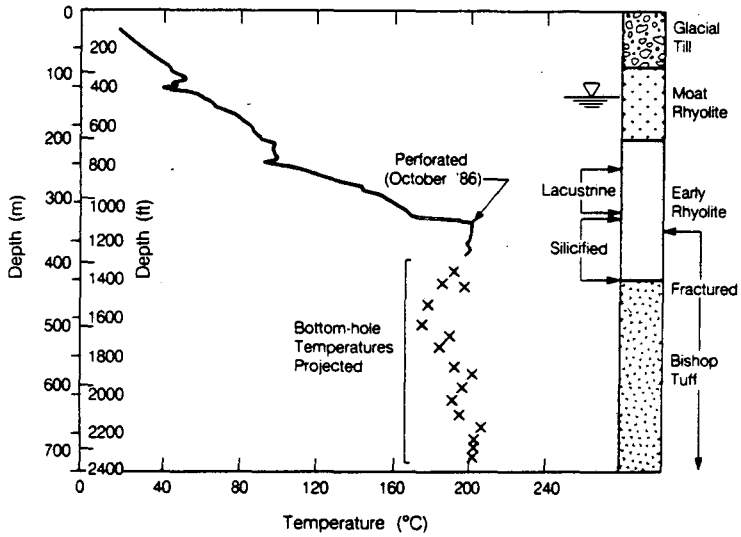
Hydrothermal systems in tuffaceous and older sedimentary rocks contain evidence of the interaction of radionuclides in fluids with rock matrix minerals and with materials lining fractures, in settings somewhat analogous to the candidate repository site at Yucca Mountain, NV. Earlier studies encompassed the occurrences of U and Th in a "fossil" hydrothermal system in tuffaceous rock of the San Juan Mountains volcanic field, CO. More recent and ongoing studies examine active hydrothermal systems in calderas at Long Valley, CA and Valles, NM. At the Nevada Test Site, occurrences of U and Th in fractured and unfractured rhyolitic tuff that was heated to simulate the introduction of radioactive waste are also under investigation. Observations to date suggest that U is mobile in hydrothermal systems, but that localized reducing environments provided by Fe-rich minerals and/or carbonaceous material concentrate U and thus attenuate its migration.

INTRODUCTION

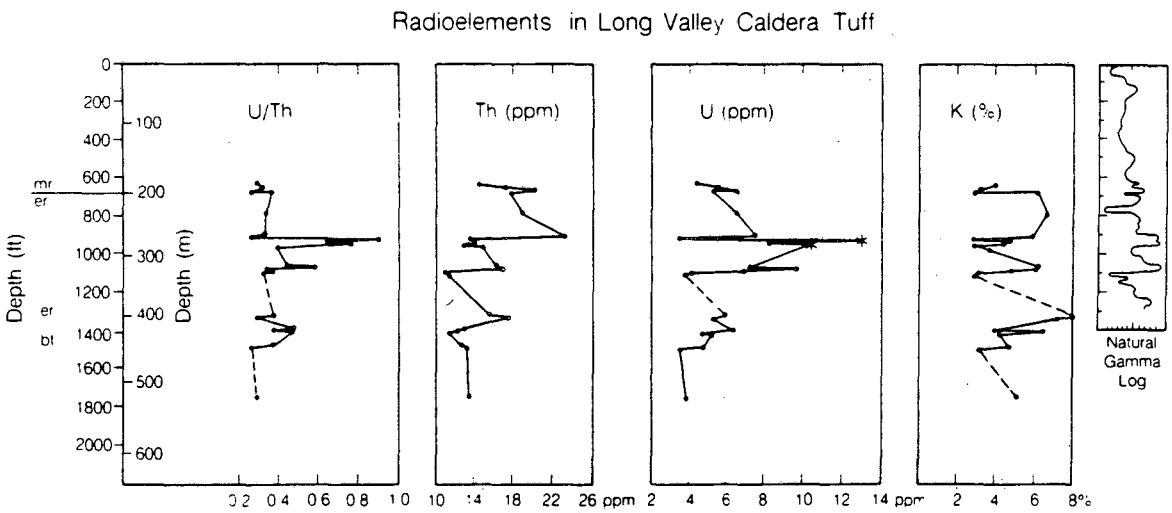
Hydro-geochemical processes must be understood if the movement of radionuclides away from a breached radioactive waste canister is to be modeled and predicted. Hydrothermal systems in tuffaceous and underlying sedimentary rocks contain evidence of the interaction of radionuclides in fluids with materials lining fractures, in settings that are somewhat analogous to the candidate repository site at Yucca Mountain, NV. Earlier studies [1,2] encompassed the occurrences of U and Th in a "fossil" hydrothermal system in tuffaceous andesitic rock of the San Juan Mountains volcanic field, CO. At this site,where a regional hydrothermal system occurred in response to intrusion of monzonite into andesitic tuff, U and Th were confined to accessory minerals, and thus were essentially unaffected by hydrothermal alteration or by intense heating at the monzonite-tuff contact. More recent and ongoing studies examine active hydrothermal systems at the Long Valley caldera, CA and the Valles caldera, NM. The occurrences of U and Th in fractured and unfractured rhyolitic tuff that was heated to simulate the introduction of radioactive waste are also under investigation. In these studies high-resolution gamma spectrometry and fission-track radiography are coupled with observations of alteration mineralogy, stable-isotope ratio measurements, and thermal profiles to deduce the evidence of, or potential for movement of U and Th in response to the thermal regimes.

LONG VALLEY CALDERA

Samples of core were examined from a 730 m-deep hole in rhyolitic tuff of the active hydrothermal system of the Long Valley caldera [3]. The hole penetrates a thermal regime from near ambient temperature to over 200°C (Fig.1,2). Evidence of disequilibrium in the U decay series was observed in calcite-cemented breccia of a fracture zone at ~150°C, in a region of rapidly increasing temperature with depth where oxygen isotope ratios concomitantly decrease from +3 to -2. Illite is the principal clay mineral in this zone[4]. Fission-track radiography shows that U associated with Fe-rich mineral phases in the breccia is concentrated to 30 to 50 ppm, compared to 11 to 13 ppm in the calcite and ~6 ppm in unbrecciated tuff. Thorium in the high-U zone is also somewhat elevated, ~24 ppm, compared to a local background of ~20 ppm. The U/Th ratio in this zone, ~1, is anomalously high, compared to ~0.3 in the rest of the core. High-resolution gamma spectrometry



1. Thermal and lithologic diagram of a hole cored in tuff of the Long Valley caldera. Projected temperatures are from bottom-hole measurements made during coring (from [3]).



2. Distribution of radioelements over a temperature range 60 to 150°C in the Long Valley core hole. Asterisks in the U diagram indicate U-series disequilibrium. mr = Moat Rhyolite, er = Early Rhyolite, bt = Bishop Tuff.

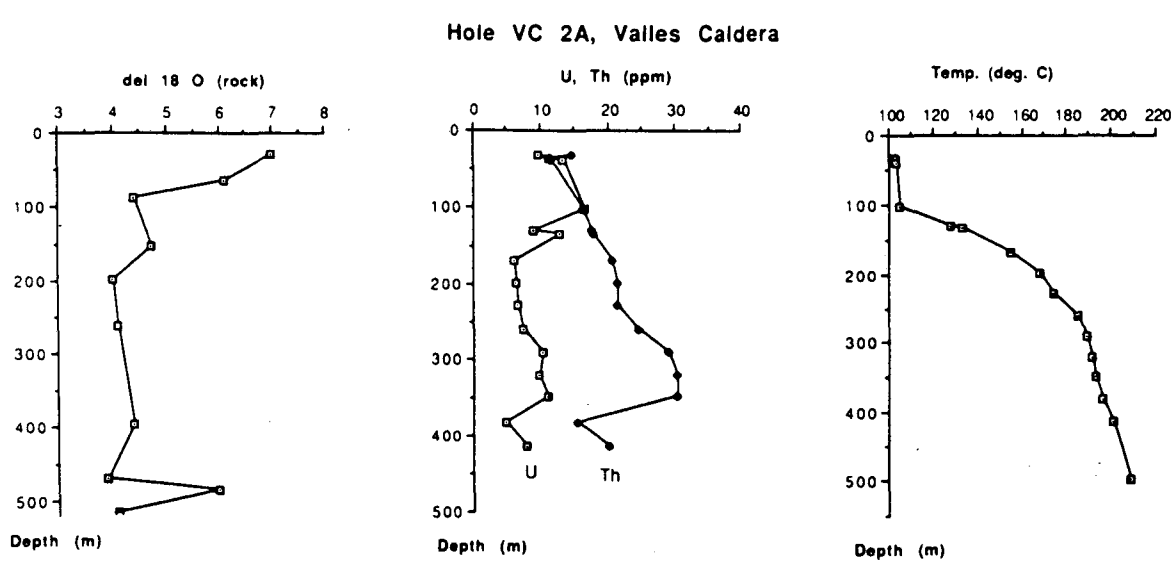
indicates that the U in the breccia zone is not in secular equilibrium with its daughter elements, (in some cases Ra is in excess with respect to U , in others U daughters appear depleted), suggesting localized mobilization/deposition of parent U and/or its daughters in the hydrothermal environment.

VALLES CALDERA

In quartz-rich welded rhyolitic tuff of the Valles caldera, a ~530 m-deep core hole intersected the vapor zone (at temperatures ~100° C) that caps the active fluid-saturated hydrothermal system [5]. Relatively high concentrations of U (9 to 16 ppm) are observed in this zone (Fig. 3); they are nearly equal to Th concentrations [6]. The high-U zone also contains relatively high concentrations of Mo (in the form of poorly crystalline molybdenite), suggesting that it was deposited in an earlier saturated regime at ~200°C [7]. The presence of an earlier saturated regime is substantiated by the decrease in whole-rock oxygen isotope ratios over the upper ~ 100 m of the hole (Fig. 3). Gamma-spectrometric evidence of equilibrium in the U-decay series in these high-U samples suggests that there has been little if any mobility of U over the life of the vapor-dominated system. In the underlying saturated zone where temperature rapidly increases with depth (Fig. 3), U concentrations drop to 6 to 8 ppm, while Th continues to rise with depth. However, in the saturated zone the pattern of U distribution generally follows that of Th. Fission-track radiography is underway to determine the mineral asociations of U in the tuff of the vapor-dominated and saturated zones, and will help explain the cause of the enrichment of U at depths below ~ 150 m.

In the outflow zone of the caldera's hydrothermal system [8] Ra in anomalously high concentrations occurs at sites in the Paleozoic calcareous Abo shale (80° C) that underlies the Quaternary volcanic rocks. At these sites, Ra is unsupported by parent U, suggesting preferential removal of U or addition of Ra by hydrothermal fluids [9]. Uranium concentrations of several tenths of a percent are associated with carbonaceous material in the underlying Madera limestone (at ~120° C).

The Valles and Long Valley studies thus provide evidence for at least localized mobility of U and its daughters in tuff and underlying sedimentary rocks, at temperatures comparable to those expected in a repository environment.



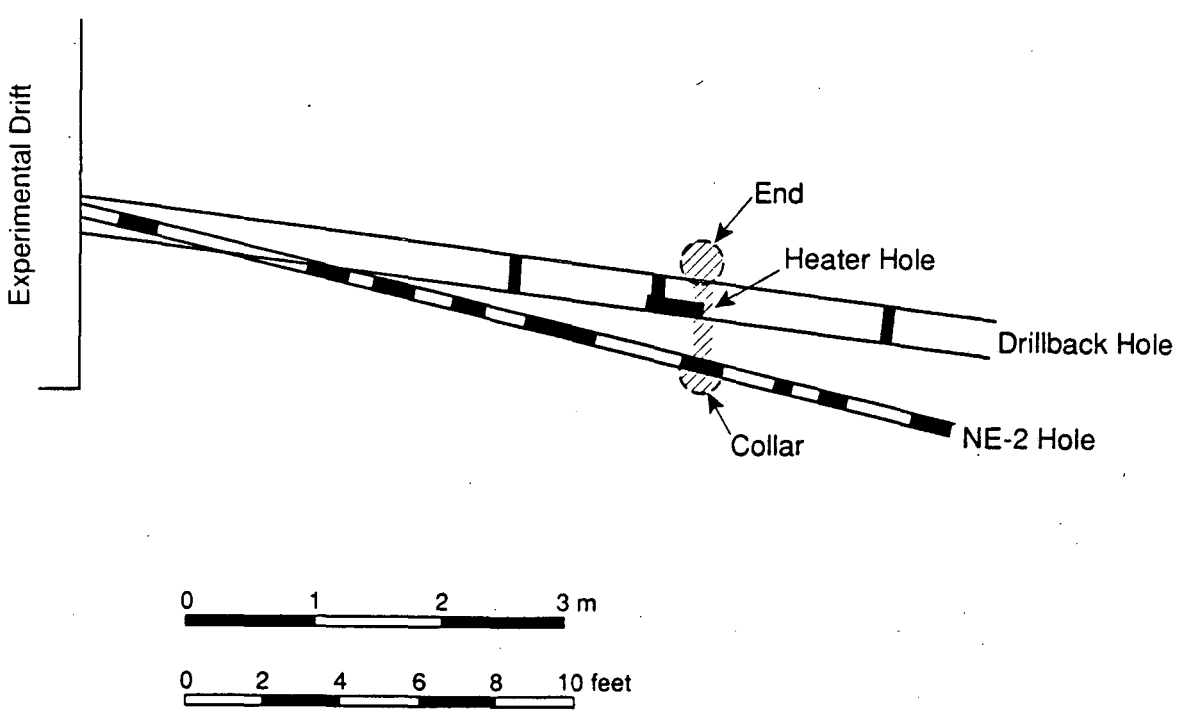
(Data from Musgrave et al., 1989)

3. Radioelement, temperature, and O-isotope diagrams for hole VC-2A, in rhyolitic tuff of the Valles caldera (data from [6]).

NEVADA TEST SITE

At the G-tunnel test facility, Nevada Test Site, core has been obtained for mineralogical, geochemical and geomechanical studies of welded tuff from the unsaturated zone that has been artificially heated to repository temperature. The mineralogical and physical properties of this tuff, the Grouse Canyon, are similar to those of the densely welded Topopah Springs tuff, the candidate repository medium [10]. In an experiment conducted by Lawrence Livermore National Laboratory (LLNL), an electric heater simulated the localized thermal field caused by introduction of high-level waste [11]. The heater was at full power for 4 months, with a temperature of 240° C at the heater edge and 120° C in rock at a distance of 0.7m. A small steam-dominated system developed in the rock within 0.6-0.7m of the heater and lasted for at least 70 days.

To provide baseline data, we selected unheated core from a hole, designated NE-2, that passes within 1 m of the electric heater (Fig. 4). The distribution of radioelements in this core was investigated by gamma spectrometry, and results showed a relatively even distribution of U and Th over the length of the core (mean values: U=3.4 +/- 0.4 ppm, Th= 15.6 +/- 2.1 ppm). More detailed gamma spectrometry indicated high concentrations of U and Th associated with an open fracture, coated partially with amorphous silica. This occurrence was examined by fission-track radiography, disclosing that U, at ~20 ppm, is concentrated by a factor of 5 in the silica coating relative to the tuff matrix. This U-rich coating could have been associated with the hydrothermal system that developed soon after deposition of the tuff, or with a cooler, fracture-controlled groundwater system that subsequently developed.



4. Vertical section perpendicular to heater hole in G-tunnel, Nevada Test Site, showing sampled intervals in core from the NE-2 hole, drilled prior to the heater hole, and the "drillback" hole that intersected the heater hole. The heater hole projects into the figure, with the end of the hole ~1 m above the elevation of its collar.

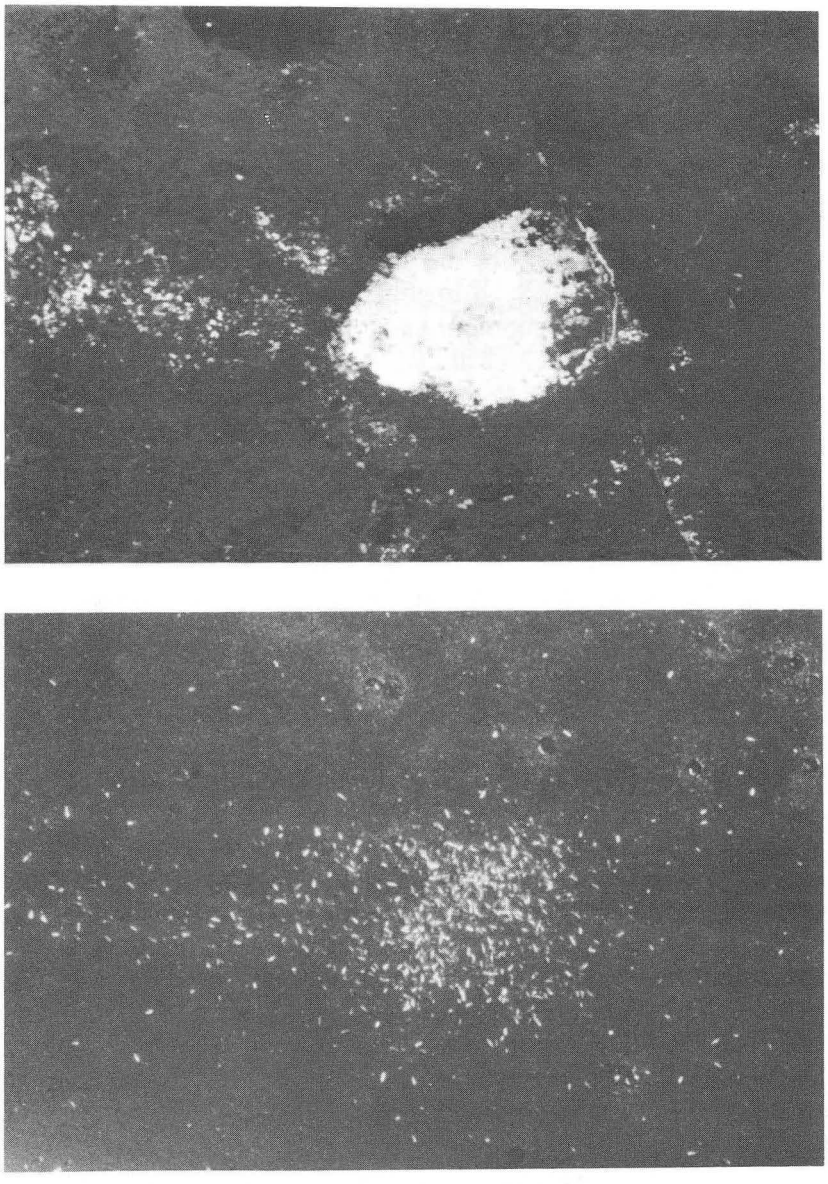
Investigations of heated core, obtained by drilling through the heater hole are presently underway. We are examining the core from sites where localized heating may have affected fracture-lining and rock-matrix constituents; preliminary results are presented here. Five subcores perpendicular to the axis of the 30 cm-diameter drillback core and 1 core parallel to the axis have been obtained, covering a span of 30 cm from the edge of the heater hole . Whole-rock gamma spectrometry of these subcores indicates a slightly lower U concentration (3.3 ppm) in the core closest to the heater hole (3.5 cm) than in the more distant cores, which average 3.5 ppm U. Thorium, averaging 16.5 ppm is nearly the same in all cores, with only a small depletion (to16.2 ppm) evident in the subcore at 10 cm from the heater hole. The mean concentrations of U and Th in the heated subcores are similar to those of the unheated core. Preliminary comparison of radioelement correlations in heated and unheated rock (Table 1) indicates that U and Th are correlated similarly, while U and K are more strongly correlated in the heated than in the unheated rock. Th and K are strongly correlated in both the heated and unheated rock.

Table 1. Correlations (r^2) Between Radioelements

	U with Th	U with K	Th with K
Heated tuff	0.47	0.59	0.96
Unheated tuff	0.43	0.28	0.93

The apparently more independent behavior of U than of Th and K in both heated and unheated tuff might be influenced by the loci of U in the rock. This is indicated by the aforementioned association of U with fracture - lining silica and also by the results of fission-track radiography of tuff close to the heater. Radiography in combination with x-ray spectroscopy (EDAX)on the scanning electron microscope show that U is asociated both with primary magnetite and ilmenite, and with secondary disseminated Mn-oxyhydroxide minerals (Fig. 5). Uranium has probably been localized in the secondary minerals by adsorption, while it appears to be incorporated in the grains and on the surfaces of the primary minerals. Fission-track determinations of U in 5 thin sections from within 10 cm of the heater hole (Fig. 6) show that U is concentrated 8 to 10 times above whole-rock values where it is associated with the primary Fe-Ti-oxide minerals and 4 to 5 times whole-rock values where it is associated with secondary, mainly Mn-oxide minerals. Where U is associated with Fe-Ti-oxide minerals in unheated core from the NE-2 hole, U concentrations are ~150 ppm, considerably higher than the concentrations shown in Fig. 6. This, together with the apparent gradient in U shown in Fig. 6 suggests a relative depletion of U associated with Fe-Ti-oxide minerals in close proximity to the heater. Electron microscopy with EDAX is being used to determine more accurately the composition of these opaque minerals. Detailed fission-track radiography and EDAX are proceeding as well on thin sections from the 5 subcores, covering a broader range (30 cm) of distance from the heater.

Taken together, observations to date suggest that U is mobile in hydrothermal systems, but that localized reducing environments provided by Fe-rich minerals and/or carbonaceous material concentrate U and thus attenuate its migration.



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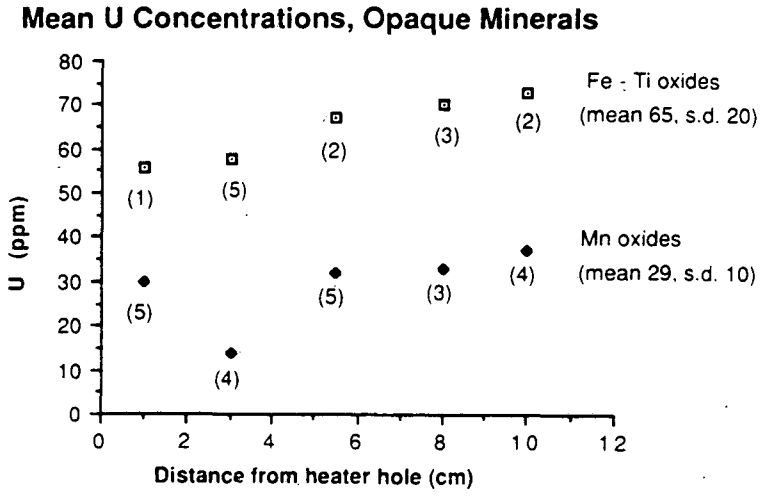
5. Uranium associated with primary and secondary opaque minerals in heated tuff. Top: Backscattered electron image of primary Fe-rich grain (center) and secondary disseminated Mn-rich mineral (left). Bottom: Associated fission tracks. Length of field 1.3mm.



6. Uranium concentrations, by fission-track radiography, in primary Fe-Ti and secondary Mn-oxyhydroxide minerals in welded tuff within 10 cm of the heater hole. Numbers of observations are shown in parentheses.

ACKNOWLEDGEMENTS

We thank Abelardo Ramirez of LLNL for his help in arranging the drillback coring at G-tunnel, and William Glassley of LLNL for his collaboration in obtaining samples of the core. This work was sponsored by the Director, Office of Civilian Radioactive Waste Management, Office of Facilities Siting and Development, Siting and Facilities Technology Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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