Radionuclide Mobility in the Shallow Portion of an Active High-Temperature Geothermal System

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Introduction

Accurate knowledge of the behavior of radionuclides in natural rock-water systems is crucial for the prediction of the consequences of failure of a high-level nuclear waste repository. Work in progress at Argonne National Laboratory involves the detailed geochemical analysis of rock, mineral, and water samples from shallow drill holes in a thermal area of Yellowstone National Park [1]. This study is designed to provide data that will increase our understanding of the behavior of a group of radionuclides in an environment similar to that of the near field of a high-level nuclear waste repository.

Samples and Their Environment

Samples being studied are from U.S.G.S. research drill holes Y7 and Y8 [2]. The petrography and mineralogy of the samples has been thoroughly characterized [3]. Briefly, the samples consist of hydrothermally altered rhyolite vitrophyre breccia and pumiceous tuff from the Biscuit Basin Flow. Obsidian was the primary constituent of the samples (70-80%) when fresh, but effects of hydrothermal alteration include hydration of obsidian and replacement of hydrated obsidian by zeolites and clays. Vein and pore filling deposits of zeolites, clays, silica, and other secondary phases are present in cleanly separable quantities sufficient for geochemical analysis.

Samples from depths of 174 to 242 feet (~120-140°C) in Y7, and 182 to 499 feet (~160-170°C) in Y8, have been studied. Samples of dilute (~2 g/L T.D.S.), near-neutral pH thermal water from the drill holes and nearby hot springs have been analyzed.

Methods of Study

Whole rock samples, mineral separates, and thermal waters have been analyzed by instrumental neutron activation analysis and inductively-coupled plasma atomic emission spectroscopy.

Results

The group of elements studied, and their corresponding analogs in high-level nuclear waste, are listed in Table 1. Whole rock compositional changes are summarized in Table 2 as follows:

(1) Initial rock composition is assumed to have been homogeneous, which is consistent with data for immobile elements such as Ti, Zr, Th, REE, etc.

(2) Whole rock concentration of each element is normalized by weight to TiO_2, which is assumed to be immobile.

(3) Ti-normalized concentration of each element is divided by that of the least altered sample, which is assumed to represent the initial rock composition before hydrothermal alteration.

(4) Range of values calculated in step (3) above is listed in Table 2.

The data in Table 2 suggest that:

(1) Zr, Sm, and Th are immobile in this system on the scale of the samples analyzed.

Table 1

Element	Analog
Cs	Cs
Sr	Sr
Ba	Ra
Sb	Sb
Zr	Zr
Sm	REE, 3+ Actinides
Th	Th, 4+ Actinides
U	U

Table 2. Whole Rock Composition Changes

Element	$(C_{Altered}/C_{Unaltered})_{Ti}$
Cs	1.0 - 50
Sr	1.0 - 1.5
Ba	0.5 - 1.5
Sb	1.0 - 30
Zr	1.0
Sm	1.0
Th	1
U	0.8 - 7.5

(2) Moderate to large increases in whole rock concentration of Sr, Sb, Cs, Ba, and U are associated with hydrothermal alteration. The enrichment in U observed in some samples has been found, by fission track radiography, to be associated with magnetite surfaces, possibly by adsorption on a thin oxidized layer [1].

Empirical mineral-water distribution ratios (R_d) having been calculated using compositions of mineral separates and thermal water samples from either the same drill hole or a nearby geyser. These empirical R_d values (Table 3) demonstrate the contributions that various secondary minerals have to the observed whole rock compositional changes. Note that the R_d values are generally very high, especially for Sr, Cs, and Ba in zeolites and for Cs, Ba, Zr, Sm, Th, and U in clay. Zeolites and clays are the most abundant secondary phases in these samples, as they also are in the volcanic rocks of the Nevada and Washington repository candidate sites. Precipitates of beta-cristobalite and calcite have high R_d values for U and Sr, Ba, Sm, Th, and U, respectively.

Discussion

It appears that the elements studied are effectively retarded as a result of geochemical processes operating in the shallow portion of this high-temperature geothermal system. This may imply that similar behavior could be expected for these elements in the event of their release from a repository located in saturated, altered vitric volcanic rock.

Table 3. Empirical Distribution Ratios*

	Clinoptilolite	Mordenite	Analcime	Celadonite	Beta-Cristobalite	Calcite
Cs	-	3.6	4.4	2.2	-	-0.7
Sr	>4.0	>3.9	-	-	-	>4.2
Ba	4.9	>4.7	>4.0	3.9	-	3.4
Sb	-	-	-	1.1	1.0	-0.5
Zr	-	-	-	>4.3	-	-
Sm	-	-	-	>5.4	-	>4.4
Th	-	-	-	>5.1	-	>3.8
U	-	-	-	3.6	3.2	2.2

*R_d = $\frac{\text{concentration of element in mineral}}{\text{concentration of element in water}}$
Reported values are in units of $\log_{10} R_d$
All minerals analyzed are vein precipitates, except clinoptilolite, which is a glass replacement phase.

- = Value not determined.

References

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2. White, D., R. Fournier, L. Muffler, and A. Truesdell, "Physical Results of Research Drilling in Thermal Areas of Yellowstone National Park, Wyoming," U.S. Geological Survey Professional Paper 892, 70 pp. (1975).

3. Keith, T.E.C., D. E. White, and M. H. Beeson, "Hydrothermal Alteration and Self-Sealing in Y-7 and Y-8 Drill Holes in Northern Part of Upper Geyer Basin, Yellowstone National Park, Wyoming," U.S. Geological Survey Professional Paper 1054-A, 26 pp. (1978).

Questions and Answers

1. Is any consideration given to the short time dynamic nature of steam-water cyclical phase changes?

The mineralogy of these drill cores does not indicate that vapor-dominated conditions have ever been a significant factor affecting rock sampled from drill holes Y7 and Y8. There are presently no acid-sulfate springs in the immediate vicinity. Thus is appears that the hydrothermal alteration at this location has mainly involved Na-HCO_3-Cl water similar to that now being discharged in Upper Geyser Basin.

2. What is the redox state of this system?

The minerals goethite, hematite, and pyrite occur as hydrothermal alteration products in the drill cores. This may indicate redox potentials near the hematite-pyrite equilibrium value. Thermal waters sampled from the drill holes generally contain both oxidized and reduced sulfur species. Oxidized sulfur species are considered to form from reduced sulfur species by reaction with dissolved oxygen in cool recharge waters; deeper reservoirs probably contain primarily reduced sulfur species. It is likely that redox conditions at a given point may vary with time, depending on water circulation patterns.

3. Are the distribution ratios that you presented equilibrium values?

These have been referred to as empirical distribution ratios because there is some uncertainty as to whether or not they reflect equilibrium, and if so, what is the nature of the equilibrium that

they represent. It is noteworthy that the empirical Rd values determined for Sr and Ba in clinoptilolite compare closely to those determined in sorption experiments at Los Alamos.

4. Is the water chemistry controlled by leaching of the rhyolite glass?

To some extent this is probably true, although undoubtedly the secondary mineral phases, once formed, also have significant effects upon water chemistry.