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BEHAVIOR OF NUCLEAR WASTE ELEMENTS DURING HYDROTHERMAL
ALTERATION OF GLASSY RHYOLITE IN AN ACTIVE GEOTHERMAL
SYSTEM: YELLOWSTONE NATIONAL PARK, WYOMING

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NEIL C. STURCHIO AND MARTIN G. SEITZ

DE85 002730

Chemical Technology Division, Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

The behavior of a group of nuclear waste elements (U, Th, Sr, Zr, Sb, Cs, Ba, and Sm) during hydrothermal alteration of glassy rhyolite is investigated through detailed geochemical analyses of whole rocks, glass and mineral separates, and thermal waters. Significant mobility of U, Sr, Sb, Cs, and Ba is found, and the role of sorption processes in their observed behavior is identified. Th, Zr, and Sm are relatively immobile, except on a microscopic scale.

INTRODUCTION

Most disposal options currently under consideration for high-level nuclear waste involve the construction of a deep repository in a geologic environment where the potential release rates of radionuclides from the repository to the biosphere are within regulatory limits [1]. Flowing groundwater is generally considered to be the most probable medium of radionuclide transport. If the rate of transport by flowing groundwater is sufficiently low, then a significant quantity of radionuclides will not reach the biosphere. Geochemical retardation by sorption processes (including adsorption, ion exchange, and precipitation) along groundwater flow paths may further limit radionuclide mobility and is an important factor in the assessment of the safety of a given repository environment. A thorough understanding of sorption phenomena is best approached through the integration of knowledge derived through laboratory experiments, theoretical models, and empirical observations of natural rock-water systems.

Among the scientific attributes of studying natural systems in relation to nuclear waste disposal is that they contain information that allows long-term extrapolations of laboratory results and theoretical models be evaluated. Nature also contains valuable examples of the long-term stability of waste form analogs, e.g., volcanic glass and crystalline actinide-bearing phases, in contrasting geologic environments.

This paper summarizes initial results of a geochemical study of the behavior, in an active geothermal system in silicic volcanic rock, of a group of elements of concern in high-level nuclear waste disposal (U, Th, Sr, Zr, Sb, Cs, Ba, and Sm). The results of this study demonstrate the extent of geochemical mobility of these elements and their retardation by common secondary minerals in a natural rock-water system at temperatures (120-170°C) within the range of anticipated near-field repository conditions. The rocks of this study, prior to hydrothermal alteration, consisted primarily of high-silica glass. Therefore, the small-scale redistribution of elements during alteration of this glass due to long-term exposure to heated groundwater can also be evaluated.

SAMPLE DESCRIPTIONS

The rock samples chosen for this study are from drill cores of the hydrothermally altered Biscuit Basin Flow as it was encountered in U.S.G.S.

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research drill holes Y7 and Y8 in the northern part of Upper Geyser Basin, Yellowstone National Park, Wyoming. The two holes were drilled about 130 m apart. Y7 is in an area having no surficial thermal activity, whereas Y8 is within a cluster of discharging pools and geysers. The petrography and mineralogy of the Y7 and Y8 drill core samples have been characterized in detail by Keith et al. [2]; drilling techniques and physical measurements in the drill holes are discussed by White et al. [3].

The stratigraphy is similar in Y7 and Y8, consisting of about 2 m of sinter deposits, underlain by about 50 m of silt, sand, and gravel deposits, underlain by the Biscuit Basin Flow. In Y7, the Biscuit Basin Flow consists predominantly of rhyolite flow breccia from -52.7 m to the bottom of the hole at -73.8 m. In Y8, the same flow breccia occurs from -55.2 m to -62.8 m, and is underlain by pumiceous tuff that extends to the bottom of the hole at -153.4 m. The flow breccia and pumiceous tuff are interpreted to have formed from the same magma, but through different modes of eruption, on the basis of close similarities in their bulk composition and plagioclase characteristics [2]. Bottom-hole temperatures within the Biscuit Basin Flow during drilling, considered representative of pre-drilling conditions [3], ranged from about 120 to 140°C in Y7, and from about 160 to 170°C in Y8.

Flow Breccia

The flow breccia of the Biscuit Basin Flow consists of angular cm- to m-scale clasts of perlitic vitrophyre in a matrix of more finely crushed vitrophyre. The perlitic vitrophyre clasts (hereafter referred to as "vitrophyre") range from slightly to extensively altered. Alteration is more intense adjacent to veins and matrix, thus smaller vitrophyre clasts are most altered. The matrix is more thoroughly altered than the vitrophyre, probably due to its greater porosity and permeability.

Primary (igneous) mineralogy of the vitrophyre, as preserved in relatively fresh samples, consists of 70-80 vol % high-silica glass containing phenocrysts of plagioclase, sanidine, quartz, clinopyroxene, orthopyroxene, titanomagnetite, ilmenite, zircon, and apatite. Secondary (hydrothermal) mineralogy in Y7 consists of clays (smectite, interlayered celadonite-smectite, and celadonite), zeolites (primarily clinoptilolite and mordenite), beta-cristobalite, calcite, and pyrite. Feldspars, quartz, and other primary phases are not visibly altered, except for slight oxidation of titanomagnetite. In Y8, the secondary mineral assemblage in the vitrophyre consists of celadonite, zeolites (mordenite, clinoptilolite, analcime, and laumontite), silica minerals (alpha-cristobalite, beta-cristobalite, opal, and quartz), K-feldspar, chlorite, and pyrite. The secondary minerals occur as alteration products of hydrated glass, as pyroxene replacements, and as precipitates in veins and pore-spaces. Porosity of representative samples of the flow breccia is 17% in Y7 and 13% in Y8 [2].

Pumiceous Tuff

The pumiceous tuff of the Biscuit Basin Flow consists entirely of pumice fragments that are extensively altered. The primary mineralogy of the tuff was apparently that of the flow breccia. The secondary assemblage of the tuff consists of celadonite, zeolites (mordenite and analcime), K-feldspar, silica minerals (quartz and chalcedony), calcite, and goethite. Present porosity of representative samples of the pumiceous tuff is 39% [2].

ANALYTICAL METHODS

Analyses were made of 34 whole rock samples of vitrophyre, matrix, and pumiceous tuff, 16 separates of hydrated glass and secondary minerals, and 5 thermal water samples. Zr, Sb, Cs, Sm, U, and Th in solids were determined by instrumental neutron activation analysis (INAA). Sr and Ba were determined by inductively-coupled plasma atomic emission spectroscopy (ICP). Analytical uncertainties (2 sigma) relative to reported values are, generally: 2-5% for Cs, Sm, U, and Th; 5-10% for Sr, Sb, and Ba; and 25-30% for Zr.

RESULTS

Here we report some representative analyses, summarize the present data for the elements under consideration, and briefly interpret some of the observed elemental behavior. The complete data obtained for this study, including data for other elements and analyses in progress, will be reported elsewhere.

Table I shows an analysis of hydrated glass separated from sample Y7-196. This is considered representative of the composition of the glass fraction of the samples at early stages of hydrothermal alteration, i.e., following hydration but prior to dissolution or replacement by secondary phases. Also shown in Table I is a whole rock analysis of the vitrophyre from which this glass was separated, representative of the least altered material from the Y7 drill core. By comparison of the two analyses, accounting for the fact that glass comprises 70-80 vol % of the vitrophyre, it is seen that the greatest fraction of seven of the eight nuclear waste elements considered here resides initially in the glass. The exception is Sr, that resides primarily in the plagioclase, where its concentration is about 600 ppm.

The third analysis listed in Table I is of thermal water collected from the bottom of drill hole Y7. Table II lists the concentrations of the elements U, Th, Sr, Zr, Sb, Cs, Ba, and Sm in various secondary minerals separated from Y7 and Y8 flow breccia and tuff samples. A comparison of these data with the thermal water analysis in Table I demonstrates the generally high sorption of these elements by these phases.

Whole rock analyses have been compared to detect significant changes in elemental concentrations due to hydrothermal processes; knowledge of the secondary mineralogy of the samples, in conjunction with other data such as those in Tables I and II, has been used to infer mechanisms of elemental behavior. An important assumption in this analysis is that the primary composition of the Biscuit Basin Flow was homogeneous. This is consistent with all present data for the relatively immobile elements (Ti, Zr, Hf, Th, REE, etc.) from samples of drill cores [this study and 5] and surface outcrops [6]. Nonetheless, slight initial inhomogeneities in composition would not alter the conclusions of this study. It is also noteworthy that water compositions of hot springs in Upper Geyser Basin have not changed significantly since the earliest published analyses in 1888 [7]. The inferred behavior for each element is discussed briefly in the following paragraphs.

Uranium

Figure 1 shows U concentrations vs. depth in hydrated glass, vitrophyre, and matrix from the flow breccia in Y7 and Y8. These data are interpreted to indicate significant hydrothermal addition of U to the Y7 samples, especially in the matrix, between 195 and 225 ft., where U is elevated from

Table I. Representative Analyses of Hydrated Glass, Vitrophyre and Thermal Water

wt %	Y7 196		Y7 240	
	Hydrated Glass*	Vitrophyre*	mg/L	Thermal Water†
SiO ₂	70.8	n.d.	SiO ₂	379
TiO ₂	9.20	0.42	Na	409
Al ₂ O ₃	11.1	11.8	K	91.1
FeO**	1.60	3.05	Ca	4.28
MnO	0.32	0.79	Mg	0.005
MgO	0.10	0.38	Cl	336
CaO	0.62	1.48	HCO ₃	565
Na ₂ O	2.45	2.94	SO ₄	11
K ₂ O	4.83	4.44	F	31.1
H ₂ O	6.93	n.d.	pH	7.64
<u>ppm</u>				
U	5.4	5.1	U	0.0092
Th	24.8	20.7	Th	<0.0006
Sr	40	104	Sr	<0.005
Zr	360	380	Zr	<0.01
Sb	0.11	0.13	Sb	0.028
Cs	4.5	6.0	Cs	0.05
Ba	850	940	Ba	0.012
Sm	11.4	11.6	Sm	<0.0001

*SiO₂ and Al₂O₃ in hydrated glass determined by electron microprobe; Na₂O and FeO** in hydrated glass and vitrophyre by INAA; H₂O by CHN analyzer (I. Fox, analyst); all other major oxides by ICP (E. Huff, analyst).

†Thermal water data other than U, Th, Sr, Zr, Sb, Ba, and Sm provided by J. M. Thompson [5]. U determined by laser fluorimetry (A. Essling, analyst); Th, Sb, and Sm by INAA; and Sr, Zr, and Ba by ICP.

**Total Fe as FeO.

n.d. - Not determined.

Table II. Analyses of Nuclear Waste Elements in Secondary Phases*

ppm	Y7 209CC	Y7 234CP	Y7 239CE	Y7 239CT	Y8 226AN	Y8 273MO
U	0.14	n.d.	3.4	1.42	--	n.d.
Th	0.38	n.d.	7.7	0.96	--	2.0
Sr	74	48	--	16	--	80
Zr	--	n.d.	220	13	--	--
Sb	0.008	n.d.	0.33	0.27	--	--
Cs	0.011	n.d.	8.5	3.01	2900	500
Ba	29	1030	100	220	110	520
Sm	2.27	n.d.	23.9	0.70	0.06	n.d.

*Sample numbers refer to drill hole and depth of sample in feet below surface. Ba and Sr in CC, CE, and AN determined by INAA.

Mineral Abbreviations

CC = Bladed calcite precipitated from boiling water in open fracture.

CP = Clinoptilolite replacing hydrated glass in vitrophyre.

CE = Celadonite precipitated in veinlet.

CT = Beta-cristobalite precipitated on celadonite in veinlet, contains approximately 3 wt % coprecipitated celadonite.

AN = Analcime precipitated in open fracture.

MO = Mordenite precipitated in open pore spaces.

n.d. = Not determined.

Fig. 1. Uranium Concentration vs. Depth in Vitrophyre, Matrix, and Glass Separates from Flow Breccia of Biscuit Basin Flow, Y7 and Y8 Drill Cores, Yellowstone National Park. Note addition of U to Y7 matrix and vitrophyre between 195 and 225 ft. depth.

Fig. 2. Photomicrograph of Fission Track Map (on Muscovite) Showing Extreme Concentration of U on Surfaces of Titanomagnetite. Area of map is within vitrophyre clast, several mm from contact with matrix, in sample Y7 205 (width of view = 1.4 mm).

a primary concentration of 5-7 ppm to as high as 35.2 ppm. Several lines of evidence support this interpretation: 1) the increase in U does not correlate with other (minimal) observed elemental variations in this zone, 2) fission track maps (Figure 2) show extremely high concentrations of U on and near the surfaces of titanomagnetite grains, and locally high concentrations in celadonite, especially in the matrix, in sample Y7 205, whereas this type of U distribution is not observed in sample Y7 238, and 3) U-series isotopic data (work in progress) are consistent with a large addition of U to this zone less than 30,000 years ago. The association of U with titanomagnetite may be explained either by reduction of dissolved hexavalent U by divalent Fe in titanomagnetite, causing local precipitation of less

soluble, more reduced U, or by sorption of uranyl ions on the thin layer of ferric oxyhydroxide that coats the surface of many titanomagnetite grains.

Thorium

The data do not indicate significant mobility of Th in this system. Rocks in which glass is completely replaced by secondary minerals have Th concentrations in the range of relatively unaltered samples. None of the secondary phases analyzed for Th has sufficient Th to account for its observed retention. It is suggested that Th exhibits behavior similar to that of Ti. Ti concentration of celadonite replacing glass in both Y7 and Y8 vitrophyre is 2-20 times that of celadonite precipitated in veins. Thus, Ti released during alteration of glass is nearly quantitatively retained in glass-replacement celadonite, and we infer similar behavior for Th.

Strontium

Sr is gained by many altered samples, showing increases of up to 50%. The increase in Sr is interpreted to be due to the abundance of clinoptilolite and mordenite. Both of these phases have Sr concentrations higher than that of hydrated glass (Tables I and II). The empirical distribution ratio (Rd)* for Sr in Y7 clinoptilolite given by data in Tables I and II is constrained to be greater than 9600. Present data for Y8 water constrain the empirical Rd for Sr in Y8 mordenite to be greater than 8000. Sr is also concentrated in bladed calcite that precipitated during boiling in an open fracture.

Zirconium

The behavior of Zr apparently resembles that of Th.

Antimony

Considerable addition of Sb has been noted in the more altered samples. Sb concentration in Y7 vitrophyre samples is 0.12-0.16 ppm and in Y7 matrix it is slightly elevated at 0.19-0.28 ppm; in Y8 vitrophyre and matrix samples it is 0.25-0.36 ppm. Some of the observed enrichment may be associated with celadonite and cristobalite in these samples, as these phases are relatively high in Sb (Table II), having empirical Rd values near 10. In the pumiceous tuff Sb reaches 3.49 ppm. The highest values in the tuff are in samples adjacent to the larger veins or open fractures; for example, the sample containing the most Sb (Y8 331.2) is cut by a quartz-goethite vein having 5.2 ppm Sb. No specific phase associated with Sb enrichment in the high-Sb tuff samples has yet been identified; therefore, the retardation mechanism for Sb is uncertain.

Cesium

Whole rock Cs concentrations have increased by up to a factor of 50 in samples containing mordenite and analcime. The correlation between Cs and

*The empirical distribution ratio (Rd) is defined as the observed ratio of the concentration of an element in a secondary phase to the concentration of that element in the coexisting thermal water, in units of mL/g.

analclime in these samples was first noted and discussed by Keith et al. [8], who emphasized that Cs is partitioned into analclime during crystallization and is not subject to later exchange. However, we note here the affinity of Cs for mordenite in these samples (Table II), and suggest that mordenite is susceptible to Cs exchange, with an empirical Rd of about 4200 in Y8 (3 times the calculated Kd in Daniels et al. [9]). Samples in which glass is extensively replaced by clinoptilolite (especially Y7 matrix) have as little as 2.5 ppm Cs, compared to relatively unaltered Y7 vitrophyre that has 4.7-6.0 ppm Cs. Thus, as noted by Keith et al. [8], clinoptilolite does not sorb Cs very strongly (relative to Sr and Ba) in these rocks. Celadonite is slightly enriched in Cs relative to hydrated glass (Tables I and II), and has an empirical Rd of about 170 in Y7.

Barium

Although Ba is only a minor component of high level nuclear waste, its behavior is of interest as an analog for Ra. Increases of up to 50% in whole rock Ba concentration are found where glass is extensively replaced by clinoptilolite, such as in Y7 matrix. Analysis of glass-replacement clinoptilolite from Y7 matrix (Table II) indicates that it has significantly more Ba than the glass it replaces. The empirical Rd for Ba in Y7 233.6 clinoptilolite is about 86000, that is 3.7 times the Kd proposed for this mineral at room temperature [9]. However, decreases in whole rock Ba of up to 50% are found in Y8 vitrophyre where glass is extensively replaced by mordenite. Mordenite filling pore space in Y8 273 has 520 ppm Ba, resulting in an empirical Rd of about 26000. Ba is apparently sorbed fairly strongly by all of the secondary phases analyzed (Table II), and similar behavior would be expected for Ra in this system.

Samarium

The data for Sm do not indicate significant mobility. Celadonite precipitated in Y7 has a relatively high Sm concentration (Table II), indicating an empirical Rd of at least 240,000 based on presently available Y7 water data. Calcite deposited by boiling water in Y7 also has considerable Sm. Other rare earth elements exhibit behavior resembling that of Sm.

CONCLUSION

The geochemical data of this investigation show clearly the contrasting behavior of the eight nuclear waste elements considered in this natural hydrothermal system. Th, Zr, and Sm exhibit very low mobility, due to their very low solubilities under the ambient conditions, but are apparently redistributed on a microscopic scale ($<100\ \mu\text{m}$) during alteration of glass to secondary mineral assemblages. It is suggested that, like Ti, these three elements become concentrated in secondary clays during this process. Sr and Ba exhibit significant mobility, and are strongly sorbed by ion exchange on clinoptilolite and mordenite, with empirical Rd values that compare well with those measured in the laboratory [9]. Large gains in whole rock concentrations of U (up to 7X), Sb (up to 30X), and Cs (up to 50X) are observed. The excess U is associated with titanomagnetite by adsorption on a surface coating of ferric oxyhydroxide and/or by local reduction and precipitation of dissolved uranyl ions. The excess Cs is largely present in both analclime (incorporated during precipitation) and mordenite (sorbed by ion exchange), and to a lesser extent in celadonite (sorbed by interlayer ion exchange).

The specific phase(s) associated with the excess Sb has not yet been identified, although both celadonite and cristobalite are seen to concentrate this element slightly. Calcite precipitated during boiling effectively concentrates U, Th, Sr, Ba, and Sm.

The source of the elements added to these rocks is probably similar rocks that were altered at higher temperature. The geochemical retardation processes that have resulted in these additions are seen to be a combination of sorption by physical adsorption, ion exchange, and precipitation. It is anticipated that a deeper understanding of the causes of geochemical zonations in active geothermal systems, derived in part through investigations such as this, will ultimately prove to be of value in issues of nuclear waste management.

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