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URANIUM SERIES ISOTOPE MEASUREMENTS
(University of Southern California)

Preliminary Uranium Series Isotope Measurements from June 1988 Flow Test of the State 2-14 Well.

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Abstract.   A wide range of isotopes in the ^{238}U, ^{235}U, and ^{232}Th decay chains was measured in geothermal brines collected during an extended flow test of the Salton Sea Scientific Drilling Project well (SSSDP). High concentrations of radium, radon, and lead isotopes are generated and maintained by the input of these isotopes from solid phases into brine by both recoil and leaching processes, by the high chloride content of the brine which complexes radium and lead, and by the apparent absence of suitable unoccupied adsorption sites. In contrast, uranium, thorium, actinium, bismuth, and polonium isotopes all have low concentrations due to their efficient sorption from brine to rock.

Introduction

^{238}U, ^{235}U, and ^{232}Th decay to stable isotopes of Pb through a series of shorter-lived intermediate daughters (Figure 1). In a closed system, these daughters grow into secular equilibrium with their parents, so that the daughter/parent activity (disintegration) ratio becomes unity. However, ground water and geothermal waters are not closed systems, but interact with the solid phases they contact. Because of the different geochemical properties of the intermediate isotopes in each chain, significant radioactive disequilibria often exist in these waters, and sometimes in solid phases associated with them. Both thermodynamic and kinetic factors play a role in creating and maintaining these disequilibria, and a number of workers have discussed these factors. Langmuir and his associates have provided recent reviews of the thermodynamic properties controlling the behavior of uranium, thorium, and radium in natural waters [Langmuir, 1978; Langmuir and Herman, 1980; Hsi and Langmuir, 1985; Langmuir and Riese, 1985; and Langmuir and Melchior, 1985]. Others have focused on physical factors, such as recoil during alpha decay [Tanner, 1964; Krishnaswami et al., 1982; Laul et al., 1985; Petit et al., 1985], migration of nuclides along microfractures and grain boundaries [Rama and Moore, 1984], and the possible preferential emplacement of uranium-bearing phases along grain boundaries [Krishnaswami and Seidemann, 1988].

Studies of uranium and thorium series disequilibria are of value for several reason. First, the behavior of actinides and their daughters in thermal saline waters and their associated rocks is pertinent to the management of radioactive waste, as a natural analog of nearfield conditions of radioactive waste repositories in salt

[*Elders and Moody*, 1984]. Second, while studies of saturation states can give insights to possible mineral alterations [*Langmuir and Melchior*, 1985], the radioisotope disequilibria observed in fluid and solid phases are useful for estimating rates of brine-rock interaction. Third, radioactive disequilibria may be useful for estimating parameters of geologic interest in hydrothermal systems, such as brine flow rates, fracture sizes, and ages of vein deposits [*Sturchio and Binz,* 1987; *Zukin et al.*, 1987; *Hammond et al.*, 1988]. The SSSDP well has provided a unique opportunity to study the *in situ* behavior of the naturally occurring U-Th series radionuclides in deep geothermal brines.

Methods

Details regarding the drilling and plumbing system used to produce fluid from the well are described elsewhere [*Michels*, 1986]. Brines were produced from two zones in the well during four separate flow tests. The first sampling occured when the well was 1898 m deep on December 29-30, 1985, with production presumed to come from a fracture zone near the bottom. The second set of samples was collected when the well was 3220 m deep on March 20-21, 1986, with production also originating primarily near the bottom. The third and fourth set of samples were taken during an extended flow test during June 1988, with the third set collected on June 10 and the fourth set collected on June 15, 1988 (Table 1). Because the volume of brine that could be produced during the first two flow tests was limited by the size of a pit built to receive water discharged from the well, only 4000 m^3 could be produced during each test. Measurements of major constituents and stable isotopes suggest that for the first test this brine volume was sufficient to clear the well of fluids introduced during drilling. However, the second flow test showed evidence that the fluid produced contained 5-10% of contaminant material introduced during drilling operation [*Sturtevant and Williams*, 1987]. Our measurements of radioisotopes in the brine should not be noticeably influenced by such contamination, except perhaps for isotopes of U and Th that are present in relatively small concentrations. Another possible complication is that sulfate contamination from drilling fluids may have caused some barite to precipitate during the mixing of brine and drilling fluid, and this barite may have scavenged some radium from solution. While we think this effect shoul be small, it cannot be evaluated. Thus, the radium concentrations measured during the second flow test are lower limits, but measured ratios of radium

isotopes should be accurate. Contamination is assumed to be negligible during the flow test during June of 1988, since discharge from the well was being reinjected and samples were collected after the well had been flowing for several days.

A steel pipe was attached to the wellhead to transport brine and steam to a cooling tower before its discharge into a waste pit. The pipe was fitted with a series of sampling ports separated by orifice plates, providing different pressures and temperatures for sampling the two-phase flow. Samples ports were constructed so that either brine or steam could be withdrawn from the flow line. During the June 1988 flow test samples were collected from a sampling port located just before the entry of the flow into the cyclone separator. Previous work at other SSGF sites has shown that radium and lead concentrations in the brine are not strongly influenced by the flash process [Zukin et al., 1987]. Therefore different locations in this flow line should yield equivalent samples, at least for Ra and Pb. Brine samples were collected by allowing hot brine to flow through a cooling coil immersed in an ice-water bath into a polyethylene container filled with dilute HCl (Table 1). Samples were not filtered, so measurements of uranium and thorium may be upper limits due to possible contamination with particulates transported in the brine [Zukin et al., 1987]. Gas samples for ^{222}Rn analysis were collected by allowing steam to flow through a cooling coil where condensation occurred, and the remaining non-condensable gas fraction was passed into a glass bottle fitted with inlet and outlet tubes.

Analyses for isotopes in the brine were carried out as described by Zukin et al. [1987] (Table 2), with some modifications. The CO_2 fraction in the gas sample was measured using gas chromatography, and the radon fraction using alpha scintillation techniques. The brine radon concentration was then calculated from the measuredRn/CO_2 ratio and in situ CO_2 concentration [Michels, 1981]. Results from the June 1988 flow test were calculated using the the same value for in situ CO_2 concentration as the earlier flow tests, and therefore the conentrations may have to be adjusted, but the radium ratios will be unaffected. ^{223}Ra was determined from gammas emitted by its short-lived daughters ^{219}Rn and ^{211}Pb at 401 and 405 Kev from the $BaSO_4$ precipitate collected for analysis of ^{228}Ra and ^{224}Ra (about 300 ml brine used). The ^{210}Po results are upper limits, based on an anlysis for ^{210}Po made about 0.5 days afetr sample collection. The ^{210}Po was calculated assuming that no ^{210}Bi was present initially. Pb isotope results for the June 1988 samples are not

available yet since ^{210}Pb ingrowth is necessary. In addition [227]Ac requires an ingrowth period approaching one year before measurement.

When more than one sample was taken for analysis of a constituent, the results given represent the average, weighted by the uncertainty of individual analyses. All uncertainties quoted are $\pm$ one standard deviation, derived from counting statistics. Data for the first two flow test have been corrected for evapoative losses (5-15%) prior to collection, based upon estimates of the flash fraction for different sample ports [Michels, 1986]. Results are reported as isotope activities (disintigration rate) in the brine in situ.

Results

Our results (Table 3) from the SSSDP brines generally corroborate those reported previously for saline hydrothermal systems. The measurements obtained are similar to those for other portions of the Salton Sea Geothermal field [Zukin et al., 1987], and, consequently, this discussion will include only a brief summary of the geochemistry of uranium and thorium series isotopes in saline, reducing hydrothermal waters. The June 1988 samples have lower concentrations for most isotopes, with the exception of [222]Rn and [223]Ra which had similar concentrations to the SSSDP1&2 flow tests. Until we can rule out contamination or reaction with the casing we will not attempt to interpret these difference, although they may be real. The concentrations of uranium and thorium are low, and the [234]U/[238]U ratio is also low in comparison to most groundwaters [Hammond et al., 1988]. The low uranium concentration suggests that uranium is in the +4 valence, and low uranium isotope ratio indicates either that uranium exchanges rapidly between brine and rock, or that measurements are biased by incorporation of rock fragments in samples [Zukin et al., 1987]. In contrast, radium concentrations are 1000-10000 times greater than those of their parents. These high concentrations must be maintained by input from surrounding solid phases. The persistence or radium in solution probably reflects complexation with chloride [Langmuir and Riese, 1985; Hammond et al., 1988]. Lack of suitable adsorption sites may also maintain the high concentrations that are observed [Langmuir and Melchior, 1985]. It is also possible that Ra concentrations are related to elements forming sulfides [Hammond et al., 1988]. Radon concentrations have an activity comparable to, or greater than those of its parent [226]Ra, suggesting that dissolved radium greatly exceeds

both adsorbed radium and that located within recoil range of solid surfaces [*Laul et al.*, 1985; *Zukin et al.*, 1987]. Some daughters of these isotopes(^{228}Ac, ^{228}Th, ^{210}Po) are much lower in concentration, reflecting the low solubilities of these elements and their rapid sorption from solution. In summary, in SSGF brines, radium, radon and lead are quite soluble while uranium, thorium, actinium, polonium, and bismuth have much lower solubilities.

Several samples were collected for radium analyses at different times during the flow tests, and the isotope ratios observed are of interest (Table 4). The ^{224}Ra/^{228}Ra ratio was uniform during the second flow test, although the ratio observed in each flow test is different. The lack of change in this ratio during the 14 hours of the second flow test indicates that the values of less than one that were observed here and in the nearby Fee wells [*Zukin et al.*, 1987] were not a transient effect due to intiation of flow, but must reflect steady stae *in situ* values. Formation water should have ^{224}Ra/^{228}Ra $\geq$ 1.17 if alpha recoil is the only mechanism for radium input [*Krishnaswami et al.*, 1982]. If the system is in a dynamic equilibrium, the low ratios observed here must reflect the importance of one or more of the following effects: (1) weathering of solids, (2) growth of crystals that incorporate ^{228}Th to depths comparable to the recoil range, so that the fraction of ^{224}Ra recoiled into solution from the sorbed ^{228}Th is less than the 50% expected, or (3) recoil input that is limited by slow diffusion down microfactures. The variation in ^{228}Ra/^{226}Ra ratios observed during the the 1986 and 1988 flow tests exceeds analytical error, but the cause of this variation is not apparent. It is possible that flow from multiple zones with different ratios of radium isotopes occurred during these tests, and the relative contributions from these zones varied with time.

Summary

Sampling and analyses of brines from the Salton Sea Geothermal Field have produced data for the distribution of the natural radionuclides of the ^{238}U and ^{232}Th decay series. The data are of potential use to the prediction of the behavior of radwaste radionuclides stored in geological repositories such as salt beds. The behavior of uranium and thorium series isotopes in brines from the SSSDP well is very similar to that expected in a high temperature, high salinity brine. Uranium, thorium, actinium, bismuth, and polonium are all relatively insoluble, indicating their rapid sorption from solution. In contrast, radium, lead, and radon are all found in

high concentrations. These high concentrations reflect the importance of weathering, leaching, and recoil inputs of these elements into brine from adjacent solid phases, complexing of radium and lead by chloride which helps keep these elements in solution, and lack of suitable unfilled adsorption sites capable of removing these elements from solution.

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Table 1. Sample Inventory of Geothermal Brines Collected During
June 1988 Flow Test

ID[a]	Time of sampling	Acid added(l)	Sample wt (kg)[b]	Spikes Added	Desired Analysis
3-3	1700	1	1.43	none	Ra isotopes
3-4	1700	none	2.17	none	^{222}Rn
4-53a	1848	1	2.2	none	Ra isotopes
4-106	1849	.25	.3	none	^{226}Ra
4-45	1850	4.5	12.5	^{232}U,^{228}Th	^{238}U,^{234}U, ^{232}Th,^{230}Th
4-B2	1853	1.1	2.49	^{208}Po,^{230}Th	^{210}Po,^{228}Th
4-1	1900	.25	.3	none	^{226}Ra
4-52a	1903	1	2.36	none	Ra isotopes
4-3	1915	none	2.17	none	^{222}Rn
4-2	1916	none	2.17	none	^{222}Rn
4-111	1936	.245	.?5	^{229}Th	^{228}Ac,^{212}Pb
4-108	1938	.25	.3	none	^{226}Ra
4-B3a	1940	.07	3.7	^{229}Th	^{228}Ac,^{212}Pb
4-B1	1943	1.1	2.4	^{208}Po,^{230}Th	^{210}Po,^{228}Th

a) ID# = date-sample#(3- 6/10/88, 4- 6/15/88).
b) Wt. for gases is volume in liters STP.
Line conditions P= 17.9 atm and 212 °C.

Table 2. Uranium and Thorium Series Isotopes Measured in the
SSSDP Well Brine Samples

Isotope Measured	Method of Analysis
^{238}U	Alpha-spectrometry
^{234}U	Alpha-spectrometry
^{232}Th	Alpha-spectrometry
^{230}Th	Alpha-spectrometry
^{228}Th	Alpha-spectrometry
^{228}Ra	Gamma-spectrometry
^{228}Ac	Gamma-spectrometry
^{227}Ac	Alpha-spectrometry
^{226}Ra	Alpha Scintillation/^{222}Rn ingrowth
^{224}Ra	Gamma-spectrometry
^{223}Ra	Gamma-spectrometry
^{222}Rn	Alpha Scintillation
^{212}Pb	Gamma-spectrometry
^{210}Pb	Alpha-spectrometry/^{210}Po ingrowth
^{210}Po	Alpha-spectrometry
^{210}Bi	Alpha-spectrometry

Table 3. Uranium and Thorium Series Isotopes in the SSSDP Brine Samples

Isotope	SSSDP-1 dpm/kg	n	SSSDP-2 dpm/kg	n	SSSDP-3 dpm/kg	n	SSSDP-4 dpm/kg	n
^{238}U	0.071(4)	1	0.033(4)	2	-		0.018(7)	1
^{234}U	0.077(5)	1	0.038(4)	2	-		0.026(10)	1
^{230}Th	0.043(6)	1	<0.020	1	-		<0.008	1
^{226}Ra	2190(80)	2	1060(50)	2	526(10)[a]	1	526(10)	3
^{222}Rn	2130(150)	2	2600(1400)	3	1811(96)	1	2038(74)	2
^{210}Pb	3260(115)	2	3220(80)	2	-		-	2
^{210}Bi	<740	1	<1370	1	-		-	
^{210}Po	<0.95	1	<2.8	2	-		<1.15	2
^{232}Th	0.007(4)	1	<0.007	1	-		<0.008	1
^{228}Ra	1120(60)	2	720(40)	4	244(27)	1	329(14)	2
^{228}Ac	250(170)	1	150(90)	1	-		301(86)	2
^{228}Th	0.58(4)	1	0.41(3)	2	-		0.57(6)	2
^{224}Ra	1010(60)	2	540(30)	4	292(17)	1	356(15)	2
^{212}Pb	2250(280)	1	1440(140)	1	-		-	2
^{223}Ra	6(31)	2	11(7)	4	23(10)	1	15(9)	2

Data has been corrected to pre-flash conditions, based on temperature and pressure at the sample port. The flow tests were carried out at 1898 m and the second flow test also sampled fluids from 3220 m. The analytical uncertainties in the last digit ($\pm 1\sigma$ from counting statistics) are shown in parenthese, and the numbers of samples analyzed are given as n. If more than one analysis was made, averages were weighted by the analytical uncertainties in each measurement. Radium activities for SSSDP-3 are calculated from the average of the SSSDP-4 ^{226}Ra values and measured Ra activity ratios.

Table 4. Radium Concentrations (as Activities) Observed at Different Times During SSSDP Flow Tests

Sample	Date	Time	^{226}Ra (dpm/kg)	$\dfrac{^{228}Ra}{^{226}Ra}$	$\dfrac{^{224}Ra}{^{228}Ra}$	$\dfrac{^{223}Ra}{^{226}Ra}$
SSSDP-1- 4	12-29-85	1600	2040(90)	--	--	--
-14	12-29-85	1710	2450(120)	0.51(1)	0.93(3)	0.017(27)
-18	12-30-85	1200	--	0.51(1)	--	0.001(15)
Average			2190(80)	0.51(1)	0.93(3)	0.003(18)
SSSDP-2-26	3-20-86	2210	--	0.64(1)	0.74(2)	0.020(27)
-28	3-21-86	0050	--	0.70(1)	0.74(2)	0.025(13)
-37	3-21-86	1120	1150(60)	0.75(2)	0.77(2)	0.002(9)
-45	3-21-86	1210	1020(50)	0.64(1)	0.77(2)	0.008(16)
Average			1060(50)	0.68(1)	0.76(2)	0.010(13)
SSSDP-3- 3	6-10-88	~1700	--	0.48(1)	1.12(3)	0.046(19)
SSSDP-4-53a	6-15-88	1848	500(22)	0.56(1)	1.36(4)	0.013(32)
-52a	6-15-88	1900	613(14)	0.83(1)	0.80(2)	0.037(21)
-108	6-15-88	1938	398(18)	--	--	--
Average			526(10)	0.70(1)	0.91(2)	0.030(18)

Uncertainties in the last digits ($\pm$ 1σ, derived from counting statistics) are given in parentheses. Averages are weighted means.

238U series **232Th series** **235U series**

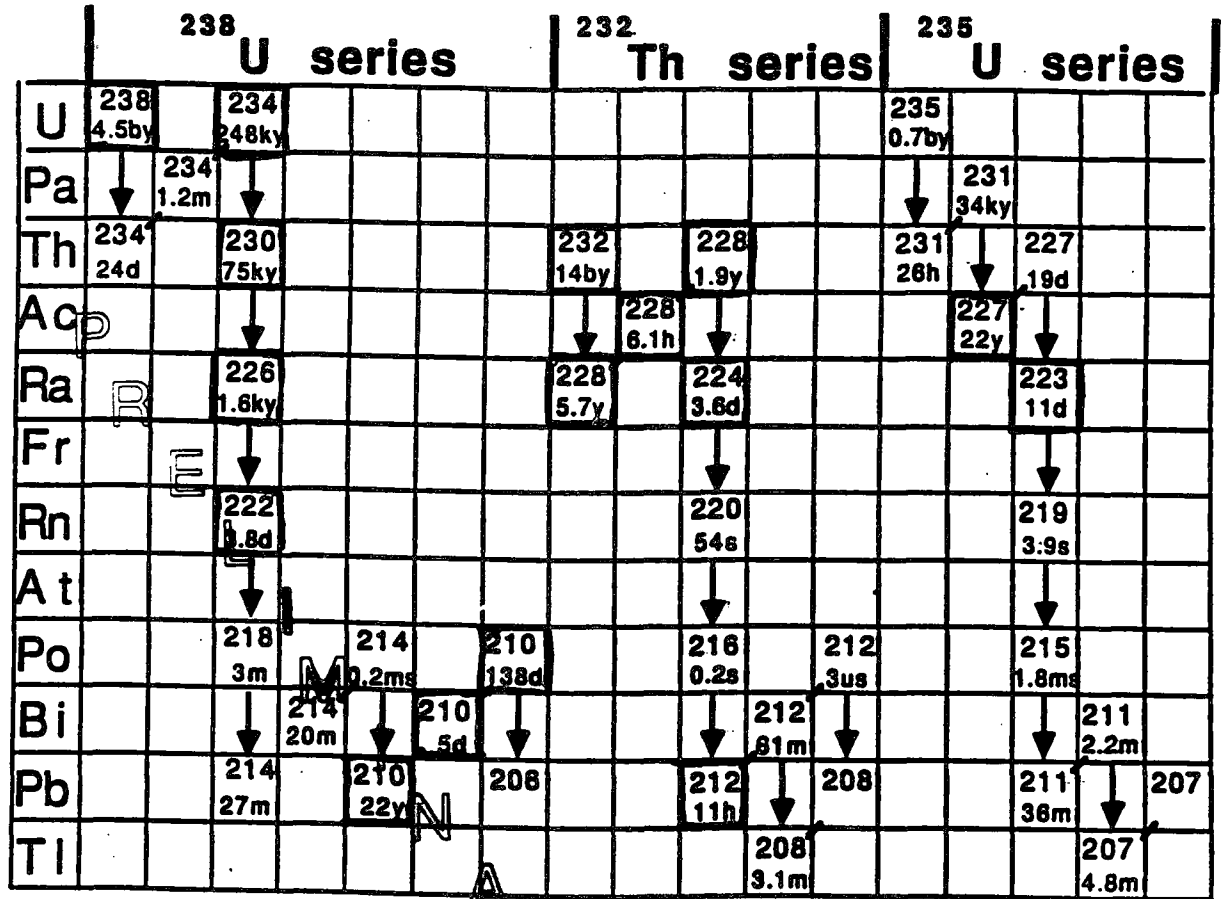| Element	Isotopes (mass number / half-life)
U	238 (4.5by); 234 (248ky); 235 (0.7by)
Pa	234 (1.2m); 231 (34ky)
Th	234 (24d); 230 (75ky); 232 (14by); 228 (1.9y); 231 (26h); 227 (19d)
Ac	228 (6.1h); 227 (22y)
Ra	226 (1.6ky); 228 (5.7y); 224 (3.6d); 223 (11d)
Fr	
Rn	222 (3.8d); 220 (54s); 219 (3.9s)
At	
Po	218 (3m); 214 (0.2ms); 210 (138d); 216 (0.2s); 212 (.3us); 215 (1.8ms)
Bi	214 (20m); 210 (5d); 212 (81m); 211 (2.2m)
Pb	214 (27m); 210 (22y); 206; 212 (11h); 208; 211 (36m); 207
Tl	208 (3.1m); 207 (4.8m)

Figure 1. The uranium and thorium decay series. Isotopes measured in this study are bordered by heavy lines. The mass number and half-life for each isotope are given.. Vertical arrows indicate alpha decays, and short diagonal bars indicate beta decays.