Application of radium isotopes to determine crustal residence times of hydrothermal fluids from two sites on the Reykjanes Peninsula, Iceland

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Abstract

Radium isotopes were used to determine the crustal residence times of hydrothermal fluids from two geothermal wells (Svartsengi and Reykjanes) from the Reykjanes Peninsula, Iceland. The availability of rock samples from the subsurface (to depths of 2400 m) allowed direct comparison of the radium isotopic characteristics of the fluids with those of the rocks within the high temperature and pressure reaction zone. The ^{226}Ra activity of the Svartsengi fluid was ~one-fourth of the Reykjanes fluid and the $^{228}Ra/^{226}Ra$ ratio of the Svartsengi fluid was ~twice that of Reykjanes. The fluid isotopic characteristics were relatively stable for both sites over the 6 years (2000–2006) of the study. It was determined, using a model that predicts the evolution of the fluid $^{228}Ra/^{226}Ra$ ratio with time, that both sites had fluid residence times, from the onset of high temperature water–rock reaction, of less than 5 years. Measurement of the short-lived ^{224}Ra and ^{223}Ra allowed estimation of the recoil input parameter used in the model. The derived timescale is consistent with results from similar studies of fluids from submarine systems, and has implications for the use of terrestrial systems in Iceland as an exploited energy resource.
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1. INTRODUCTION

The submarine ridge system that winds through 60,000 km of the deep ocean floor can be described as an "extended volcano" which produces new oceanic crust on a global scale. Hydrothermal systems within the ridge environment have been the focus of much study since their discovery at the Galapagos Spreading Center in 1977 (Corliss et al., 1979) and there remains considerable interest in the potential impact of these systems on global chemistry and biology. There was early recognition that seafloor hydrothermal systems impact the ocean chemistry of numerous elements (e.g. Edmond et al., 1979, 1982) and more recently, discovery of microbiological communities within the ocean crust has suggested the potential of this environment to harbor an extensive "subsurface biosphere" (e.g. Gold, 1992; Deming and Baross, 1993).

One of the keys to understanding the fluid flow, chemistry, and the associated microbial life within these hydrothermal systems is knowledge of the convective path length and crustal residence time of the circulating fluid. The reaction of seawater with basalt within the hydrothermal systems at mid-ocean spreading centers produces significant change in the chemical and isotopic character of seawater. Among other factors (Von Damm et al., 1985) such as temperature, extent of phase separation, rock type, degree of prior alteration (i.e. the maturity of the system) that control the composition of the exiting high temperature fluids, the convective path length and crustal residence time determine the extent of phase equilibrium and timescales over which components required for sustaining microbial life can be synthesized. Where such systems

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manifest themselves subaerially, and are exploited for energy as in Iceland, knowledge of residence time allows insight into aquifer lifetime and recovery.

Over the past twenty years, techniques have been developed for estimating these timescales by utilizing naturally occurring radioisotopes analyzed in hydrothermal material sampled from the seafloor (Kadko et al., 1985/1986; Turekian and Cochran, 1986; Kadko and Moore, 1988; Grasty et al., 1988; Stakes and Moore, 1991; Kadko, 1996; Kadko and Butterfield, 1998). Similar methods have also been applied to continental thermal areas displaying diverse chemical and physical properties (e.g. Zukin et al., 1987; Hammond et al., 1988; Clark and Turekian, 1990; Sturchio et al., 1993). For marine systems, these techniques are based on comparison of the isotopic character of the venting fluids with that of the subsurface rocks with which they react at high temperature and pressure. This emphasizes the importance of appropriate rock samples to accurately assess initial isotopic ratios in the high temperature water–rock reaction zone. However, in submarine studies, the subsurface is inaccessible, and the necessary use of seafloor rock samples (e.g. Kadko and Butterfield, 1998) has relied on the assumption that they represent the isotopic character of rocks greater than 1 km depth.

Here, we apply these techniques to two hydrothermal systems on the Reykjanes Peninsula in Iceland, a subaerial portion of the Mid-Atlantic Ridge. These systems are dominated by seawater flow, but are far more accessible than submarine systems with ready availability of both fluid and importantly, sub-surface rock substrate samples. The availability of subsurface samples for comparison to fluids represents a major advance over similar studies in submarine ridge investigation. Additionally the geology, geochemistry and mineralogy of Iceland have been well studied. These considerations allow methods used on the seafloor to be applied to Icelandic systems and be refined and tested for further application to seafloor studies.

2. BACKGROUND

2.1. Geothermal systems in Iceland

The Icelandic rift zones are part of the oceanic rift system with the consequence that the geologic and tectonic conditions observed in Iceland closely parallel those of the sea floor ridges. Continuous tectonic and magmatic activity facilitates the circulation of groundwater and seawater through the Icelandic crust that is basically oceanic in character, though generally thicker. Geothermal fields in Iceland are widespread; the water circulation extracts heat from the crust with the highest temperatures observed in the present day rift/volcanic zones and lower temperatures on the flanks. The geologic setting of the high-temperature geothermal areas, logging of presently active areas, and the internal structure of fossil systems of this kind in Tertiary and Quaternary formations, show that like seafloor systems, the heat sources are shallow (1–3 km) magma intrusions (Arnórsson, 1995 and references therein). Furthermore, heating of the convecting groundwater most likely involves its penetration into a permeable boundary that advances into the intrusive bodies by a process of cooling and cracking (Bjornsson et al., 1980, 1982) in a manner analogous to that postulated for seafloor systems (e.g. Lister, 1974). Recently, high-temperature hydrothermal vents (250 °C) and massive anhydrite deposits were found in shallow water (400 m) just 30 km off the northern coast of Iceland, with mounds and chimneys resembling deposits at sedimented seafloor ridges (Hannington et al., 2001). The most significant difference between Icelandic and deep-sea systems is that for submarine systems, pressure at 3 km water depth enables fluids to escape the seafloor at temperatures of over 320 °C, while fluids on Iceland cannot exceed 100 °C upon venting. This explains why black smoker type of activity in Iceland has only been exceptionally observed associated with intrusive activity. Another difference is that most geothermal systems in Iceland are fed by meteoric water, although others, like those on the plate boundary at the Reykjanes Peninsula, are fed by seawater and represent a close parallel to seafloor systems differing mainly in pressure. In this work we compare two systems on the Reykjanes Peninsula; a purely seawater fed area (Reykjanes) with one composed of approximately 71% seawater and 29% meteoric sources (Svartsengi).

The high temperature Icelandic areas, as the seafloor systems, are clearly driven by recent and continuous rifting and intrusive magmatic activity—with most of the high temperature fields practically on the crustal plate boundary (Arnórsson, 1995). Twenty such high temperature areas have been identified in Iceland, and all are located in active rift zones, with heat derived from magmatic intrusions found typically at the depth of about 1.5 km. Five of these areas are presently exploited by extensive drilling to depths of 2000 m.

Heat extraction from the intrusions is effective because of the brittle and porous nature of the upper crust, as is evident by the extensive hydrothermal alteration seen in fossil intrusive bodies (out of the active rift zones) exposed by erosion. Hydrogeologic considerations favor that convection is density driven and the source water for recharge is shallow groundwater in the vicinity of these systems (Arnórsson, 1995). In this regard, these systems are similar to the submarine systems in that the fluid flow results from localized circulation. However, permeability is quite variable between drilled high temperature areas, ranging over two orders of magnitude (1–150 millidarcies), and in part is reflected in substantial differences in pressure potential between sites. These different characteristics might be reflected in fluid circulation times, but the crustal residence time of these fluids in Iceland have yet to be determined.

3. METHODS

3.1. Sampling sites

The two high temperature areas, Reykjanes and Svartsengi, are situated near the tip of the Reykjanes Peninsula which forms the on-land continuation of the Reykjanes Ridge (Fig. 1). They are both exploited for electricity and hot water production with a number of drill holes in both areas. Svartsengi has been extensively exploited since 1976
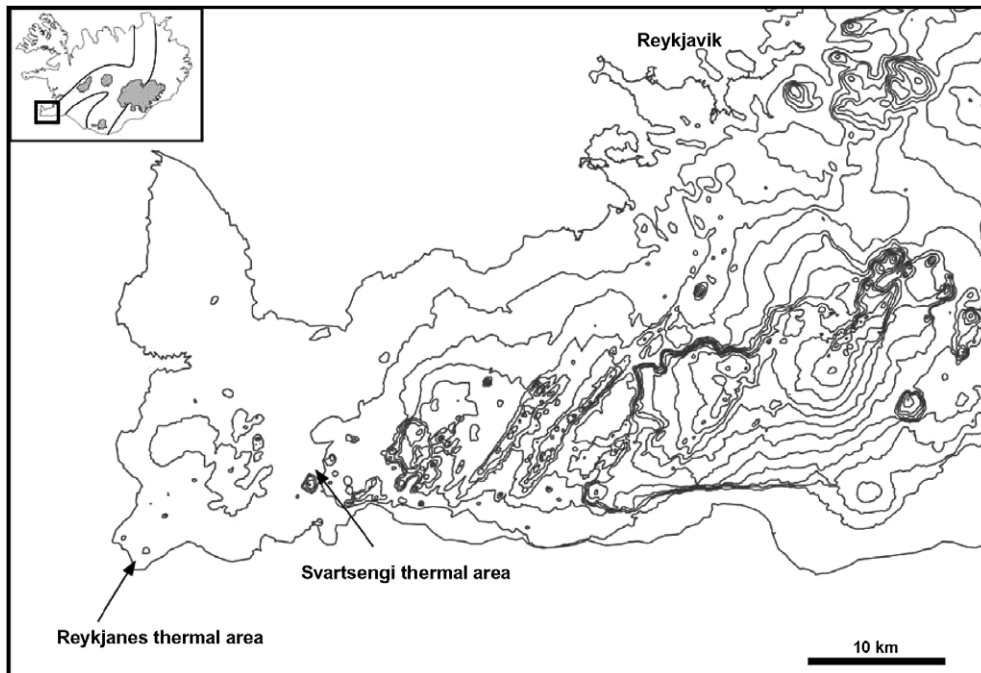
Fig. 1. Map showing the location of the Reykjanes and Svartsengi thermal areas on the Reykjanes Peninsula, Iceland.

but Reykjanes much less so until very recently. Both areas have surface manifestations of fumaroles and alteration of less than 2 km^2 but the thermal area broadens with depth.

The Reykjanes Peninsula is low lying (less than 40 m asl) and due to the highly faulted and porous nature of the rocks precipitation enters the groundwater with no surface streams in most of the peninsula. This results in a freshwater lens that is less than 30 m thick at the Reykjanes thermal area at the tip of the peninsula and about 60 m at Svartsengi, but thickening rapidly inland to the east (Sigurðsson, 1985). The fresh water lens is underlain by sea water.

Each thermal area sits at the center of swarms of active faults that facilitate hydrologic convection. Intrusions occur below about 1500 m depth. The reservoir rocks in both areas are basaltic lava flows and hyaloclastites (tuffs and breccias). The original composition is MORB-like basalts (olivine tholeiites). These have undergone extensive hydrothermal alteration and the mineralogy reflects increasing temperature with depth—with zeolites near the surface, succeeded by a mixed layer clay zone, chlorite–epidote zone and finally epidote–actinolite in the hotter Reykjanes area. Summaries of the subsurface geology and mineralogy in these regions have been made (Ragnarsdóttir et al., 1984; Lonker et al., 1993; Fridleifsson and Albertsson, 2000).

The drillholes in both areas range from 1000 to over 2500 m. They are all rotary drilled so there are no cores available but drill cuttings are sampled every 2 m during drilling. These are then used to establish the nature of the original rock type and the alteration zoning. The location and productivity of individual aquifers is estimated from the loss of circulating fluid during drilling. Casing is concreted into the holes to depths ranging from 400 to 800 m thus blocking off all aquifers shallower than that depth.

In some holes a slotted liner is inserted below the casing down to the bottom.

Borehole RN-12 in Reykjanes was drilled in 2002 and is 2500 m deep. Casing extends to a depth of 841.7 m. Loss of circulating fluid and down-hole temperature measurements indicate a number of aquifers from 980 to 2207 m with the bottom ones dominating. The reservoir temperature of RN-12 is estimated at 295 °C, but this temperature varies between 260 and 310 °C throughout the Reykjanes field (H. Franzson, personal communication). The borehole diameter is $12\frac{1}{4}''$ and no liner was put in. Borehole SV-19 at Svartsengi was drilled in 1998 down to 1600 m with casing down to 715 m and a 9.625″ liner down to 1574 m. Aquifers extend from 750 to 1560 m. The reservoir temperature is about 240 °C, similar to most of the Svartsengi drillholes (H. Franzson, personal communication). Since exploitation started in Svartsengi in 1976 there has been a marked pressure drop within the field accompanied by a drop in the water table by about 320 m. This has lowered the boiling surface from about 400 m to about 700 m forming a steam saturated cushion above 700 m.

3.2. Fluid analysis

Radium isotopes were collected by slowly (∼0.5 L/m) draining water pumped from the borehole through a copper tube filled with manganese—coated acrylic fibers. It has been shown that these fibers adsorb radium isotopes quantitatively, efficiently, and without fractionation (Moore et al., 1985). Initially, up to 200 L of fluid were drained through the fibers but it became apparent that as little as ∼20 L were sufficient to provide reasonable count rates above background.

The fibers were analyzed for the short-lived ^{224}Ra ($T_{1/2} = 3.64$ d) and ^{223}Ra ($T_{1/2} = 11.1$ d) within several days of sampling by counting their daughters with delayed coincidence scintillation detectors (Moore and Arnold, 1996). Subsequently, the fibers were packed and sealed within plastic petrie dishes and the ^{228}Ra and ^{226}Ra were determined by measurement of their daughters by gamma ray spectrometry (e.g. Michel et al., 1981). All counting systems are calibrated with known radioactive NBS sources in a geometry that matches that of the fiber samples. To check the absolute value of the radium isotopes ^{226}Ra was analyzed in separate water aliquots by the radon emanation method (Mathieu et al., 1988; Kadko and Butterfield, 1998).

The inorganic fluid chemistry of Reykjanes and Svartsengi is based on analysis done at The Iceland GeoSurvey (ISOR) (Bjarnason, 1996, 2002). In addition, we analyzed representative samples of the RN12 and SV19 wells for major and minor elements by ion chromatography, atomic absorption and ICPMS (methods described in Butterfield et al., 2004). These results are in good agreement with the ISOR results.

3.3. Rock analysis

Approximately 80 g of chips were sealed in a plastic petrie dish, and subsequently analyzed by gamma ray spectrometry as described above for the fiber samples. Each rock sample was counted on two different detector systems to check for precision.

3.4. Modeling fluid residence time

The activity of ^{228}Ra ($T_{1/2} = 5.77$ years) has been modeled as a chronometer for the time that the fluid has resided under high temperature conditions of the crust. It is normalized to the long-lived ^{226}Ra ($T_{1/2} = 1622$ years), which mitigates the effect of secondary removal processes such as precipitation. The ratios are thus more accurate indicators of aging (e.g. Kadko and Butterfield, 1998).

In the basic model of hydrothermal circulation (e.g. Bischoff, 1980; German and Von Damm, 2005) the convective circulation of the hydrothermal fluids consists of downwelling limbs of cold seawater that become heated at depth in proximity to magma chambers beneath the ridge axis. Under these high temperature and pressure conditions extensive fluid–rock reactions occur. The heating of the fluid is ultimately limited by increasing expansion and buoyancy, but achieves such elevated temperature and low pH that it can solubilize tens of parts per million of heavy metals, numerous radionuclides, and H_2S from rocks. The recharge area for the seawater is probably large with respect to fluid discharge zones, and the recharge flow is low compared to the discharge rate.

The circulating fluid adopts the ^{228}Ra/^{226}Ra ratios of the basalt upon the initiation of basalt alteration, where extraction of heavy metals from the rock into the hydrothermal fluid occurs. These ratios will evolve as a function of time until the fluid is sampled at the surface. The time rate of change of these ratios will depend on the decay rate of ^{228}Ra and the

supply, or production rate of the nuclide in the system. The residence time of the hydrothermal fluid or "clock" is defined here as the time elapsed between the onset of basalt alteration and discharge at or near the surface.

Models describing the behavior of radionuclides in terrestrial groundwater systems can be applied to the fluid-basalt interaction occurring within the convective hydrothermal system at mid-ocean ridges. Krishnaswami et al. (1982) applied a steady-state equation to naturally occurring radionuclides in terrestrial aquifers:

$$\partial C/\partial t = P - \lambda C + k_2 C^* - k_1 C = 0 \qquad (1)$$

where

C = concentration of nuclide in solution (atom kg^{-1});
C^* = concentration of nuclide adsorbed on aquifer solids, per unit volume of fluid (atoms kg^{-1});
P = supply rate of nuclide to solution (atoms min^{-1} kg^{-1});
t = time (min^{-1});
λ = radioactive decay constant (min^{-1});
k_1, k_2 = adsorption and desorption rate constants, respectively (min^{-1}).

Krishnaswami et al. (1982) used a steady-state solution for terrestrial groundwater systems. However, for convective hydrothermal systems, steady state may not be attained for all isotopes because for a particular pressure, temperature and chemical environment, the residence time of the hydrothermal fluid may be short compared to the decay rate of the nuclide of interest. Therefore, $\partial C/\partial t$ will not be equal to zero in the formulation described here. Relating C^* and C by a distribution coefficient, K, the non-steady state solution in terms of dissolved isotope activity A is:

$$A = [\lambda/(\lambda - k_2 K + k_1)] \cdot P[1 - \exp(-\lambda + k_2 K - k_1)t] \qquad (2)$$

where $A = (\lambda C)$ and $C^* = KC$

As described in earlier work (e.g. Kadko and Moore, 1988; Kadko and Butterfield, 1998), the effects of adsoption can be ignored under the high temperature, saline, and low pH of water–rock interaction in seafloor hydrothermal systems. Eq. (2) can therefore be simplified to:

$$A = P(1 - e^{-\lambda T}) \qquad (3)$$

where T = crustal residence time of the fluids as previously defined.

Because the systems at Reykjanes are high temperature, low pH and marine dominated the same approach is used here.

Radium-228 is produced by the decay of its parent ^{232}Th ($T_{1/2} = 1.39 \times 10^{10}$ years) and ^{226}Ra by the decay of ^{230}Th ($T_{1/2} = 7.5 \times 10^4$ years). Input (P) of radium isotopes to the hydrothermal fluid results from the sum of: (P_i) in-situ decay of their parents in solution. (P_{ii}) input from basalt alteration by the corrosive hydrothermal fluid. (P_{iii}) recoil into the fluid from decay of their parent in the basalt. In this model, the hydrothermal fluid will initially adopt the ^{228}Ra/^{226}Ra ratio of the basalt at the onset of high temperature basalt alteration. If the residence time of a fluid is short relative to the half-life of ^{228}Ra, then the ^{228}Ra/^{226}Ra

ratio of the fluid will be similar to the ratio in the basalt. If the residence time is long, then a combination of radioactive decay and the above input mechanisms will cause the $^{228}Ra/^{226}Ra$ fluid ratio to progressively depart from the basalt value.

(P_i): In-situ production (P_i) can be readily determined by measuring the activity of parent in solution. For both radium isotopes in-situ production (^{228}Ra from ^{232}Th and ^{226}Ra from ^{230}Th) is negligible because of the very low activities of the parent nuclides in solution (Chen et al., 1986).

(P_{ii}): Input by high temperature basalt alteration (P_{ii}) can be evaluated by examination of the $^{228}Ra/^{226}Ra$ ratio of basalts from the spreading centers. Prior work relied on measurements of the $^{228}Ra/^{226}Ra$ ratio (or the $^{232}Th/^{230}Th$ ratio assuming radium–thorium secular equilibrium) from rocks collected near the seafloor with the assumption that these were similar to subsurface values, and thus representative of the initial basalt $^{228}Ra/^{226}Ra$ ratio that circulating hydrothermal fluids would adopt at depth in the high-temperature reaction zone (Grasty et al., 1988; Kadko and Moore, 1988; Stakes and Moore, 1991). However observations of excess ^{226}Ra over ^{230}Th in young axial lavas indicate that radium is more incompatible than thorium in magmas (e.g. Rubin and Macdougall, 1988, 1990; Volpe and Goldstein, 1993; Lundstrum et al., 1995; Kokfelt et al., 2003). Thus, assumptions of radium–thorium secular equilibrium and constancy of $^{228}Ra/^{226}Ra$ ratio with depth are not necessarily valid. Here, the ready availability of subsurface samples has allowed a more accurate assessment of the initial ratio. The input of the radium isotopes as a result of the high-temperature water–rock reaction is given by

$$P_{ii} = A^* / W \cdot T \cdot \lambda \cdot 10^{-3} \qquad (4)$$

where

A* = activity of nuclide in basalt (dpm g^{-1});
W = water–rock ratio (mass of fluid participating in reaction with a given mass of rock, g g^{-1}).

Because λ is in the denominator of Eq. (4), nuclide input through rock alteration is of greatest significance for the longer-lived species.

(P_{iii}): The most uncertain of the production terms is the recoil input, P_{iii} (Kadko and Moore, 1988; Kadko and Butterfield, 1998). It has been suggested that the recoil supply rate of all alpha decay products can be approximated by the ^{222}Rn activity in solution (Krishnaswami et al., 1982). Radon-222, a short-lived species ($T_{1/2} = 3.85$ d) is emplaced predominately by recoil from its parent ^{226}Ra. Input by rock alteration (Eq. (4)) is unimportant for nuclides with short half-lives (Krishnaswami et al., 1982; Dymond et al., 1983). Steady-state is rapidly approached for the short-lived radon activity such that the activity (dpm/kg) will equal the recoil input (atom/min kg):

$$A_{Rn\text{-}222} = P_{iii} \qquad (5)$$

Krishnaswami et al. (1982) suggest that because the U series is more or less in secular equilibrium in the basalt, then the recoil supply of all products of alpha decay should be within a factor of two of the recoil supply of ^{222}Rn. Then, the recoil supply of ^{226}Ra would equal the ^{222}Rn activity and the ^{228}Ra recoil supply rate would equal [^{222}Rn activity $\times$ $^{232}Th/^{230}Th$ activity ratio of the basalt]. However, unlike the chemically inert radon, non-gaseous, reactive nuclides (Th, Pb, Ra) could be involved in secondary reactions or adsorbed onto crystal grains (Rama and Moore, 1984). While the high temperature, low pH conditions here likely mitigate this possibility, the use of the ^{222}Rn activity as an estimate of the recoil input could lead to an overestimate of this parameter. These discussions have been recently summarized by Porcelli and Swarzenski (2003). The use of ^{224}Ra ($T_{1/2} = 3.64$ d) might provide a better estimate for the model recoil parameter, as it is an isotope of radium with a half-life similar to that of ^{222}Rn. However it too could be susceptible to secondary precipitation reactions. The ^{224}Ra is produced from the alpha decay of ^{228}Th ($T_{1/2} = 1.9$ years), which is in turn produced by ^{228}Ra decay. Assuming that there is little ^{228}Th in solution, any ^{224}Ra activity in the circulating fluid is produced from recoil from rock. If the Krishnaswami model is correct, then the $^{224}Ra/^{222}Rn$ activity ratio should equal the basalt ratio of $^{228}Ra/^{226}Ra$. For a study on the Juan de Fuca Ridge in the NE Pacific, the recoil efficiency of ^{224}Ra was determined to be approximately 20% of that expected from the radon activity (Kadko and Butterfield, 1998). This could be a lower limit as the ^{224}Ra was not determined on fibers, but rather directly on fluids from which radium precipitation was possible.

The input of the radium isotopes as a result of the recoil process is then:

$$P_{iii} = 0.2 \times (^{222}Rn) \times \tau \qquad (6a)$$

where $\tau = {}^{232}Th/^{230}Th$ activity ratio in basalt for ^{228}Ra recoil, and unity for ^{226}Ra recoil, and the recoil efficiency (.20) from the Juan de Fuca study is used.

In terms of ^{224}Ra activity, recoil is represented by:

$$P_{iii} = (^{224}Ra)/\tau \qquad (6b)$$

where $\tau = {}^{232}Th/^{230}Th$ activity ratio in basalt for ^{226}Ra recoil, and unity for ^{228}Ra recoil.

At depth, radium–thorium equilibrium is likely and therefore we use the down-hole $^{228}Ra/^{226}Ra$ ratio for τ.

Eqs. (3), (4) and (6) are combined to give the $^{228}Ra/^{226}Ra$ activity ratio in the hydrothermal fluid as a function of time:

$$\frac{(^{228}Ra)}{(^{226}Ra)} = \frac{[P_{iii} + A8^*/W \cdot T \cdot \lambda_8 \cdot 10^{-3}](1 - e^{-\lambda_8 T})}{[P_{iii} + A6^*/W \cdot T \cdot \lambda_6 \cdot 10^{-3}](1 - e^{-\lambda_6 T})} \qquad (7)$$

where

λ_8 and λ_6 = the decay constants of ^{228}Ra and ^{226}Ra, respectively;
A8* = the activity of ^{228}Ra in basalt;
A6* = the activity of ^{226}Ra in basalt.

3.4.1. Application of model to Icelandic systems

In order to apply a residence time model to the data, one has to understand or make assumptions about the structure of the hydrothermal system. The Reykjanes wells are clearly dominated by seawater circulation and we apply the model

used for seafloor systems (Kadko and Butterfield, 1998). It has been proposed that for Svartsengi, meteoric groundwater is mixed and incorporated into seawater in the downwelling portion of the circulation cell and subsequently this mixture reacts at high temperature and pressure with the rock substrate (Ragnarsdóttir et al., 1984). Under these circumstances, the same residence time model can be applied to the Svartsengi system.

The Reykjanes system displays strong upflow which reaches the surface, while the groundwater table is lower in the Svartsengi system and surface discharge was nearly absent prior to well production (Lonker et al., 1993). This is reflected in the resistivity structure and alteration mineralogy of the two areas (Arnason et al., 2000). As already noted, the high-temperature reaction zone at Svartsengi is also overlain by a thick lens of cold meteoric and salt water. There is therefore the possibility that infiltrating cold water can interact with the high-temperature fluid within the upwelling limb at Svartsengi.

4. RESULTS AND DISCUSSION

Radium isotope data for fluids and rock are given in Tables 1 and 2, and fluid chemistry data are given in Table 3. The depth profiles of the ^{226}Ra activity and the ^{228}Ra/^{226}Ra activity ratio for both drill holes are shown in Fig. 2. It is seen that the ^{228}Ra/^{226}Ra activity ratio of the Svartsengi fluid is approximately twice that of the Reykjanes fluid and that the ^{226}Ra activity of the Svartsengi fluid is approximately one-fourth that of the Reykjanes fluid.

4.1. Model parameters

4.1.1. Water–rock ratios
Water–rock ratios provide a measure of the mass transfer between fluid and rock, indicating the extent that elements are removed from rocks into the circulating fluid during hydrothermal alteration. The concept of water–rock ratio (W) does not however have a single meaning that is independent of a specific reaction, and there are several methods in use to estimate water–rock ratio for hydrothermal fluids (e.g. Ragnarsdóttir et al., 1984; Berndt et al., 1988). For example, B and Li are readily removed from rocks and remain soluble in the hydrothermal solution and yield low ratios for a system; their fluid concentrations give an estimate of the total amount of rock encountered by

Table 2
Rock radium analyses

Sample	^{226}Ra (dpm/g)	^{228}Ra (dpm/g)	^{228}Ra/^{226}Ra
Reykjanes[a]			
RNJ12-202m	0.220 ± 0.017	0.154 ± 0.016	0.70 ± 0.09
RNJ12-392m	<0.02	<0.02	nd
RNJ12-603m	0.191 ± 0.018	0.117 ± 0.009	0.61 ± 0.08
RNJ12-800m	0.072 ± 0.024	0.074 ± 0.014	1.03 ± 0.40
RNJ12-1000m	0.063 ± 0.018	0.061 ± 0.003	0.97 ± 0.28
RNJ12-1200m	0.148 ± 0.018	0.096 ± 0.007	0.65 ± 0.09
RNJ12-1400m	0.075 ± 0.007	0.058 ± 0.008	0.78 ± 0.13
RN10-1430m	0.071 ± 0.010	0.055 ± 0.008	0.78 ± 0.16
RN10-1432m	0.063 ± 0.007	0.051 ± 0.007	0.81 ± 0.15
RNJ12-1800m	0.174 ± 0.016	0.085 ± .005	0.49 ± 0.05
RNJ12-2400m	0.157 ± 0.018	0.056 ± 0.007	0.36 ± 0.06
Svartsengi			
SJ19-100m	0.296 ± 0.024	0.206 ± 0.012	0.695 ± 0.07
SJ19-300m	0.212 ± 0.015	0.170 ± 0.017	0.80 ± 0.10
SJ19-380m	0.114 ± 0.013	0.085 ± 0.012	0.74 ± 0.14
SJ19-600m	0.083 ± 0.003	0.047 ± 0.003	0.56 ± 0.04
SJ19-908m	0.074 ± 0.007	0.035 ± 0.008	0.47 ± 0.12
SJ19-1000m	0.029 ± 0.009	0.017 ± 0.008	0.58 ± 0.32
SJ19-1200m	0.10 ± 0.013	0.084 ± 0.008	0.84 ± 0.13
SJ19-1290m	0.059 ± 0.012	0.045 ± 0.008	0.76 ± 0.21
SJ19-1300m	0.088 ± 0.014	0.051 ± 0.005	0.58 ± 0.11

[a] Samples from borehole no. 12 unless indicated otherwise.

the fluid (Berndt et al., 1988). Other elements display higher water–rock ratios indicating lower extraction efficiencies (e.g. Von Damm et al., 1985) suggestive of effects such as secondary precipitation reactions or incomplete reaction.

Under the conditions of the two boreholes in this study, lithium is highly soluble in the hydrothermal fluid, and its extraction efficiency should be nearly unity. Rock compositions are very similar at the Reykjanes and Svartsengi sites, and the inferred conditions in the deep reservoir are also similar (Ragnarsdóttir et al., 1984). Using a typical MORB Li concentration for the rock (6.5 ppm) and our measured fluid Li concentrations, we get W_{Li} values of ~1.5 for Reykjanes and 2.0 for Svartsengi. Boiling and steam segregation also have very minor effects on the ratios of Li or major elements to chloride. The ratio of major elements (Na, K, Ca) to chloride at Reykjanes and Svartsengi are the same to within 2%. However, it is clear that many other elements are depleted in Svartsengi relative to Reykjanes, which

Table 1
Fluid radium analyses

Sample	Year	^{226}Ra (dpm/L)[a]	^{228}Ra/^{226}Ra [b]	^{224}Ra/^{226}Ra[b]	^{224}Ra/^{223}Ra[b]
Svart (SV-07)	Dec. 2000	7.32 ± 0.24	1.70 ± 0.05	—	—
Svart (SV-19)	May 2004	6.71 ± 0.21	1.97 ± 0.04	1.68 ± 0.19	67 ± 8
Reykjanes (RN-09)	Dec. 2000	25.41 ± 0.36	1.04 ± 0.02	—	—
Reykjanes (RN-12)	May 2004	26.46 ± 0.49	—	—	—
Reykjanes (RN-12)	Feb. 2005	—	1.05 ± 0.05	1.3 ± 0.3	26.2 ± 5.4
Reykjanes (RN-12)	July 2005	22.85 ± 0.53	0.99 ± 0.03	1.1 ± 0.2	24.7 ± 3.0
Svart (SV-19)	June 2006	6.01 ± 0.35	1.89 ± 0.04	0.99 ± 0.03	63 ± 9

[a] Radon emanation method.
[b] Mn fiber.

Table 3
Fluid chemistry[a]

	Reykjanes	Svarstengi
Temperature (°C)	295	240
pH[b]	5.00 (RN-9, 295 °C)	5.46 (SV-11, 240 °C)
pH[c]	5.44	7.04
Li (μmol/kg)	687	476
Na (mmol/kg)	456.3	317.28
K (mmol/kg)	40.0	28.93
Mg (mmol/kg)	0.116	0.11
Ca (mmol/kg)	45.4	31.24
Cl (mmol/kg)	576.9	394.5
Ba (μmol/kg)	74.3	15.4
Si (mmol/kg)	13.0	8.42
Sr (μmol/kg)	158	69

[a] Values from holes RN-12 and SV-19, unless indicated otherwise.
[b] Calculated pH of the reservoir at the reported temperature (Lonker et al., 1993).
[c] Measured pH at surface.

may be due to conditions in the reaction zone (slightly lower temperature and higher pH in Svartsengi) or in the upflow zone (possible boiling, mixing and/or cooling).

Strontium isotopes provide an integrated view of the water–rock ratio based on Sr exchange between fluid and rock. Using the Sr isotopic ratio of Reykjanes (0.7042) and Svartsengi (0.7040) fluids and unaltered local rock (0.7032) from Elderfield and Greaves (1981), our measured fluid Sr concentrations (Table 3), and the equations for single-stage continuous reaction (Berndt et al., 1988), we get W_{Sr} values of 5.0 for RN12 and 7.5 for SV19.

The barium content of Svartsengi (Table 3) is approximately 20% of the Reykjanes value, consistent with a secondary removal process for barium and by implication, radium as well. Sturchio et al. (1993) discuss how precipitation of just trace amounts of barite could effectively control aqueous radium concentration, but under these circumstances the isotopic ratio $^{228}Ra/^{226}Ra$ acquired in the high temperature and pressure reaction zone would be unaffected (e.g. Hammond et al., 1988; Berndt et al., 1988).

Here, the water–rock ratio for radium (W_{Ra}) is estimated from the ratio $(dpm/kg)_{rock}/(dpm/kg)_{fluid}$. This is an apparent value which effectively combines the water-to-rock ratio yielded by elements quantitatively removed from rocks (e.g. alkalis) with an extraction efficiency reflecting secondary precipitation reactions (Von Damm et al., 1985). The value for W_{Ra} is chosen to yield the ^{226}Ra activity observed in the fluids. The integrated value of the rock radium activity (below the casing depth) is used and compared to the average fluid activities. The calculation for Reykjanes yields $W_{Ra} = 5.5$, while a larger value ($W_{Ra} = 10$) is required for the Svartsengi system to account for the lower observed fluid ^{226}Ra activity. Because the input of radium isotopes as a result of the high-temperature water–rock reaction (Eq. (4)) reflects a W_{Ra} within the deep reaction zone, the values calculated here are upper limits if radium loss occurs within the upflow zone. The $^{228}Ra/^{226}Ra$ ratio and the activity of the short-lived isotopes ^{224}Ra and ^{223}Ra will further constrain the water–rock ratio.
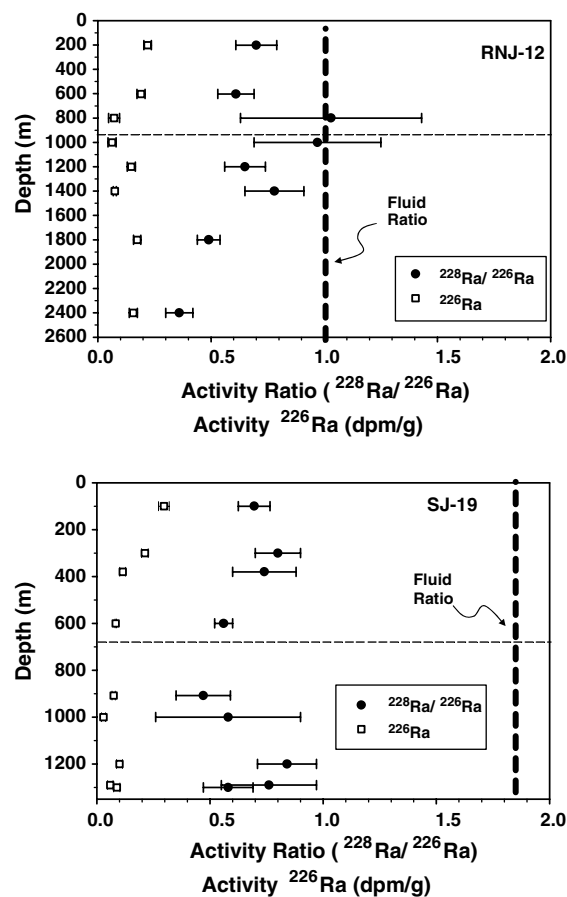

Fig. 2. (Top) The activity ratio $^{228}Ra/^{226}Ra$, and the activity of ^{226}Ra for rock samples down the Reykjanes-12 drill hole. (Bottom) The activity ratio $^{228}Ra/^{226}Ra$, and the activity of ^{226}Ra for rock samples down the Svartsengi-19 drill hole. The dashed vertical lines show the $^{228}Ra/^{226}Ra$ activity ratio of the fluids. The radium isotopic characteristics of the rocks are similar, but the fluid activity ratio of Svartsengi is ~twice that of Reykjanes. For both cores, the depth of casing (above which fluids are isolated from the rock) is indicated by the horizontal dashed line.

4.1.2. Recoil input

The recoil input is evaluated here by both the ^{222}Rn and ^{224}Ra approaches. Radon-222 was not measured in these fluids. However, radon in submarine hydrothermal fluids is typically ~500 dpm/kg (Kadko, 1996), and a compilation of radon from hydrothermal systems from South Iceland suggest similar values (Jónsson, 1994). Using the recoil efficiency (0.2) from the Juan de Fuca, and $\tau = 0.7$, the ^{228}Ra recoil input based on ^{222}Rn would therefore be 70 atom/min kg.

The ^{224}Ra activity is derived from multiplying the $^{224}Ra/^{226}Ra$ ratio of the Mn fiber by the ^{226}Ra determined from the radon emanation method. The ^{224}Ra activity at the Reykjanes site suggests a ^{228}Ra recoil input ~35 atom/min kg, and for Svartsengi only ~9 atom/min kg. Particularly for the Svartsengi fluids, this is likely a lower limit because of mixing processes during upflow discussed below.

The $^{224}Ra/^{223}Ra$ ratios of the exiting fluids give some insight into the behavior of the fluids during late stages of venting, as these isotopes have half-lives of days. The input

of these short-lived nuclides is dominated by recoil, such that the activity would be:

$$A = R[1 - \exp(-\lambda t)] \tag{8}$$

where R is the recoil rate (in atom/min kg).

The ratio of the recoil inputs for ^{224}Ra and ^{223}Ra is

$$R_{224}/R_{223} = 21.7(^{228}\text{Ra}/^{226}\text{Ra})_{\text{rock}} \tag{9}$$

as the ^{238}U/^{235}U activity ratio is 21.7.

If we assume for simplicity that the ^{228}Ra/^{226}Ra is unity then after several days as steady-state is approached the ^{224}Ra/^{223}Ra activity ratio of the fluid would be ~ 21.7 in the absence of scavenging. This is close to the value observed for the Reykjanes site suggesting that processes such as mixing or precipitation during upwelling are minimal. This is consistent with the strong upflow which reaches the surface within this system (Lonker et al., 1993).

In the presence of scavenging, the activity of the short-lived radium isotopes can be represented by:

$$A = \lambda/(\lambda + k) \cdot R[1 - \exp(-(\lambda + k)t)] \tag{10}$$

where k = scavenging constant.

For large k, the activity ratio A_{224}/A_{223} approaches the ratio of 21.7 $(\lambda_{224}/\lambda_{223})$ = 66 at steady state.

In contrast to the Reykjanes system, the groundwater table in the Svartsengi system is lower and surface discharge was nearly absent prior to well production (Lonker et al., 1993). This would be consistent with infiltration of surficial waters. Such waters, in the absence of high temperature reaction, would have little long-lived radium activity, but would attain short-lived radium isotopes by recoil. For Svartsengi, we suggest that a shallow circulating groundwater described by Eq. (10) mixes with the hot, upwelling fluid over some time t, such that:

$$\begin{aligned} A = {} & \lambda/(\lambda + k) \cdot (1 - f) \cdot R[1 - \exp(-(\lambda + k)t)] \\ & + f \cdot A^\circ \cdot \exp(-\lambda t) \end{aligned} \tag{11}$$

where

f = fraction of deep source water;
A° = the activity attained within the deep high temperature water–rock reaction zone (Eq. (8)). As an example, with A° for ^{224}Ra = 35 dpm/kg, A° for ^{223}Ra = 35/21.7 = 1.61 dpm/kg.

Then, the ^{224}Ra/^{223}Ra activity ratio (A_{224}/A_{223}) is:

^{228}Ra/^{226}Ra ratios set during the high temperature–pressure alteration stage of flow would not be affected by this late-stage mixing. Absolute activities could however be affected by mixing.

4.2. Model results

The model results are shown in Figs. 3 and 4, and model parameters shown in Table 4.

4.2.1. Reykjanes

The water–rock ratio of 5.5 (calculated from the fluid and rock radium values) is used since the short-lived radium isotopes indicate little late-stage mixing processes. A range of recoil inputs (based on the ^{224}Ra and ^{222}Rn approximations) for ^{228}Ra are shown yielding a residence time in the range 1.0–4.0 years. The importance of the recoil input mechanism is readily seen here. While input as great as that suggested by radon activities is not required, values at least as great as suggested by the ^{224}Ra activity levels (35 atom/min kg) are needed to account for fluid ^{228}Ra/^{226}Ra activity ratios that are substantially greater than the rock substrate with which they interact. The results here are comparable to a residence time estimate of less than 50 years that was based on observed partial equilibration of sulfur isotopes in the Reykjanes fluids (Sakai et al., 1980).

4.2.2. Svartsengi

For the Svartsengi fluid, the estimated W_{Ra} based on the fluid and integrated rock radium activities is 10, but this is likely an upper limit because mixing during upwelling would dilute the measured ^{226}Ra. We do not know the parameter f (fraction of deep source water), but because the fluids appear to be dominated by high-temperature fluid–rock interaction, it must be large. We can make the calculation using a range of W_{Ra}, which essentially adds a constraint on f. In Fig. 3, the calculations are made with a W_{Ra} of 10 with the range of recoil inputs used for Reykjanes. These calculations suggest a residence time in the range 1.0–2.0 years. In Fig. 4, the calculation is made using a recoil input of 35 atom/min kg and a range of W_{Ra} from 6 to 10, equivalent to respectively a range of f from 0.6 to 1. The lower value of W_{Ra} is comparable to that used for Reykjanes and the W_{Ra} of 7.5 is based on Sr isotopes. The calculations in Fig. 4 extend the residence time range to between 1.0 and 5.0 years. Also in Fig. 4, the calculated

$$\frac{A_{224}}{A_{223}} = 21.7 \frac{\lambda_{224}/(\lambda_{224} + k) \cdot R[1 - \exp(-(\lambda_{224} + k)t)](1 - f) + f \cdot A^\circ{}_{224} \cdot \exp(-\lambda_{224})t}{\lambda_{223}/(\lambda_{223} + k) \cdot R[1 - \exp(-(\lambda_{223} + k)t)](1 - f) + f \cdot A^\circ{}_{223} \cdot \exp(-\lambda_{223})t} \tag{12}$$

For large k, the steady-state activity ratio A_{224}/A_{223} approaches the ratio of 21.7 $(\lambda_{224}/\lambda_{223})$ = 66 which is comparable to the value observed at Svartsengi. Note that because the timescale of upflow and mixing must be much less than the decay time of ^{228}Ra and ^{226}Ra, and that groundwater has relatively small activities of these isotopes, the

^{226}Ra activities are shown as a function of W_{Ra}.

Although the fluid ^{228}Ra/^{226}Ra ratios and ^{226}Ra activities are quite different between sites, similar calculated residence times, within the model resolution, are derived. Recoil parameters chosen for the sites are similar. The adjustment of the water–rock ratio and the similarity of
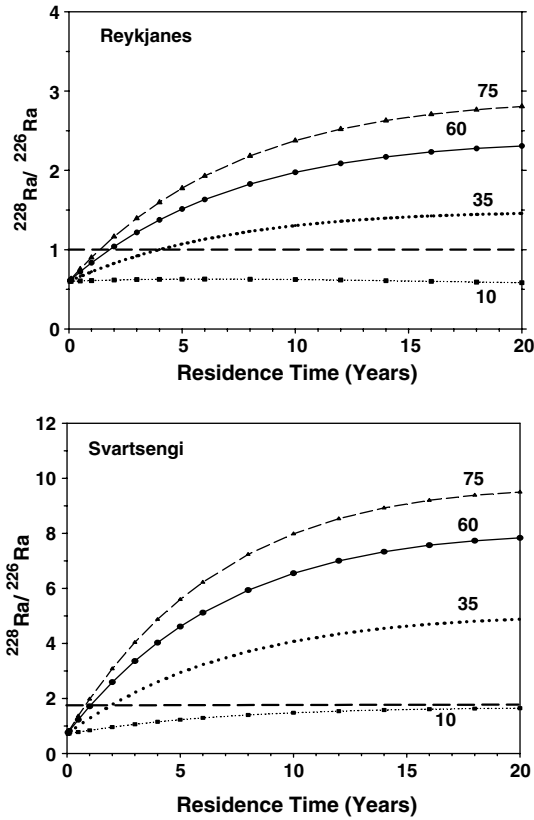
Fig. 3. The modeled fluid activity ratio $^{228}Ra/^{226}Ra$ (see Eq. (7) in text) as a function of residence time for various ^{228}Ra recoil inputs (the value of 35 atom/min kg corresponds to the measured ^{224}Ra fluid activity in Reykjanes). The measured $^{228}Ra/^{226}Ra$ activity ratio of the fluids is indicated by the horizontal dashed line. (Top) Reykjanes system; (bottom) Svartsengi system.
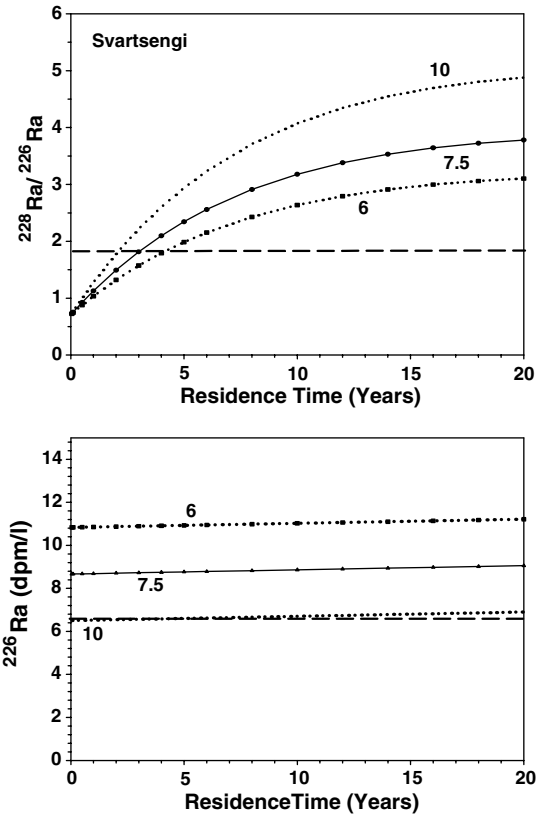

Fig. 4. (Top) Modeled fluid activity ratio $^{228}Ra/^{226}Ra$ (see Eq. (7) in text) for Svartsengi as a function of residence time for various W_{Ra}. The measured $^{228}Ra/^{226}Ra$ activity ratio of the fluids is indicated by the horizontal dashed line. (Bottom) Modeled ^{226}Ra activity in Svartsengi fluid as a function of residence time for various W_{Ra}. The measured ^{226}Ra activity of the fluids is indicated by the horizontal dashed line. The ^{228}Ra recoil input value of 35 atom/min kg is used for each calculation.

the Ra/Ba ratios between the sites are internally consistent. Given that the sites are separated by only 14 km with similar rock substrate and heat source it is perhaps not surprising that the calculated residence times are similar.

The circulation model proposed for Svartsengi, whereby meteoric water mixes with seawater before entering the high-temperature reaction zone (Ragnarsdóttir et al., 1984), is upheld by the radium isotope ratios. Given that long-lived radium isotopic activities (concentration) are very low in meteoric groundwaters with low temperature and high pH, it is not feasible to raise the $^{228}Ra/^{226}Ra$ activity ratio significantly by mixing meteoric groundwater into a high-temperature hydrothermal fluid. This supports the observations that the lower temperature and salinity, higher pH, lower Ra and Ba mobility, lower transition metal content and lower dissolved silica concentration at Svartsengi (relative to Reykjanes) are primarily properties acquired in the reaction zone, and not due to processes in the upflow zone.

The calculated residence time for these systems has implications for these sites as exploited energy sources. The results here do not include the low-temperature infiltration path and thus are lower limits, but suggest that perturbations within a human timescale could impact the hot water reservoir that is mined. This implies a limited reservoir that can be depleted by withdrawal of hot water. The lateral extent of the fluid reservoir at Svartsengi is approximately 4 km^2 and the rocks have a porosity of about 8% (Ragnarsdóttir et al., 1984). Assuming that the reservoir extends to 2.5 km, then the fluid volume is 8×10^{11} kg, or about 9×10^8 tons. If as a lower limit the residence time is 5 years, the steady state input rate would be 180×10^6 tons/year. If the residence time is 100 years, then the input rate would be 9×10^6 tons/year which is comparable to the rate at which water is currently being pumped from

Table 4
Model parameters

Site	W_{Ra}[a]	^{228}Ra recoil input (at/ min kg)	Initial ^{226}Ra activity (dpm/g)[b]	Initial $^{228}Ra/^{226}Ra$ ratio (τ)[c]
Reykanes	5.5	35–75	0.138	0.6
Svartsengi	10	35–75	0.065	0.7

[a] Water–rock ratio based on average radium fluid activity and depth-integrated rock activity.
[b] Depth-integrated rock activities below casing depth.
[c] Depth-integrated activity ratio below casing depth.

the system (ÍSOR tech. report). This is not inconsistent with the observed drop of the water table of 320 m and the generation of a steam cushion down to 700 m in the center of the Svartsengi field, which has been exploited since 1976.

5. SUMMARY AND CONCLUSIONS

Radium isotopes were used to determine the crustal residence times of hydrothermal fluids from two seawater-dominated geothermal wells (Svartsengi and Reykjanes) from the Reykjanes Peninsula, Iceland. The availability of rock samples from the subsurface (to depths of 2400 m) allowed a direct comparison of the ^{226}Ra activity and ^{228}Ra/^{226}Ra activity ratio of the fluids with those of the rocks within the high temperature and pressure reaction zone. This represents an advance over earlier studies of seafloor hydrothermal systems, where subsurface samples are generally inaccessible.

The fluid isotopic characteristics were relatively stable for both sites over the six years (2000–2006) of the study. The ^{226}Ra activity of the Svartsengi fluid was ∼one-fourth of the Reykjanes fluid and the ^{228}Ra/^{226}Ra ratio of the Svartsengi fluid was ∼ twice that of Reykjanes. Using a model that predicts the evolution of the ^{228}Ra/^{226}Ra with time, we determined that the fluid residence times for both sites, from the onset of high temperature water–rock reaction, is less than 5 years. The ^{224}Ra/^{223}Ra ratios of the exiting fluids provided insight into the behavior of the fluids during late stages of venting and allowed estimation of the recoil parameter for the model. The timescale for fluid residence times derived here is consistent with results from similar studies of fluids from submarine systems, and has implications for the use of terrestrial systems in Iceland as an exploited energy resource.

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