RADIUM ISOTOPES CONTRIBUTION TO GEOTHERMAL EXPLORATION IN CENTRAL ITALY

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ABSTRACT

Naturally occurring uranium and thorium decay series have recently shown to be potential tools for the study of water dominated geothermal systems. Ra-223, Ra-224, Ra-226, Ra-228 and Rn-222 measurements together with environmental isotopes and chemical elements determinations have been performed in thermal springs and geothermal fluids from deep wells of Central Italy. This region is characterized by a positive heat flow density anomaly, geothermal reservoir is generally made up by mesozoic limestones covered by low permeability rocks. The main lithotypes of the region have been characterized for the radioactivity. The obtained results, evaluated on the basis of a conceptual model provided new insights in the kinetics of interaction between geothermal fluids and host rock. The principal results provide information on mixing processes. on the source rocks and on the contact time between water and host rocks.

1. INTRODUCTION

Studies of uranium and thorium series disequilibria were found to be useful for estimating parameters of chemical and hydrogeological interest in hydrothermal systems (Hammond et al., 1988). In particular, measurements of radium isotopes yielded insight into the mechanisms controlling radioisotope exchange, and they permitted estimation of rates of fluid-rock chemical interaction (Ku et al., 1992). Therefore, an investigation was initiated to study the potential of radium isotopes for geothermal exploration in Italy, particularly regarding the identification of the main reservoirs and the assessment of the dynamics of such geothermal systems. The activity was principally aimed to carry out field experiments with the purpose to measure concentrations of radium isotopes and radon in geothermal fluids in a water dominated geothermal area. The investigation was extended to a considerable number of thermal springs in order to elucidate the effect of the temperature on the principal geochemical and radioactivity parameters. The stable isotopes and tritium concentrations were also determined in order to get information on the hydrology of the area. Moreover a series of laboratory experiments was carried out to study dissolution of radium isotopes and potassium from syenite and limestone under different conditions with respect to temperature, pressure and chemical composition of the fluids. The detailed description of these experiments and the results are in progress.

2. TEE STUDY AREA

The study area covers the Tuscan Latium geothermal region: particularly the Latera field and some areas of Monte Amiata (Fig. 1). The geological setting of the region is characterized by a superposition of several sedimentary and metamorphic complexes and the presence of neoauthoctonous deposits and of recent volcanic products. From the hydrological point of view all the geothermal fields of the region are featured by a low permeability cap rock overlying the reservoirs formations. The cover consists mainly of flysch complexes and neoauthoctonous sediments. The geothermal reservoir is represented by the mostly carbonatic-evaporitic sequence of the Tuscan complex. In deep strata, also regional metamorphic complex sometimes acts as a geothermal reservoir. The effective porosity of the rocks in the reservoirs is estimated to be about 2 %. The thickness both of the cover and of the reservoir is extremely variable, even at short distances, because of intense tectonic phenomena.

3. SAMPLING AND ANALYSIS OF RADIUM ISOTOPES

Sampling of geothermal fluids and groundwater for radiometric analysis were performed by a specially designed filtration/sorption apparatus in order to separate particulate matter and to preconcentrate the radium content in liquid phase. The sample processing was carried out on the site as follows. Fluids were collected from the weir tubes near the geothermal wells and cooled down to abut 30°C; they were filtered on line by a series of filter cartridges; the last one was a 0.6 μm porous membrane filter. The dissolved radium isotopes were collected by exchanger or adsorber beds: ion exchange resins, alumina, $BaSO_4$ activated alumina. Pretreatment of the fluids usually results in a 1000 to 5000 fold enrichment of radium isotopes. Furthermore this procedure allows to determine the chemical form (cationic, anionic, non-ionic) of the dissolved radionuclides. Alumina beds retain only radium which is in non-ionic form, whereas $BaSO_4$ activated alumina retain both the cationic and non-ionic forms (Perkins, 1968). The sampler is similar to the Battelle Large Volume Water Sampler (Silker et al., 1971); it has been extensively used for radiological characterization of river water (Battaglia et al., 1984) and seawater (Battaglia et al., 1988). The alumina beds are 30 cm i.d. and 7 mm thick; the flow rate is abut 8 l/min and the sample volumes range from 1 to 3 m^3. $BaSO_4$ activated alumina was produced by a simple procedure (Perkins, 1968) using neutral alumina and boiling solutions of Na_2SO_4 and $Ba(NO_3)_2$. Laboratory tests showed that the yield recovery of one activated alumina bed ranges from 0.75 to 0.83. Under field conditions, the recovery was calculated by the expression: $R = (A_n - A_{n+1})/ A_n$, where A_n and A_{n+1} are the radium isotope activities of two consecutive beds. (Nevissi and Schell, 1975). The total activity follows from the expression: $A = A_1 + \ldots A_{n-1} + A_n/R$. Using a cascade of three beds the overall recovery usually was 0.99.

The activity of the radium isotopes retained on filters and adsorbers was determined by low background gamma spectrometry. Two measurements were performed: the first one was carried out immediately after processing the samples in order to determine the short-lived Ra-223 and Ra-224. The second measurement was carried out about one month later to determine Ra-226 activity through the radon daughters ingrowth. The sampling technique combined with high sensitivity gamma measurements resulted in an detection limit of 1 Bq/m^3 for Ra-223 and 0.2 Bq/m^3 for the other radium isotopes. The total uncertainty of the analysis is about 5 %. The Ra-223 activity was determined by a specifically designed computer code. Rn-222 dissolved in water was measured by conventional emanation technique using scintillation cells. The radium isotopes concentration in rock samples was measured directly by gamma spectrometry.

4. EXPERIMENTAL RESULTS

The anionic composition of the thermal springs of the region is dominated by bicarbonate or sulphate ions while geothermal fluids are characterized by high chloride content. Considering also the alkali and alkaline earth ions, a different degree of maturity of these waters can be identified (Giggenbach, 1988).

In Fig. 2 the measured ion concentrations are compared with theoretical values reflecting full equilibrium between geothermal waters and average crustal rock at different temperatures . This plot demonstrates that the geothermal fluids and most of the spring waters approach a trend line from immature to mature waters. Geothermal fluids G and I appear to be in equilibrium with rocks at about 300°C whereas the other fluids have reached a lower degree of maturity (H, C, F, D).

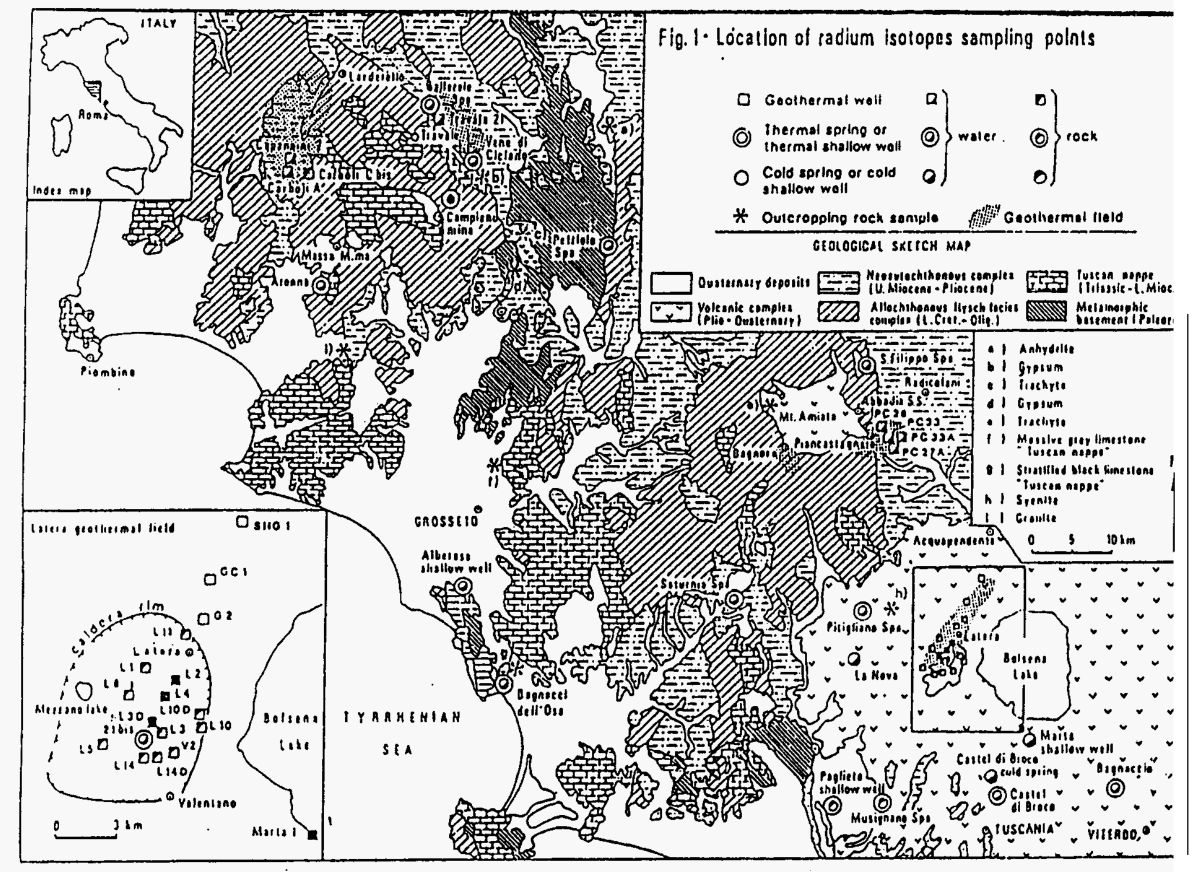
Fig. 1· Location of radium isotopes sampling points

Geothermal well E represents a relatively low maturity stage which probably reflects the influence of fresh water injected during a production test conducted prior to the sampling. In general, the spring waters are out of this kind of equilibrium. These findings are corroborated also by examining the environmental isotope composition of these waters.

Concerning the stable isotopes H-2 and 0-18, the spring waters fall close to the Meteoric Water Line. This indicates that these waters are isotopically not altered by water-rock interaction, which is also suggested by their relatively low temperature. In general, the tritium content of the well and spring waters was found to be less than a few TU which indicates a fairly high residence time of these waters.

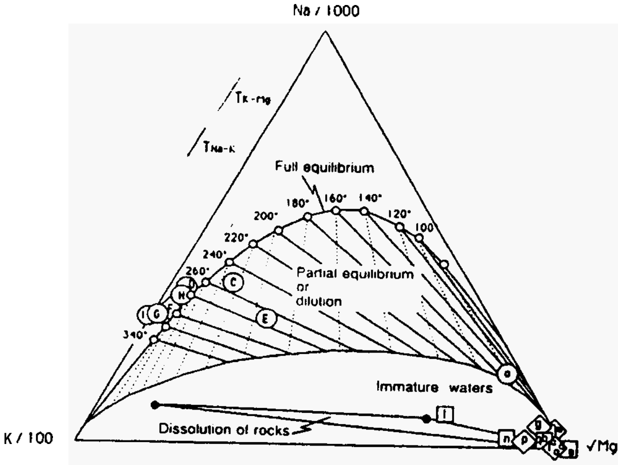

Fig. 2. Geochemical maturity of the fluids and thermal waters

Table I. Radium isotopes data of the thermal springs and geothermal fluids of the study area

Name	Label (1)	Temp. [°C]	Ra-223 [Bq/m³]	Ra-224 [Bq/m³]	Ra-226 [Bq/m³]	Ra-228 [Bq/m³]	Rn-222 [Bq/l]
ALBERESE	h	28.5	n.d.	20.2±0.9	58.0±1.4	11.3±0.5	6.6±0.2
V. CICIANO	e	22	n.d.	5.0±0.2	8.5±0.3	2.8±0.2	23.0±0.
S. FILIPPO	d	47	50.1±2.6	44.6f1.8	587±14	65.4i2.0	53.4±3.
ARONNA	c	23	1.6±0.6	6.2±0.3	16.0±0.3	3.3±0.2	16.6±0.
GALLERAIE	f	32	28.0±1.2	32.0i0.4	59.9±1.4	33.8±1.7	n.d.
MIN. CAMP.	g	75	69±5	Mi2	787±10	141±2	39.3
B. MUSIGN.	h1	43	4.7±0.6	59.3±1.5	23.1±0.6	56.8±1.2	31.4±1.
B. MUSIGN.	h2	39.5	8.0±0.9	45.6±1.5	13.0±0.8	50.6±1.2	35.7±2.
C. BROCO	i	23	49±5	1276±63	242±10	775±33	243±27
BAGNACCI	l	67	16.4±1.7	299±11	120±3	166±3	1.4±0.1
B. PITIGL.	m	38	1.1±0.5	23.5±1.0	36.6±1.9	13.7±3.0	129±3
P. 21 BIS	n	29	n.d.	59.9±1.7	15.3±1.7	37.1±3.0	3.1±0.4
SATURNIA	o	37	3.5±1.0	81.2±3.0	157±3	78.3±2.0	5.5±0.2
PAGLIETO	p	35.9	32.3±0.6	9.4±0.8	23.3±0.9	6.5±0.4	41.7±4.
PETRIOLO	q	45	32.5±0.9	22.9±0.6	399±5	8.7±0.3	10.8±0.
LA NOVA	s	15	nd.	1.7±0.3	2.0±0.2	1.5±0.2	45.3±2.
C. BROCO f.	t	17	n.d.	30.2±2.3	9.2±1.0	17.7f0.4	77.5±3.
GEOTH. WELLS							
LATERA 2	C	204	86.6i6.5	303±4	228±3	15352	150
LATERA 3D	D	238	126	432	85.0	216	92
LATERA 4	E12	195-210	77.7±2.8	315±9	168±3	98.2±1.7	371
MARTA 1	F	183	19.9±2.2	167±5	222±5	148±3	n.d.
PC 26 (2)	G	300	n.d.	23.1±1.7	128±2	32.1±1.1	1.9
PC 27/A (2)	H	300	I.0i0.3	7 1f0.4	10.0±0.2	6.5i0.3	n.d.
PC 33 (2)	I	300	n.d.	22.4±9.2	21.7±6.8	9.9f4.0	35.3
PC 33/A (2)	J	300	n.d.	7±2	9.3±1.5	3.6±0.3	n.d.

(1) Capital letters = wells; Small letters = thermal springs
2) Monte Amiata wells

The radium isotope concentrations in thermal waters and geothermal fluids are found to cover a range from a few Bq/m^3 up to more than 1000 Bq/m3 (Tab. 1). Some thermal springs show a considerably higher radium isotope content than deep geothermal fluids (d, g, q). This is probably due to the host rock composition, which in all these *cases* is dominated by anhydrites mostly in proximity to occurring sulphide mineralizations. In these rocks a secondary enrichment of uranium due to phreatic aquifer fluctuations in the redox conditions (Locardi and Mittemperger, 1971) could be the *cause* of the high Ra-226 content. The other springs are comparable with the geothermal fluids in respect to the radium isotope concentration. It is interesting to note that in the geothermal fluids the radium isotopes were found in non-ionic form whereas in the water collected from thermal springs, cationic, anionic and non-ionic radium was present in different proportions.

The mean Ra-228/Ra-226 activity ratio characterizing the Th/U ratio of the host-rocks, taken from outcrops or cores in the study area, ranges from 0.2 to 1.6 (the radioactivity data of rock samples are summarized in Tab. 3). The cover of the reservoir formations is generally low in Ra-226 (10 to 20 Bq/kg) with a mean Ra-228/Ra-226 ratio of about 1.6. The lowest Ra-226 content of rocks from the region was found in the carbonatic-evaporitic sequence representing the geothermal reservoir (about 10 Bqlkg with the ratio of 0.2). The radioactivity of limestones which were altered by thermal metamorphism with metasomatism, depends mainly of the degree of interaction with hydrothermal fluids. Phyllites and micascists show similar Ra-228/Ra-226 ratios of about 1.3 with Ra-226 concentrations ranging from 20 to 60 Bqlkg. Volcanites and plutonic rocks are generally characterized by a high U and Th content and a very high K-40 activity. Their Ra-228/Ra-226 activity ratio is between 1.2 and 1.3 at a Ra-226 concentration ranging from *80* Bqlkg (granites) to more than 250 Bqlkg (syenites).

Concerning the Ra-228/Ra-226 activity ratio, a clear distinction can be made between rocks of the carbonatic sequence (ratio at about 0.2) and the all the other rocks of the study area which cover a range from 1 to 1.6.

The activity ratios Ra-228/Ra-226 and Ra-224/Ra-228 as well as Ra-224/Ra-223 are expected to provide useful information on fluid-rock chemical interaction (Ra-223 is normalized for the U-238/U-235 activity ratio). The triangular diagram of Fig. 3 representing the relative concentrations of Ra-224, Ra-226 and Ra-228 clearly shows that most of the data of the Ra-224/Ra-228 ratio (including data taken from Laul, 1985 , Dickson, 1985 and Clark and Turekian, 1990) range between 1 and 3. This seems to indicate the dominance of recoil ejection in transferring radium isotopes from the host rock into the liquid, with respect to the chemical dissolution. (Alpha-recoil ejection is a physical displacement of the atom produced by alpha decay of the precursor atom (Osmond and Cowart, 1992)). The spread around the theoretical value of about 1.2 is indicative of other processes or conditions affecting this ratio; among them are nonequilibrium processes with respect to Ra-228 and sorption processes which have a greater influence on the Ra-228 concentration than on the Ra-224 concentration.

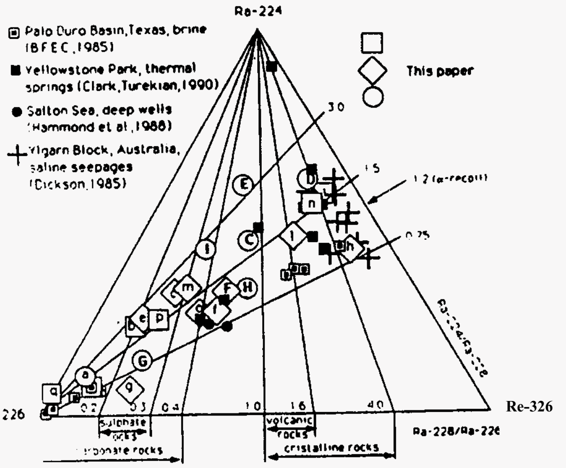

Fig. 3. Triangular diagram of Ra-226, Ra-224 and Ra-228 of the water samples.

For practical applications the Ra-228/Ra-226 ratio of thermal fluids was of particular interest: it is expected to represent the Th/U ratio in the host rock and thus to provide infomation on the origin of the fluid in the geothermal system. The measured ratios in fluids were subdivided in three groups (Fig.3). The first group ranged from 0 to 0.4 and was found to be in good correspondence with the ratios of sulphate and *carbonate* rocks of the main reservoir in the region (Tab. 3). The second group, which included five geothermal wells, is ranging between 0.4 and 1 and appeared to represent fluids derived from different host rocks, especially from carbonatic rocks affected by metamorphism. The third group was represented by ratios higher than about 1 and thus could be attributed to metamorphic and volcanic rocks. It is noticed that a quite similar pattern with respect to the Th/U host rock composition is also exhibited by Ra-224/Ra-223 ratios.

During september 1988 a production test was carried *out* on the Latera 4 wells and 12 consequential radiochemical analysis of the fluids were performed, in order to follow the evolution of radium isotope concentrations. The results are reported in Tab. 2.

Table 2. Radium isotopes and radon concentrations during the production test carried out on the Latera 4 well in 1988.

Date	Label (I)	Temp. [°C]	Ra-223 [Bq/m^3]	Ra-224 [Bq/m^3]	Ra-226 [Bq/m^3]	Ra-228 [Bq/m^3]	Rn-222 [Bq/l]
1/9/88	E1	195-210	32.3±1.9	226±4	87.5±1.2	44.1±0.9	37a
1/9/88	E2	195-210	35.8±1.9	247±5	92.2±1.1	47.3±0.7	37a
2/9/88	E3	195-210	61.5±2.3	279±9	105±2	56.6±1.3	378
2/9/88	E4	195-210	47.4±1.5	308±16	137±3	66.8±1.9	378
3/9/88	E5	195-210	65.5±1.9	348±6	139±2	75.3±1.2	378
4/9/88	E6	195-210	63.4±2.0	303±10	124±3	67.9i1.6	378
5/9/88	E7	195-210	70.7±1.6	339±7	145±2	82.9±1.3	37a
7/9/88	E8	195-210	69.8±2.1	325±10	150±3	81.4±2.0	3 n
8/9/88	E9	195-210	88.4±1.7	363±7	169±2	94.6±1.4	378
9/9/88	E10	195-210	85.8±1.8	386±6	161±2	88.0±1.4	371
15/9/88	E11	195-210	70.8±2.0	303±6	136±2	85.3±1.4	378
19/9/88	612	195-210	77.7±2.8	315±9	168±3	98.2±1.7	378

Concerning the data obtained for geothermal well Latera 4 (E1 to E12, Tab. 2). Fig. 4 seems to reveal an evolutionary trend. These samples were successively taken from the well during a production test conducted between 1 and 19 September 1988 where a fluid volume of 26,400 tons was produced. The test was carried out about 5 month after injection tons fresh water into *the* well. Plotting Ra-224/Ra-228 vs. 1/Ra-228 (Fig. 4) it turns out that the data reflect a mixing between the injected fresh water and the undisturbed geothermal fluid. The area covered by the data points appears to be triangular. Thus a third component probably represented by fresh water slightly alterated by water-rock interaction during its residence time of a few months, could additionally be taken into account.

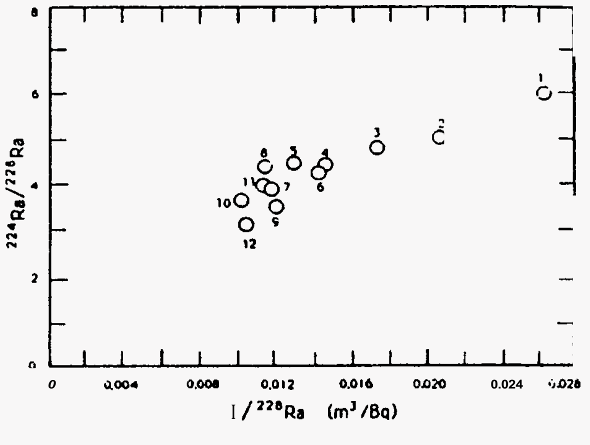

Fig. 4. Values for Ra-224/Ra-228 versus 1/Ra-228 in the water samples taken in the Latera 4 production test.

Table 3. Radioactivity in Central Italy rock samples

ROCK	N(*)	Ra-226 [Bq/kg]	Ra-228 [Bq/kg]	K-40 [Bq/kg]	Ra-228/Ra-226
CAP ROCKS					
Volcanites	16	197±147	254±172	2030±830	1.30±0.29
Flysch complex	5	16.0±6.1	25.9±11.9	494±314	1.58±0.17
Varicoloured shales	3	11.3±4.6	17.7f5.4	341±97	1.64±0.18
POTENTIAL RESERVOIR					
Sandstone	1	209	30.6	467	1.46
Carbonatic sequence	9	12.8±3.6	2.9±1.2	78±60	0.26±0.15
Marble	6	135±140	145±196	316±310	1.09±0.55
Anhydrites	3	3.5±2.4	0.9±0.4	4.6±2.8	0.24f0.05
Phyllites and Micascists	11	45±20	52.6±8.6	933±152	1.32f0.38
Syenite	6	250±127	296±155	2270±560	1.18±0.08
Granite	1	82.5	95.2	1440	1.15

(*) Number of samples examined

5. INTERPRETATION AND DISCUSSION

The experimental results were evaluated by a model based on transport equation of natural radionuclides, (Froehlich and Gellermann, 1987, Ivanovich et al., 1991). The model describes physico-chemical interaction between the radionuclides in the fluid and in the rock phase. in terms of first-order dissolution and precipitation processes and fast reversible exchange following a linear adsorption isotherm. In addition to dissolution, recoil ejection due to alpha decay of the radioactive progenitor is incorporated in the model. Fluid transport is described in terms of dispersive/advective flow. The analytical solution of the transport model for steady-state conditions and negligible dispersive and diffusive transport is given in Ivanovich et al., 1991. The model was specifically studied for the radium isotopes by K. Froehlich (Battaglia et al., 1992).

In the case of radium isotopes it is assumed that their progenitors (Th isotopes) are fixed on the solid phase. Furthermore it is considered that a fluid sample taken from a geothermal spring or geothermal well represents a mixture of components with different residence times in the systems. Characterizing this mixture by a simple exponential residence time function, the following expression describing the evolution of the activity concentration a_i of a given radium isotope i (i = 3: Ra-223. i = 4: Ra-224, etc.) is obtained:

$$a_i = \frac{a_{i0}+a_{is}K_iT}{1+K_iT} \qquad (1)$$

where:

a_{i0} = initial activity concentration
K_i = $R\lambda_i + p$ = effective decay constant
R = retardation factor (reversible sorption)
λ_i = decay constant
p = precipitation rate (irreversible sorption)

$$a_{is} = \frac{e+\gamma_i\lambda_i}{n\,K_i}\,a_{ir} \qquad (2)$$

a_{is} = stationary (equilibrium) concentration
e = chemical dissolution (leaching) rate
$\gamma_i\lambda_i$ = m i l ejection rate
n = porosity of the rock
a_{ir} = activity of the rock per volume of rock matrix
T = mean residence time of the fluid in contact with the host-rock of the system (water-rock reaction time) prior to supply to surface

For the short living radium isotopes Ra-224 and Ra-223 it can be assumed that $K_iT << 1$ and thus their concentrations approach the stationary (equilibrium) value. Considering that their decay rate is very high, the slower chemical precipitation and leaching processes can be assumed to be of negligible influence on the equilibrium concentration of these two radium isotopes. Hence, from eq. (2) it follows:

$$a_i = \frac{\gamma_i}{n\,R}\,a_{ir}, \qquad i = 3, 4 \qquad (3)$$

Equations (1) to (3) show that measurements of U/Th decay series radionuclides in hydrothermal fluids can be used to estimate parameters of geological interest in hydrothermal systems, such as rates of fluid-rock interaction.

First of all, equation (3) can be employed to derive information on the rock (a and n) as well as on the recoil ejection supply and the retardation factor. However it has been noted that this information is related to the proximity of the outlet of the thermal springs and of the borehole of the geothermal wells. This is due to the short migration length of these short-living radium isotopes. Ra-223 and Ran-222 which have similar half-lives can be used to estimate the retardation factor. As the precursors U-238/U-235 activity ratio is invariant in rocks and it corresponds to 21.6, from equation (3) it follows:

$$R = \frac{a_2/a_3}{21.6+a_6/a_3} \qquad (4)$$

In deriving equation (4) it is considered that Rn-222 is not subject to sorption processes (noble gas) and is produced by decay of Ra-226 in liquid and rock phase. The recoil ejection factor γ is assumed to be the same for both radionuclides (Krishnashwami et al., 1982). This assumption ignores possible differences in the migration of these. radionuclides trough microfractures and thus might under such conditions overestimate the sorption characteristics of the radium isotopes (Dickson, 1990).

Deriving equations (1) and (2) it is assumed that the rate constants of sorption and desorption of radium are short with respect to the decay constants of Ra-223 and Ra-224. In the following this assumption is given up. With k1, the sorption rate constant, and k2, the desorption rate constant, the activity concentration of a given radium isotope in solution, a_i, and at the rock surface, $a_{ad\,i}$, follows equation (1) and (2), respectively:

$$\frac{da_i}{d\tau^*} = P_i - (\lambda_i+k_1')\,a_i+k_2a_{ad\,i} \qquad (5)$$

and

$$\frac{da_{ad\,i}}{d\tau^*} = k_1a_i-(\lambda_i+k_2)\,a_{ad\,i} \qquad (6)$$

where:

$$P_i = \frac{(e+\gamma_i\lambda_i)\,a_{r\,i}}{n}$$

and

$$k_1' = k_1 + p$$

τ^* is the residence time of radium in the system, P_i denotes the production in the rock phase and p stands for the irreversible sorption rate constant (precipitation rate). The solution of the differential equations (1) and (2) yields for Ra-223, Ra-224 and Ra-228, which are assumed to be in stationary state and for which production by dissolution from the rock is negligible in comparison to recoil ejection, the following expression:

$$a_i = \frac{\gamma_i\lambda_ia_{r\,i}}{n\lambda_i[1+k_1/(\lambda_i+k_2)]} \qquad (7)$$

with i = 3,4,8. For Ra-226 it follows:

$$a_6 = \frac{(e+\gamma_6\lambda_6)a_{r\,6}}{nR\lambda_6(1+p/R\lambda_6)}(1-\exp[-(R\lambda_6+p)\tau]) \qquad (8)$$

where τ is the residence time of the water in the system considered. In this approach, the retardation factor of the radium isotopes is defined by the expression:

$$R = 1+\frac{k_1}{\lambda_i+k_1} \qquad (9)$$

Equation (9) shows that R depends also on the decay rate constant of the respective radium isotope.

On the basis of equations (7) and (9), the rate constants k_1 and k_2 and the retardation factor R can be derived from the experimental values of **Ra-223, Ra-224, Ra-226** and Rn-222. The values obtained are compiled in Tab. 4. The results show that K_2 ranges between $4\cdot10^{-5}$ to $5\cdot10^{-4}$ min^{-1}, that is the same order of magnitude of the decay rate constant of **Ra-224** ($1.32\cdot10^{-4}$ min^{-1}) and of **Ra-223** ($4.2\cdot10^{-5}$ min^{-1}). The retardation factor has to be derived from the equation (9) rather than eq. (4). For **Ra-226** and **Ra-228.** however, the decay rate constant is negligible compared with k_2, and thus the retardation factor is given by:

$$R = 1 + \frac{k_1}{k_2}$$

The uncertainty of sorption/desorption rate constants and the retardation factor depends on the analytical error of the radium isotopes and radon measurements. It ranges between about 10 % to 50 %. Moreover, the full set of experimental data, necessary for the rate constants and retardation factor determination, is only for a small fraction of all geothermal springs and wells available so far. Furthermore, it can be shown that realistic estimates of k_1, k_2 and R can only be obtained if the activity ratio Ra-224/Ra-228 is higher than about 1.2. However, for several thermal springs and geothermal wells this ratio turned out to be considerably lower (springs d,f,g and well G).

It is interesting to observe that one can derive the Th/U of the host rock by another approach from the following expression:

$$Th/U = \frac{R\, a_8}{0.8\, a_2} \tag{10}$$

where the factor 0.8 stands for the ratio of the **Ra-228** and **Rn-222** recoil factors (Krishnashwami et al., 1982).

In the following, an attempt is made to indicate the potential of the radium isotopes in deriving useful information on the dynamics of the geothermal system. Combining the expression (I) for **Ra-226** with equation **(3)** for **Ra-223,** and defining F by the expression:

$$F = \frac{(a_6/a_3)\,(1+k_1/k_2)}{21.6\,(\gamma_6/\gamma_3)\,[1+k_1/(\lambda_3+k_2)]} \tag{11}$$

and **E,** which represents the ratio between dissolution and recoil ejection rate for **Ra-226,** it follows:

$$F = \frac{1+E}{1+p/(R\lambda_6)}\;\frac{a_{6\,0}/a_{6\,s}+R\lambda_6 T}{1+R\lambda_6 T} \tag{12}$$

As a first approximation, it is assumed that $p/(R\,\lambda_6) << 1$ and $(1+E) \approx 1$. With these assumptions it follows:

$$T \approx \frac{1}{R\lambda_6}\;\frac{F-a_{6\,0}/a_{6\,s}}{1-F} \tag{13}$$

If the F value derived from the experimental data (eq.11) is $<< 1$ (and thus also $a_{6\,0}/a_{6\,s} << 1$) equation (13) yields an estimate of the mean residence time of water in geothermal systems.

The results of this attempt (Tab. 4) suggests that the mean residence time of thermal spring water is in the order of magnitude of a few years. Considering the definition of T which is based on an exponential residence time distribution function, this result would be consistent with the conclusion that 63 % of the water discharged by the respective thermal spring or geothermal well is less than T years (i.e. a few years) in contact with the geothermal system.

On the other hand, the total subsurface residence time of the water discharged by the spring or well can be estimated from measurements of the environmental isotope tritium. The values obtained are in the order of magnitude of some tens to hundreds of years. For thermal springs, this subsurface residence time corresponds approximately with the ratio of the subsurface water volume related to the spring and the discharge rate of the spring.

Table 4: Sorption/desorption rate constants, retardation factor and maximum residence time in geothermal fluids and thermal waters.

Name	Label (1)	k_1 [min^{-1}]	k_2 [min^{-1}]	R [$1+k_1/k_2$]	Th/U ratio	T [yrs]
LATERA 2	C	1.80±0.15E-3	1.90±0.84E-4	98±7	0.12±0.01	4.3
LATERA 3D	D	7.40±0.40E-3	1.8E-4	41 f2	0.12±0.01	2.3
LATERA 4	E1	4.40±0.50E-2	3.90±0.14E-5	113I f 126	0.16±0.02	*0.8*
LATERA 4	E2	3.90±0.44E-2	3.80±0.12E-5	1034±112	0.16±0.02	0.8
LATERA 4	E3	2.40±0.26E-2	4.10±0.21E-5	578±60	0.11±0.02	0.8
LATERA 4	E4	3.20±0.40E-2	4.50±0.35E-5	718±76	0.16±0.02	1.2
LATERA 4	€5	2.3OiO.248-2	4.40±0.14E-5	520±51	0.13±0.02	1.1
LATERA 4	E6	2.40±0.27E-2	4.70±0 26E-5	526±53	0.12±0.02	1.0
LATERA 4	E7	2.30±0.24E-2	5.20±0.19E-5	446±43	0.12±0.02	1.1
LATERA 4	E8	2.4OiO.278-2	5.40±0.30E-5	445±45	0.12±0.02	1.2
LATERA 4	E9	2.00±0.20E-2	5.70±0.20E-5	343±33	0.11±0.01	1.3
LATERA 4	E10	1.80±0.18E-2	4.80±0.14E-5	384±37	0.11±0.02	1.2
LATERA 4	E11	2.60±0.27E-2	6.40±0.25E-5	409±40	0.12±0.02	1.0
LATERA 4	E12	2.60±0.30E-2	7.50±0.39E-5	351 i 3 6	0.11±0.02	1.3
ARONNA	e	1.20±0.53E-1	2.10±0.44E-4	575±219	0.14±0.06	5.5
C. BROCO	i	8.4±2.2E-2	3.2±0.7E-4	265±40	1.04±0.20	3.3
BAGNACCI	l	8.3±1.4E-4	2.40±0.28E-4	4±1	0.66±0.12	343
B. PITIGL.	m	1.7±1 4E+0	2.80±0 19E-4	6300±2900	0.83±0.43	
PAGLIETO	p	3.4±1 9E-2	5.4±2.9E-4	64±7	0.01±0.00	1.4
PETRIOLO	q	2.10±0.17E-3	10.0±0.8E-5	21±1	0.02±0.00	4.2

Consequently it seems to be possible, by combining available hydraulic and hydrologic information (such as discharge rate of the spring or well) with information derived from environmental isotopes and U/Th decay series radionuclides, to gain new insights in the dynamics of the geothermal systems.

6. CONCLUSIONS

The correlation between activity ratios Ra-224/Ra-228 and Ra-223/Ra-226 yields information on the relative contribution of recoil ejection and chemical dissolution in transferring these isotopes from the rock into the liquid phase.. Including **Rn-222** in this evaluation, the rate constant of recoil ejection and chemical leaching can be estimated. Apart from **Ra-226** in geothermal fluids, the transfer of the other radium isotopes from rock to fluid *appeared* to be controlled by recoil ejection rather than by chemical dissolution.

Evaluating **Ra-224** and **Ra-228** data of samples taken during a production test carried out with geothermal well Latera **4 (E)** it is demonstrated that radium isotopes can provide useful information on mixing between fresh water and old geothermal fluid. This information is of practical interest in connection with re-injection of fresh water in geothermal wells and in attempts to identify mixing between deep geothermal fluids and shallow cold groundwater in thermal springs.

The identification of host-rocks of geothermal systems and thus of the origin of geothermal fluids is of particular practical interest for geothermal exploration. In this contest the activity ratios Ra-224/Ra-223, Ra-228/Ra-226 and particularly eq. (10) appeared to be a suitable indicator of the host-rock composition.

Furthermore this study demonstrates that a detailed consideration of the chemistry of the geothermal system including environmental isotopes is essential for the evaluation and interpretation of radium isotopes in thermal waters and geothermal fluids. Finally it is important to take samples successively during production tests or production life of a well: measurements of such samples could facilitate a more detailed study of the dynamics of the system.

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