

## Radiochemical constraints on the crustal residence time of submarine hydrothermal fluids: Endeavour Ridge

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**Abstract**—The <sup>210</sup>Pb/Pb and <sup>228</sup>Ra/<sup>226</sup>Ra ratios measured in fluids and particles venting from the Endeavour Ridge are used to constrain the crustal residence time of the convecting hydrothermal fluid from the initiation of basalt alteration where Mg<sup>+2</sup> loss from seawater results in rapidly falling pH conditions, to termination at seafloor venting. The <sup>210</sup>Pb/Pb ratios of hot, low Mg fluids are close to that of the basalts, suggesting a residence time of no greater than ten years. Particles associated with these vents have slightly higher ratios which may in part be due to scavenging of seawater <sup>210</sup>Pb. The <sup>228</sup>Ra/<sup>226</sup>Ra ratios of the fluids and an associated Ba-rich particle sample were also close to the basalt ratio, further constraining the residence time to 3 years or less. These estimates indicate that the mass of fluid interacting with newly formed crust at any one time is less than  $9 \times 10^{13}$  kg, if the axial heat flux is to be no greater than 30% of the total advective heat loss from the oceanic crust.

### INTRODUCTION

THE HYDROTHERMAL CIRCULATION of seawater associated with the generation of new oceanic crust at spreading centers has been the subject of intensive study over the past decade. Since the initial discovery of the low temperature (<20°C) venting of hydrothermal fluids from the Galapagos Spreading Center in 1977 (CORLISS *et al.*, 1979), discoveries of seafloor venting of fluids attaining 350°C, or higher, have been made at several sites along the medium-to-fast spreading East Pacific Rise (EPR) (SPEISS *et al.*, 1980; LONSDALE *et al.*, 1980; HEKINIAN *et al.*, 1983; THE MERGE GROUP, 1984). Recently, an impressive vent field has also been found in the TAG area of the slow spreading mid-Atlantic Ridge (RONA *et al.*, 1986).

This discharge of hot water at oceanic ridges has important consequences to the global heat and geochemical budgets. Near mid-ocean ridges, the convective flow of seawater is responsible for 15–30% of the total heat loss from the oceanic crust (CONVERSE *et al.*, 1984). The reaction of seawater with basalt within the convective cycle also produces profound chemical mass transfer and isotopic exchange which may have a significant impact on the chemical budget of the ocean (EDMOND *et al.*, 1979, 1982). While there is a general similarity between the solution chemistry of the venting fluids from all these sites, differences do exist between sites and even between vent fields of any one site (VON DAMM *et al.*, 1985). Several factors exist which can account for this variability, including rock type and degree of prior rock alteration, temperature, convective path length, flow rate and residence time. These parameters are not independent of one another. The residence time, flow rate and path length are all related, and influence the nature of reactions that are occurring, the effective water/rock ratio of these reactions, and whether equilibrium is achieved between the water and rock in these systems (VON DAMM *et al.*, 1985).

Furthermore, a feedback process probably exists whereby the products of reaction ultimately alter the parameters which initially brought about the reaction (NORTON, 1984). In this work we attempt to constrain one of these parameters, namely

the crustal residence time of the hydrothermal fluid from the initiation of high temperature rock alteration. Geophysical modeling, flow rate measurements and chemical data suggest that transit through the upflow zone is very fast ( $\ll 1$  year) (MACDONALD *et al.*, 1980; LISTER, 1982; MOTT, 1983; CONVERSE *et al.*, 1984) but there have been few results which provide insight into the residence time of fluid within the zone of basalt-seawater reaction. Such information is required to determine the rates of reaction and to ascertain the extent to which equilibrium for specific reactions is attained.

Several recent studies indicate that measurement of naturally occurring radionuclides in the hydrothermal fluids and associated basalts may offer constraints to this residence time. KRISHNASWAMI and TUREKIAN (1982) measured the concentration of <sup>210</sup>Pb (half-life = 22.3 y) in vent waters of the Galapagos Rise and suggested that when compared to the rate of production from *in situ* <sup>222</sup>Rn could yield an estimate of the crustal residence time of the hydrothermal fluid. They recognized, however, that the extremely low <sup>210</sup>Pb activities of their samples were probably due to precipitation of Pb within the system, and hence could not be used to accurately assess a time scale. KADKO *et al.* (1985/86) overcame this problem by normalizing the <sup>210</sup>Pb values of sulfides deposited in the Juan de Fuca Ridge to stable Pb. Their results suggested that the residence time of hydrothermal fluids, from the onset of basalt alteration, was much less than the 22.3 year half-life of <sup>210</sup>Pb. TUREKIAN and COCHRAN (1986) measured the <sup>228</sup>Ra/<sup>226</sup>Ra ratio of clam shells collected near vents from the Galapagos area and used this information to calculate the crustal residence time of fluids. They estimated a 22 to 45 year time period for basalt-seawater interaction, but the measurements and model results in this paper suggest a much shorter time scale.

We present here the first <sup>210</sup>Pb/Pb ratio measurements on hydrothermal solutions vented from the seafloor and will compare these to values obtained from associated sulfide material. We have also determined the <sup>228</sup>Ra/<sup>226</sup>Ra ratio of these solutions and will use this data to model the residence time of the circulating fluid.

## METHODS

*Vent fluid samples*

Samples analyzed in this study were collected in 1984 during the University of Washington expedition to the Endeavour Ridge, where an active vent field was discovered at 47°57'N, 129°06'W (THE MERGE GROUP, 1984). Vent fluids were obtained by 755 ml titanium syringes deployed in parallel on a T-handle by ALVIN's hydraulic arm. This system is described in VON DAMM *et al.* (1985). An aliquot of 90–720 ml was drawn from one of the syringes into an evacuated erlenmeyer flask fitted with a bubbler head for  $^{222}\text{Rn}$  collection. The remainder of the syringe was drawn for  $\text{CH}_4$  analysis.

The radon was stripped from the erlenmeyer flask by bubbling He through the sample with collection on an activated charcoal column at dry ice temperature. The column was heated and the radon transferred to an evacuated ZnS coated scintillation cell. This cell was placed in a photomultiplier tube counting system calibrated with  $^{226}\text{Ra}$  standards (MATHIEU, 1977). Approximately 5 ml of  $\text{HNO}_3\text{-HCl}$  were then added to the water sample and this was combined with the aliquot which had been stripped of  $\text{CH}_4$  and similarly acidified. The samples were then stored in 1-liter polyethylene bottles.

On land, the samples were spiked with approximately 30 dpm  $^{209}\text{Po}$  and 25 mg Pb carrier. They were again placed in the erlenmeyer flasks, flushed to remove radon, and then stored to allow regrowth of radon for  $^{226}\text{Ra}$  determination. Several radon milkings were performed and the results averaged. After the radium determination,  $\text{FeCl}_3$  and  $\text{Na}_2\text{CrO}_4$  were added to the sample and enough NaOH was added to form a mixed precipitate of  $\text{Fe}(\text{OH})_3$  and  $\text{PbCrO}_4$ . Polonium was then plated and counted on a low background alpha spectrometer. The solution was then passed through a series of ion exchange columns, Pb was eluted, and  $\text{PbCrO}_4$  precipitated. This was respiked with  $^{209}\text{Po}$ , stored for a few months to develop  $^{210}\text{Po}$ , and replated for polonium. The initial  $^{210}\text{Pb}$  activity is calculated from the  $^{210}\text{Po}$  ingrowth. Where less than a few months passed between sample collection and the first plating, the initial  $^{210}\text{Po}$  value, with a correction for ingrowth from  $^{210}\text{Pb}$ , could be determined. Details of this procedure are presented in THOMSON and TUREKIAN (1976).

The Pb and Mg values reported here were determined on aliquots of fluid taken from the companion titanium bottle to that used for the radionuclides and  $\text{CH}_4$ . Magnesium values for the two bottles generally agreed to within 5% of each other for the high temperature vent samples, and to within 0.4% for the low temperature vent samples. The Pb was determined by atomic absorption spectrophotometry and Mg was determined by EDTA titration of Ca + Mg corrected for Ca determined by EGTA titration. The analyses were performed by R. McDuff of the University of Washington.

*Manganese fiber experiment*

Manganese-impregnated acrylic fibers have been used successfully to extract radium from large volumes of seawater (MOORE, 1976; MICHEL *et al.*, 1981). In this work, a Mn-fiber sampler that could readily be deployed by ALVIN was developed for the purpose of determining the  $^{226}\text{Ra}/^{228}\text{Ra}$  activity ratio in vent water. The device (Fig. 1) was a 17.5 cm × 17.5 cm × 3.8 cm stainless steel box covered on two sides by a mesh of about 3 cm × 3 cm. The top was removable and a Mn-fiber cartridge could be placed in the sampler. Cartridges were simply 100 gms or so of fiber wrapped in a stainless steel mesh of about 0.6 cm × 0.6 cm. The unit had a T-handle for ALVIN use, and was placed in a close fitting stainless steel sheath during ascent and descent to prevent flow-through of ambient seawater.

The device could not be placed directly at the vent orifice, because the high heat and flow rate destroyed the fiber. Also the low pH of the unmineralized vent fluid would preclude efficient extraction of the radium isotopes. Optimum results were obtained by holding the device several inches above the orifice. Contamination with ambient bottom water was not of great concern because the concentration of radium in the hydrothermal endmember is many times that of seawater (see Results section).

Upon retrieval at the surface, the cartridges were rinsed with distilled water, and the fiber was removed from the wire mesh and stored in plastic bags. On land, the radium was removed from the fibers by a

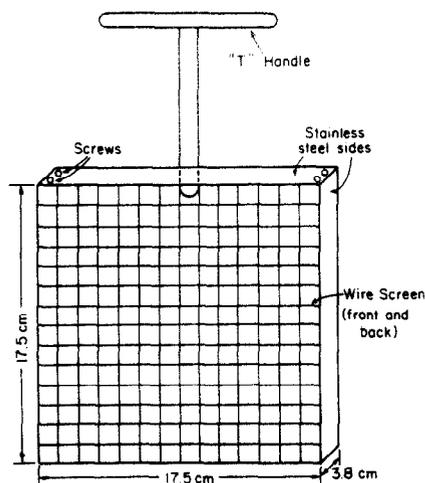


FIG. 1. Device for containing Mn-fibers for extraction of radium isotopes from vent water. The device fits into a sheath during ALVIN ascent and descent to prevent ambient water contamination.

mixture of hydroxylamine and dilute HCl, then concentrated by precipitating  $\text{BaSO}_4$  with the addition of 10 ml saturated  $\text{BaCl}_2$  solution and 50 ml  $\text{H}_2\text{SO}_4$ . The precipitate was placed in 20 ml plastic vials and counted in a Ge crystal well gamma detector. Details of this procedure are presented in MICHEL *et al.* (1981).

*Vent particle samples*

Vent particle samples were collected on 1.2  $\mu\text{m}$  millipore filters by the Grapple *in situ* pump system which was mounted on ALVIN's sled behind the sampling basket. The intake nozzle was mounted on the basket for easy access by the manipulator. Samples of 'black smoke' taken directly from the vents, and 'ambient smoke' from near field of the vents were collected. The recovered filters were covered with a substantial layer of black material which was carefully rinsed with approximately 500 ml of distilled water. These filters were air dried in a laminar flow hood and stored in a desiccator until further analysis. In addition to the vent particle samples, material collected in a sediment trap deployed 20 m above the vent field by J. Dymond of Oregon State University was also analyzed.

On land the samples (typically on the order of 200 mg) were divided into aliquots for mineralogic studies, neutron activation, atomic absorption analysis and for radiochemical determinations. For radiochemical analysis, 14–63 mg of sample was dissolved in a  $\text{HNO}_3\text{-HCl-HF}$  acid mixture to which approximately 4 dpm  $^{209}\text{Po}$ , 4 dpm  $^{227}\text{Th}$  spike and 25 mg Pb carrier were added. As for the vent water samples, polonium was first plated and then  $\text{PbCrO}_4$  was made to allow a new growth of  $^{210}\text{Po}$  for  $^{210}\text{Pb}$  determination. Thorium isotopes were separated from U and Fe by an 8 N HCl anion exchange column and purified on a 7 N  $\text{HNO}_3$  anion column. The Th was then plated from a TTA-benzene solution onto stainless steel disks and counted on a low background alpha detector. The U and Fe fraction was eluted with 0.1 N HCl from the 8 N HCl column and was then spiked with approximately 1 dpm  $^{232}\text{U}$ , purified on a 7 N  $\text{HNO}_3$  anion exchange column, and plated onto stainless steel disks from TTA for alpha counting.

One sample (M 12-4) was found from neutron activation analysis to contain 2.5% Ba (J. DYMOND, pers. commun.), and was assumed to have enough radium activity for analysis. Therefore, after the first polonium plate, and before the solution was sent through the ion exchange columns, the solution was stored for radon ingrowth as was described for the vent water samples and several  $^{226}\text{Ra}$  determinations were made. The  $\text{PbCrO}_4$  precipitation and Th plating followed.

TABLE 1  
 Radiochemistry - Vent Water 1984 Endeavour Ridge

Dive #	Vent Temp (°C)	Mg (mmol/kg)	<sup>222</sup> Rn (dpm/l)	<sup>226</sup> Ra (dpm/kg)	<sup>210</sup> Pb (dpm/kg)	<sup>210</sup> Po (dpm/kg)	Pb <sup>c</sup> ( <sup>210</sup> Pb) (μg/kg)	<sup>210</sup> Pb
1436	1.7 <sup>a</sup>	52.7	5.7±0.2	NA	NA	NA	NA	-
1438	315	7.08	613.2±2.0	2.70±.42	33.44±.96	NA	60	0.56
1439	186	51.28	38.8±0.5	-	6.93±.22	NA		
1445	345	21.60	598 ±80 <sup>b</sup>	2.09±.36	21.50±.52	11.53±3.87	<10	>2.1
1446	56	51.16	43.7±9.5 <sup>b</sup>	NA	NA	NA		
1447	250	17.04	293.6±1.2	1.01±.39	7.6 ±.5	NA	<10	>0.7
1447	15	50.48	75.2±0.7	NA	30.66±.90	NA		
1451	370-390	7.86	905 ± 2	2.40±.19	9.52±.44	10.81±2.11	18	0.53
1453	340	0.86	215.1±0.8	4.18±.62	13.05±.84	9.73±5.77	30	0.43

<sup>a</sup> ambient bottom seawater  
<sup>b</sup> uncertain cell efficiency  
<sup>c</sup> assume  $\rho = 1.025$   
 NA - not analyzed

## RESULTS

The radiochemical results from the vent fluids are presented in Table 1. The highest temperature recorded with each sample is also shown, but since the titanium syringes often entrained ambient seawater with the vent fluid, a measure other than temperature is needed to characterize the samples that were obtained. Because Mg is quantitatively removed from seawater during high temperature reaction with basalt at low water/rock ratios (BISCHOFF and DICKSON, 1975) the Mg content of the sample can serve as an indicator of the extent to which ambient water has mixed with hydrothermal fluid in each sample (VON DAMM *et al.*, 1985). For the high temperature vents, this represents mixing as an artifact of the sampling procedure, but for the lower temperature vents, Mg may also be introduced during subsurface mixing between the high temperature endmember fluid and groundwater of composition essentially that of the overlying water (EDMOND *et al.*, 1979). For non-conservative elements, this mixing process may preclude extrapolation of the low temperature concentrations to zero magnesium for the purpose of determining the high temperature endmember values.

### Radon-222

The radon results (Fig. 2) from the low temperature vents in this study are consistent with those obtained from the low temperature fluids sampled from the Galapagos area (DYMOND *et al.*, 1983). In both instances, the radon content increases linearly with decreasing Mg content. The radon values here extrapolate to a value of about 1540 dpm/l at zero Mg content. This value is probably not realistic, as none of the high temperature vents (low Mg content) contained such high values. Rather, the data suggest the existence of a lower temperature crustal endmember which does not correspond to zero Mg, and thus would not have the extrapolated Rn concentration. The Rn content of this component should be comparable to that of the high temperature vents, as recoil from radium decay, rather than high temperature basalt alteration, is the dominant mode of Rn production in either case (DYMOND *et al.*, 1983). The production from alpha-

recoil will depend on the uranium content of the crust as well as on factors controlling the surface area to volume of the hydrothermal conduits.

The higher temperature samples showed considerable scatter in the data, and several samples had radon activities 2-3 times greater than the extrapolated 350°C endmember value of 320 dpm/kg reported at the 21°N EPR site (KIM and FINKEL, 1980). It should be noted that the radon samples were not collected from the 'gas-tight' syringes used for <sup>3</sup>He determination (J. LUFTON, pers. commun.), and thus it is

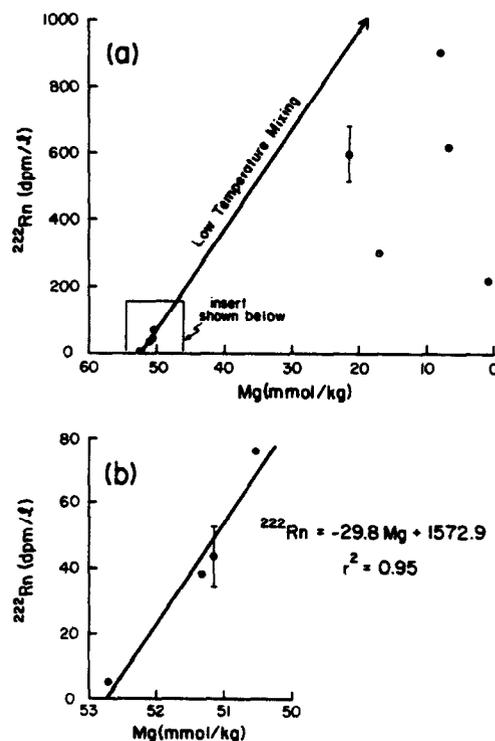


FIG. 2. a) <sup>222</sup>Rn versus Mg for all vents sampled on the Endeavour Ridge in 1984. b) <sup>222</sup>Rn versus Mg for the low temperature vents sampled on the Endeavour Ridge in 1984.

not known to what extent, if any, degassing from the samplers may have contributed to the scatter observed in the high temperature data.

### Radium

The radium-226 concentrations shown in Fig. 3a are most likely not indicative of the actual high temperature endmember concentration. VON DAMM *et al.* (1985) show that just trace amounts of sulfate in these samples will cause barite precipitation from the barium-rich vent fluids (Fig. 3b) and this should result in removal of radium. The highest value measured here,  $4.18 \pm 0.62$  dpm/kg, is about 14 times that measured in the bottom water of this area ( $0.30 \pm 0.1$  dpm/kg; KADKO, unpublished data), but is less than the 44.1 dpm/kg value extrapolated for 21°N fluids (KIM and FINKEL, 1980) and less than the range of extrapolated values at the Galapagos vents (12.8–40.3 dpm/kg; DYMOND *et al.*, 1983). Laboratory studies have demonstrated that Ba is strongly leached from basalts by hydrothermal fluids (MOTTL and HOLLAND, 1978) and Ra should be expected to show similar behavior. Assuming the alkali element water/rock ratio of 2 from the EPR at 21°N (VON DAMM *et al.*, 1985), and a uranium concentration of about 0.1 dpm/g in basalts, the  $^{226}\text{Ra}$  concentration in the fluids would be about 50 dpm/kg. However, barite deposition in the walls of vent chimneys indicate that even barring sampling artifacts, Ba (and Ra) can be subject to secondary precipitation reactions at depth. If the higher 'effective' water/rock ratios (10–30) for Ba derived from 21°N are then used, which reflect the effects of sampling loss and perhaps secondary precipitation reactions, then the  $^{226}\text{Ra}$  concentration would be in the range 3–10 dpm/kg.

Fortunately, for the purpose of determining fluid residence

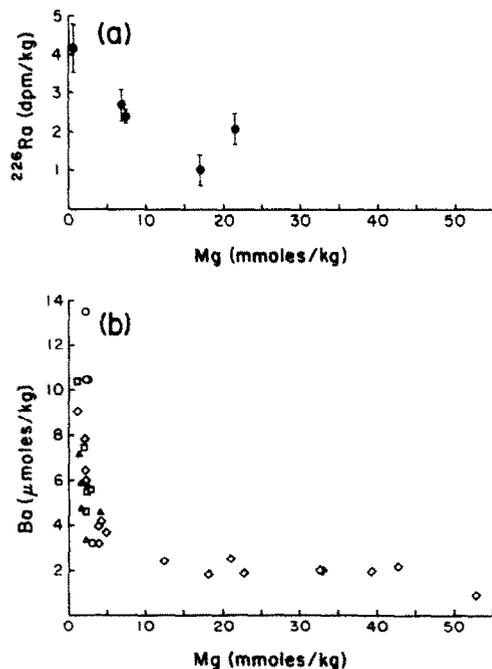


FIG. 3. a)  $^{226}\text{Ra}$  versus Mg for samples collected from the Endeavour Ridge in 1984. b) Ba versus Mg for samples from the EPR 21°N vents (VON DAMM *et al.*, 1985).

Dive #	$^{224}\text{Ra}$ (dpm)	$^{228}\text{Ra}$ (dpm)	$^{228}\text{Ra}/^{226}\text{Ra}$
1446 345°C vent	$36.50 \pm 2.0$	$37.8 \pm 3.0$	$1.04 \pm 0.10$
1451 >370°C vent	$48.5 \pm 1.0$	$42.7 \pm 1.5$	$0.88 \pm 0.04$
1445 -275°C vent	$14.5 \pm 0.8$	$14.1 \pm 0.8$	$0.97 \pm 0.07$
1438 Ambient	$29.7 \pm 0.6$	<1	<0.03
1437 Ambient	$5.5 \pm 0.5$	<1	<0.2
Blank	$0.60 \pm 0.10$	<0.5	

times, the  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratio is of more importance than the absolute concentrations. The  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios determined by the Mn-fiber technique are presented in Table 2. The values for the high temperature samples are in the range 0.86–1.16 which includes counting uncertainty, while the two ambient samples recorded low  $^{228}\text{Ra}/^{226}\text{Ra}$  activity ratios expected of bottom water. Figure 4 shows that the results from the Mn-fibers, which were held several inches above the vent openings, are not sensitive to different mixtures of hydrothermal fluid and ambient seawater that the fibers may have sampled. The dashed lines are mixing models between a dilute endmember of one isotopic composition with a much more concentrated endmember of differing isotopic composition. Because the radium content of vent fluids is 20–200 times greater than that in normal seawater, fibers "seeing" greater than only about 10% vent water will be sampling a  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio dominated by the vent signal.

The radium isotopic ratio was also determined on the bar-

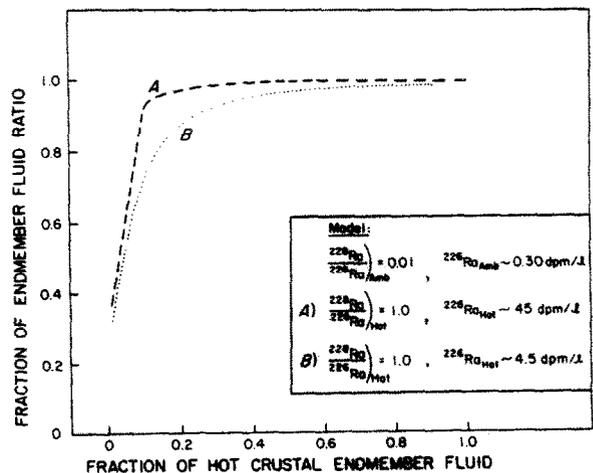


FIG. 4. Mixing model between a more concentrated endmember of one isotopic composition with a dilute endmember of another isotopic composition. The ordinate is the resultant mixture's isotopic ratio normalized to the concentrated endmember's ratio. The abscissa is the fraction of the mixture which is the hydrothermal (more concentrated) endmember. Case A is the mixing line if the hot endmember radium-226 content is 45 dpm/kg, while case B represents the mixing line if the hot endmember radium-226 content is only 4.5 dpm/kg.

TABLE 3  
 Radiochemistry - Particle samples 1984 Endeavour Ridge

Sample	$^{210}\text{Pb}$ (dpm/g)	Pb (ppm)	$^{210}\text{Pb}/\text{Pb}$ (dpm/ $\mu\text{g}$ )	$^{228}\text{Th}$ (dpm/g)	$^{232}\text{Th}$ (dpm/g)	$^{231}\text{Pa}$ (dpm/g)	$^{228}\text{Thb}$ (dpm/g)	$^{226}\text{RaC}$ (dpm/g)	$^{226}\text{Ra}$ (dpm/g)	$^{235}\text{U}$ (dpm/g)	$^{238}\text{U}$ (dpm/g)
JDF trap 20 m above vent site	302.2 $\pm$ 36.0	225	1.35	1.7 $\pm$ .3	$\leq$ .15	$\leq$ .8	10.2 $\pm$ 1.3	27 $\pm$ 3	n.a.	4.00 $\pm$ .20	3.22 $\pm$ .18
M12-8 Dive 1447- Ambient 'smoke' near vents	129.7 $\pm$ 10.0	-	-	$\leq$ 2	b.d.	$\leq$ .9	5.5 $\pm$ 0.7	14 $\pm$ 2	n.a.	b.d.	b.d.
M12-3 Dive 1451- hot vent	419.3 $\pm$ 30.6	602	0.70	$\leq$ 1.8	b.d.	b.d.	$\leq$ 1.3	-	n.a.	1.49 $\pm$ .15	1.36 $\pm$ .15
M12-10 Dive 1446, 56°C vent	1001.2 $\pm$ 24.9	1340	0.75	$\leq$ 1.6	b.d.	b.d.	14.8 $\pm$ 2.0	38 $\pm$ 5	n.a.	b.d.	b.d.
M12-4 Dive 1451- Ambient 'smoke' near hot vents	606.1 $\pm$ 11.9	763	0.79	3.2 $\pm$ .4	$\leq$ .3	b.d.	46 $\pm$ 6	107 $\pm$ 13	140 $\pm$ 6	n.a.	n.a.

a) from  $^{227}\text{Th}$  counts  
 b) at time of analysis  
 c) Calculated from  $^{226}\text{Ra}$ , assuming no initial  $^{228}\text{Th}$   
 b.d. = below detection  
 n.a. = not analyzed

ite-rich (2.5%) particles filtered from 'smoke' sampled near high temperature venting (Table 3, sample M12-4). The  $^{228}\text{Ra}$  was calculated from the ingrown  $^{228}\text{Th}$  activity (1.8 years after sample collection) assuming no initial  $^{228}\text{Th}$ . The negligible  $^{232}\text{Th}$  activity indicates that this assumption is probably valid. With the  $^{226}\text{Ra}$  determined by the radon emanation method the resulting  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio of  $0.76 \pm 0.10$  is close to the range obtained for the high temperature endmember fluid by the Mn-fiber experiment.

#### $^{210}\text{Pb}$ and $^{210}\text{Pb}/\text{Pb}$ ratios

The  $^{210}\text{Pb}/\text{Pb}$  ratios of hydrothermal fluids and the sulfides forming from the fluids should reflect the  $^{210}\text{Pb}/\text{Pb}$  ratio of the basalts undergoing hydrothermal alteration. Additionally, if the residence time of the fluid is long compared to the half-life of  $^{210}\text{Pb}$ , then excess  $^{210}\text{Pb}$  over that derived from the basalt alone should be generated by ingrowth from the very high activity of its parent  $^{222}\text{Rn}$  in the system (KRISHNASWAMI and TUREKIAN, 1982; KADKO *et al.*, 1985/86).

The  $^{210}\text{Pb}/\text{Pb}$  ratios determined on six vent fluid samples are shown in Fig. 5. The high temperature, low Mg samples on the extreme right of the figure have  $^{210}\text{Pb}/\text{Pb}$  ratios which are  $\leq 0.56$  dpm/ $\mu\text{g}$ , agreeing with values measured in fresh sulfide chimney fragments dredged from two locations on the JDF (KADKO *et al.*, 1985/86). These ratios are within the range measured in basaltic glass dredged from several locations along the Juan de Fuca Ridge (Table 4), implying that the transit time of the fluid from the onset of basalt alteration was short enough to preclude  $^{210}\text{Pb}$  generation from radon. This will be elaborated upon in the discussion section.

The samples to the left of Fig. 5 (low temperature vents, or high temperature vents contaminated by low temperature water) show much higher values of the  $^{210}\text{Pb}/\text{Pb}$  ratio. Because the aliquot used for  $^{210}\text{Pb}$  determination was not filtered, the high  $^{210}\text{Pb}$  values of these samples could be derived from particles of ambient 'smoke.' The concentration of  $^{210}\text{Pb}$  in sulfide material can be several hundred dpm/g (Table 3).

Alternatively, the higher  $^{210}\text{Pb}/\text{Pb}$  ratios of the lower temperature vent fluids could in part be a consequence of a longer residence time.

The  $^{210}\text{Pb}/\text{Pb}$  ratios of the particle samples are shown in Table 3. Two were taken directly from venting fluids. Sample M12-3 from a 380°C vent, had a  $^{210}\text{Pb}/\text{Pb}$  ratio of 0.70, which was higher than that measured on the fluid (0.53) from the same vent. We do not have a mechanism to explain this difference; however, the particulate ratio is still within the range expected from basalt alteration. Sample M12-10, from the 56°C vent, had a slightly higher ratio of 0.75.

The ambient 'smoke' sample, M12-4 ( $^{210}\text{Pb}/\text{Pb} = .79$ ) possibly, and the sediment trap sample ( $^{210}\text{Pb}/\text{Pb} = 1.35$ ) probably, have ratios that reflect scavenging of  $^{210}\text{Pb}$  from seawater. KADKO *et al.* (1986/87) found substantial deficiencies of  $^{210}\text{Pb}$  in seawater near the seafloor at the EPR, 8°45'N. The trap

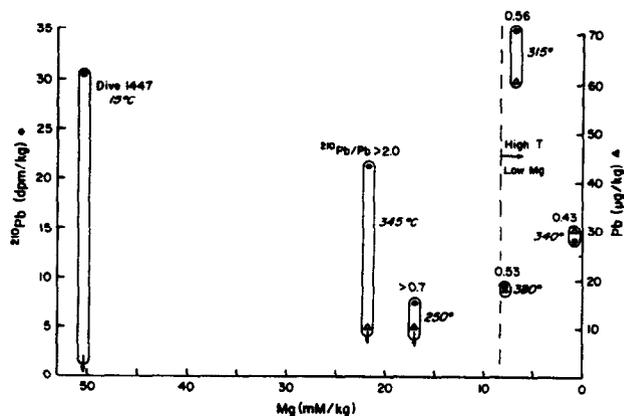


FIG. 5.  $^{210}\text{Pb}$  (solid circles) and Pb (open triangles) plotted against [Mg]. The  $^{210}\text{Pb}$  and Pb values from individual samples are coupled and the  $^{210}\text{Pb}/\text{Pb}$  ratio is indicated for each pair. The Pb concentration from the 15° 1447 vent is assumed to be very low. High temperature, low [Mg] samples on the extreme right have  $^{210}\text{Pb}/\text{Pb}$  ratios  $\leq .56$ , which are within the range measured in basalts.

TABLE 4  
Summary -  $^{210}\text{Pb}/\text{Pb}$  ratios from the Juan de Fuca Ridge

Fluids	RANGE	$^{210}\text{Pb}/\text{Pb}$ (dpm/ $\mu\text{g}$ )	MEAN (no. samples)
Low Mg	0.43-0.56		0.50 (3)
High Mg	>0.7		-
Sulfide chimney <sup>a</sup> fragments	0.285-0.60		0.48 (16)
Sulfide particles			
vents	0.70-0.79		0.75 (3)
trap	1.35		-
Basalt glass <sup>a</sup>	0.33-0.77		0.53 (4)

a) Data from KADKO *et al.*, 1985/86

result here supports the idea that venting particles scavenge reactive species from seawater.

## DISCUSSION

### Radionuclides in ocean ridge hydrothermal systems

Models describing the behavior of radionuclides in terrestrial groundwater systems can be applied to the seawater-basalt interaction occurring within the convective hydrothermal systems of mid-ocean ridges. KRISHNASWAMI *et al.* (1982) applied the following equation to naturally occurring radionuclides in terrestrial aquifers:

$$\frac{\partial C}{\partial t} = P - \lambda C + K_2 C_d \left[ \frac{\rho(1 - \phi)}{\phi} \right] - K_1 C = 0 \quad (1)$$

where

$C$  = concentration of nuclide in solution (atom  $\text{kg}^{-1}$ )

$C_d$  = concentration of nuclide adsorbed on aquifer solids (atoms  $\text{g}^{-1}$ )

$P$  = supply rate of nuclide (atoms  $\text{min}^{-1} \text{kg}^{-1}$ )

$\rho$  = density of aquifer solids ( $\text{g kg}^{-1}$ )

$\phi$  = porosity of aquifer

$\lambda$  = radioactive decay constant ( $\text{min}^{-1}$ )

$K_1$  = adsorption rate constant ( $\text{min}^{-1}$ )

$K_2$  = desorption rate constant ( $\text{min}^{-1}$ ).

For the case of convective hydrothermal systems, steady state may not be attained for each isotope because at least over 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 used here. Additionally, because we will be concentrating on that part of the convective cycle where basalt is undergoing alteration by seawater under conditions of high temperature and low pH, the effects of adsorption will not be considered. Prior to the rock alteration component of the circulation, however, isotopes of radium, thorium and lead are adsorbed rapidly during the shallow levels (to at least 0.5 km) of downwelling, where oxidizing and near neutral pH conditions prevail. This situation is similar to that of groundwater where low rock dissolution rates and rapid adsorption preclude significant mobility of these nuclides (KRISHNASWAMI *et al.*, 1982; RAMA and MOORE, 1984). The drop in pH accompanies the loss from seawater of  $\text{Mg}^{+2}$  to silicate phases and

can occur at temperatures at least as low as  $150^\circ\text{C}$  (BISCHOFF and DICKSON, 1975; SEYFRIED and BISCHOFF, 1977). The large uptake of Mg by pillow lavas metamorphosed in the greenschist facies suggests that large volumes of seawater can be heated rapidly to  $250^\circ\text{C}$  within the upper 1 or 2 km of the downwelling limb of circulation (MOTTL, 1983). Thus, conditions of low pH may occur relatively early in the system. Some experimental work suggests that after the initial drop in pH, and depending on the water/rock ratio and temperature, protons may gradually be consumed by hydrolysis of silicates and initially released metals may be taken up in alteration phases (BISCHOFF and DICKSON, 1975; SEYFRIED and BISCHOFF, 1977, 1981). Because we will be investigating radium and  $^{210}\text{Pb}/\text{Pb}$  ratios however, the effects of these secondary reactions should be mitigated. Our 'clock' therefore begins at the onset of basalt alteration defined as the initiation of falling pH conditions, and ends at the time of venting at the seafloor. Under these conditions Eqn. (1) is simplified to:

$$\frac{\partial C}{\partial t} = P - \lambda C. \quad (2)$$

The production term,  $P$ , for a U or Th decay series nuclide in the hydrothermal fluid consists of (1) production from *in situ* decay of its dissolved parent nuclide, (2) recoil into the fluid from decay of its parent nuclide in the basalt, and (3) input from basalt alteration by the erosive hydrothermal fluid.

The *in situ* production rate can be readily determined by measuring the activity of the parent in solution. The recoil supply rate of all alpha decay products, on the other hand, is best approximated by the  $^{222}\text{Rn}$  activity in solution (KRISHNASWAMI *et al.*, 1982). Because  $^{222}\text{Rn}$  is chemically inert and has a short half-life (3.85 d) it should reach steady state in solution and be unaffected by adsorption or any secondary reactions. Therefore, its governing equation is

$$P = \lambda C \quad (3)$$

as described in DYMOND *et al.* (1983). Because the activity of  $^{222}\text{Rn}$  is much greater than that of its parent  $^{226}\text{Ra}$ , *in situ* production is not an important supply term and, furthermore, nuclide input from basalt alteration is not important for short-lived isotopes (KRISHNASWAMI *et al.*, 1982; DYMOND *et al.*, 1983). As we will discuss here, the recoil process of nuclide injection becomes dominant as the half-life of the nuclide decreases. From Eqn. (3), therefore, the  $^{222}\text{Rn}$  activity,  $\lambda C$  (dpm  $\text{kg}^{-1}$ ) is equivalent to its recoil input rate,  $P$  (atoms  $\text{min}^{-1} \text{kg}^{-1}$ ). As the U series is more or less in secular equilibrium in the basalts, then the recoil supply of all products of alpha decay in the chain should be within a factor of two of the recoil supply of  $^{222}\text{Rn}$  (KRISHNASWAMI, 1982). RAMA and MOORE (1984), however, argued that nuclides are first recoiled into nanopore spaces of crystal grains and that unlike radon, non-gaseous, reactive nuclides (Th, Pb, Ra) would be rapidly adsorbed before diffusing into the intergranular porewater. Using the  $^{222}\text{Rn}$  activity as an estimate of recoil supply would lead to a gross overestimate of this parameter under those circumstances. In the case of low pH, hydrothermal fluids however, adsorption will be minimal and the  $^{222}\text{Rn}$  activity probably is a realistic measure of recoil input. For the Th series nuclides, the recoil supply rate equals the  $^{222}\text{Rn}$  activity times the  $^{232}\text{Th}/^{230}\text{Th}$  activity ratio of the basalt.

The activity ( $A$ ) of a nuclide in the fluid resulting from both the recoil process and *in situ* decay of its parent may be expressed as a function of time. The solution to Eqn. (2) is:

$$A = (Q + R)(1 - e^{-\lambda T}) \quad (4)$$

where

$Q$  = Activity of parent in solution ( $\text{dpm} \cdot \text{kg}^{-1}$ )

$R$  = Recoil supply rate ( $\text{atom} \cdot \text{min}^{-1} \cdot \text{kg}^{-1}$ )

$\lambda$  = Decay constant of nuclide ( $\text{yr}^{-1}$ )

$T$  = Residence time of hydrothermal fluid (yr).

It can be seen that the importance of these processes is strongly dependent on the half-life of the nuclide. For short-lived nuclides (large  $\lambda$ ) these processes will be the dominant mode of nuclide supply to the hydrothermal fluid.

The importance of recoil in supplying nuclides into groundwater has been recognized experimentally (KIGOSHI, 1971; FLEISCHER and RAABE, 1978). Recently, excess activity of another short-lived species in the  $^{238}\text{U}$  series,  $^{234}\text{Th}$  (24.1 d), was observed with  $^{222}\text{Rn}$  in the hydrothermal plume over the Endeavour Ridge (KADKO *et al.*, 1986). The activities of the two nuclides were comparable (2–5 dpm/l) which is further evidence that recoil is an important mechanism for introducing short-lived nuclides to hydrothermal fluids.

The activity of a nuclide in the fluid resulting from basalt alteration can also be expressed as a function of time:

$$A = \frac{A^*}{W \cdot T \cdot \lambda \cdot 10^{-3}} (1 - e^{-\lambda T}) \quad (5)$$

where

$A^*$  = Activity of nuclide in basalt ( $\text{dpm} \cdot \text{g}^{-1}$ )

$W$  = Water/rock ratio ( $\text{g} \cdot \text{g}^{-1}$ ).

The input rate of the nuclide, in  $\text{atoms} \cdot \text{min}^{-1} \cdot \text{kg}^{-1}$ , is equal to  $A^*/W \cdot T \cdot \lambda \cdot 10^{-3}$ . This term implies an average, constant rate of rock alteration equaling the product  $(W \cdot T \cdot 10^{-3})^{-1}$ . The water/rock ratio calculated from the chemistry of venting solutions is the end result of all reactions transpiring between fluid and rock along the convective pathlength, and is a measure of the net addition of an element to the hydrothermal solution. Dividing this net change by the time over which the change occurs (*i.e.* the residence time) will therefore yield an average rate of basalt alteration in  $\text{g}_{\text{rock}} \cdot \text{kg}_{\text{sw}} \cdot \text{yr}^{-1}$ . Certainly the actual alteration rate and the corresponding nuclide input is not constant throughout the pathlength, but this integrated formulation allows an estimate of the residence time to be made.

Because  $\lambda$  is in the denominator of Eqn. (4), nuclide input through rock alteration is most important for the longer-lived isotopes. For all isotopes however, as the rock alteration rate decreases (or the time for a fixed quantity of nuclide to be removed from the rock increases) this mode of input becomes less important. The total activity of a nuclide in solution at  $T > 0$  is the sum of Eqn. (4) and (5):

$$A = (Q + R + S)(1 - e^{-\lambda T}) \quad (6)$$

where  $S = A^*/W \cdot T \cdot \lambda \cdot 10^{-3}$ .

#### $^{210}\text{Pb}/\text{Pb}$ ratios and crustal residence times

The  $^{210}\text{Pb}/\text{Pb}$  ratio of the hot vent fluid can be used in Eqn. (6) to constrain the residence time of the hydrothermal

fluid from the onset of basalt alteration. This ratio, as a function of  $T$  is:

$$\frac{^{210}\text{Pb}}{\text{Pb}} = \frac{\left(500 + 500 + \frac{0.23}{.002 \cdot \lambda \cdot T}\right)(1 - e^{-\lambda T}) \text{ dpm}}{250 \mu\text{g}} \quad (7)$$

The  $^{210}\text{Pb}$  and Pb contents of the basalt are respectively about 0.23 dpm/g and 0.5 ppm (KADKO *et al.*, 1985/86). To calculate the Pb concentration in solution and the contribution of  $^{210}\text{Pb}$  from basalt alteration, a water/rock ratio must be chosen. One approach is to use  $W = 2$  based on the alkali elements which are quantitatively leached from rocks. Because these elements undergo only minor secondary reactions, they are best suited to determine the water/rock ratio of the system (VON DAMM *et al.*, 1985). It is assumed here that *subsequent* to extraction, lead species undergo secondary reactions which result in higher calculated water/rock ratios for this element. If these reactions are the same for all lead species, regardless of input mechanism, then this effect is cancelled by normalization of  $^{210}\text{Pb}$  to Pb. If, however, Pb is less mobile than the alkali elements during high temperature alteration, or, if the  $^{210}\text{Pb}$  derived from radon production is not involved in the same secondary reactions, then a higher water/rock ratio must be used.

*In situ* growth of  $^{210}\text{Pb}$  from  $^{222}\text{Rn}$  could be substantial because of the high activity of that nuclide in the fluid. A radon concentration of 500 dpm/kg is chosen for the high temperature fluid and consequently a value of 500  $\text{atom} \cdot \text{min}^{-1} \cdot \text{kg}$  is used as the recoil rate, but the result of the residence time calculation is quite insensitive to the values chosen for these parameters. This is shown in Fig. 6 where the  $^{210}\text{Pb}/\text{Pb}$  ratio is plotted against residence time for the component inputs to the system. Because the  $^{210}\text{Pb}/\text{Pb}$  ratios of the hot fluids and particles are so tightly constrained near the basalt ratio, the residence time cannot be much greater than 10 years for any combination of inputs that are used. If a higher water/rock ratio is used in this calculation, the estimated residence time is greatly reduced.

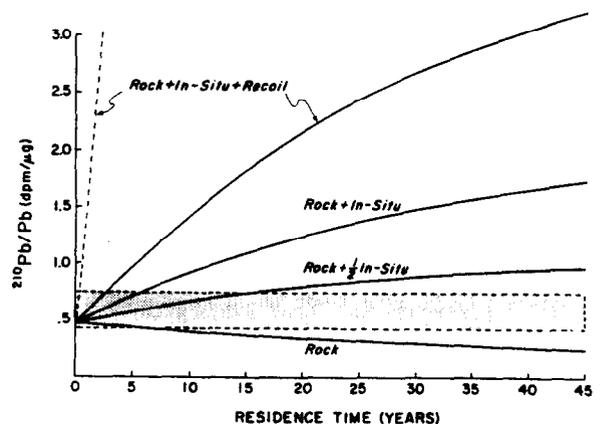


FIG. 6. The  $^{210}\text{Pb}/\text{Pb}$  ratio of hydrothermal fluids plotted as a function of fluid crustal residence time, for models comprising various modes of  $^{210}\text{Pb}$  production with a water/rock ratio of 2. The shaded box encompasses the range of ratios determined on low Mg fluid, sulfide and particle samples. The dashed line is the model result when a water/rock ratio of 20 is used.

### $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and crustal residence times

The result of the  $^{210}\text{Pb}/\text{Pb}$  calculation indicates that the residence time of the hydrothermal fluid is appreciably shorter than the 22.3 y half-life of  $^{210}\text{Pb}$ . This implies the need of a shorter-lived isotope which would allow a more sensitive evaluation of short time scale processes. The activity ratio of  $^{228}\text{Ra}$  ( $t_{1/2} = 5.77$  y) to  $^{226}\text{Ra}$  ( $t_{1/2} = 1620$  y) can be used in a manner analogous to the  $^{210}\text{Pb}/\text{Pb}$  ratio for this purpose.

For both radium isotopes, *in situ* production ( $^{226}\text{Ra}$  from  $^{230}\text{Th}$ ;  $^{228}\text{Ra}$  from  $^{232}\text{Th}$ ) is negligible because of the very low activity of the parent nuclides in the hydrothermal fluid (CHEN *et al.*, 1986). High temperature alteration of basalts, however, is a major source of radium in the hydrothermal fluids, and is the dominant source of  $^{226}\text{Ra}$ , as indicated by the similarity between the  $^{226}\text{Ra}/\text{Ba}$  ratio of MORB and the  $^{226}\text{Ra}/\text{Ba}$  of Galapagos fluids (DYMOND *et al.*, 1983; KRISHNASWAMI and TUREKIAN, 1982; TUREKIAN and COCHRAN, 1986). In fact, the  $^{226}\text{Ra}/\text{Ba}$  of the M12-4 particle sample (0.0056, Table 3) is close to the Galapagos fluid endmember ratio of 0.0065 dpm/ $\mu\text{g}$ . Input of  $^{226}\text{Ra}$  into the hydrothermal fluid by alpha recoil should not be significant because of its long half-life. However, if the residence time of the fluid is in the order of 5 years, then a significant quantity of  $^{228}\text{Ra}$  can be introduced by this mechanism. TUREKIAN and COCHRAN (1986) failed to consider this in their discussion of radium isotopes in Galapagos clams, necessitating a reinterpretation of their results.

The  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio, as a function of the residence time is

$$\frac{^{228}\text{Ra}}{^{226}\text{Ra}} = \frac{\left( R \times \frac{.14}{.23} + \frac{0.14}{.002 \cdot \lambda_8 \cdot T} \right) (1 - e^{-\lambda_8 T})}{\left( R + \frac{0.23}{.002 \cdot \lambda_6 \cdot T} \right) (1 - e^{-\lambda_6 T})} \quad (8)$$

where the  $^{232}\text{Th}$  and  $^{230}\text{Th}$  basalt activities are respectively, 0.14 and 0.23 dpm/g, and a water/rock ratio of 2 is used. This relationship is plotted in Fig. 7 for recoil input rates ( $R$ ) ranging from 0 to the radon activity of 500 atoms  $\cdot \text{min}^{-1} \cdot \text{kg}^{-1}$ . It is seen that again, the choice of this parameter is not critical because the  $^{228}\text{Ra}/^{226}\text{Ra}$  ratio of the fluid is close to that of the basalt. These results suggest that the residence time of the fluid, from the onset of basalt alteration, is less than about 3 years. If a higher water/rock ratio is used, the residence time estimate will be reduced. Note, however, that the higher water/rock ratios calculated for Ba may likely be due to artifacts of sampling, or to precipitation reactions occurring near the seafloor (VON DAMM *et al.*, 1985) and therefore not be appropriate for the present calculation. The actual  $^{232}\text{Th}/^{230}\text{Th}$  activity ratio in MORB in this model cannot be precisely known, but the values determined in basalts from several ocean ridge locations always are less than 0.9 and usually greater than 0.5 (CONDOMINES *et al.*, 1981; NEWMAN *et al.*, 1983). If we use a ratio higher than 0.6 in our model, the residence time estimate will be lowered.

TUREKIAN and COCHRAN (1986) estimated the  $^{228}\text{Ra}/^{226}\text{Ra}$  endmember ratio from clams near Galapagos vents to be much less than the basalt ratio. This can only be modeled by the 'rock input only' curve of Fig. 7 which neglects entirely

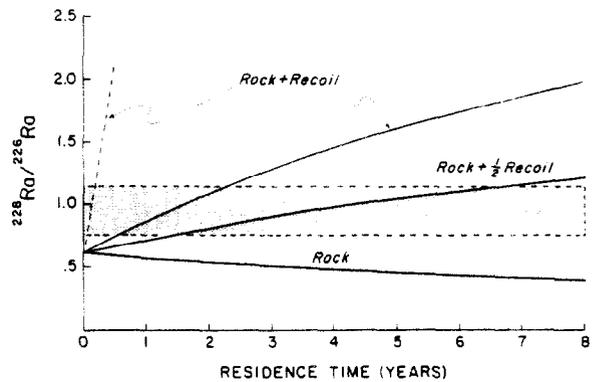


FIG. 7. The  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios of hydrothermal fluids plotted as a function of fluid crustal residence time, for models comprising a range of production from the recoil process with a water/rock ratio of 2. The shaded box encompasses the range of ratios determined by the Mn-fiber experiment and on the barite-rich M12-4 particle sample. The dashed line is the model result when a water/rock ratio of 20 is used.

the recoil input, and yields a residence time of over 20 years—which is inconsistent with the  $^{210}\text{Pb}/\text{Pb}$  geochronometer. According to those authors, the clams resided under predominantly ambient conditions (only 3% hydrothermal), which necessitated a large extrapolation to the hot endmember value. As described in Fig. 4, a substantial error can arise when estimating the endmember radium ratio from mixtures of less than 10% hydrothermal component. Our results, which are based on more direct measurements should, therefore, be more reliable.

### Flux considerations

Knowledge of the high temperature fluid crustal residence time can place constraints on the mass ( $M$ ) of the fluid interacting with newly formed crust at one time. This estimate must be consistent with both a reasonable loss of heat from the ridge crest and a fraction of newly emplaced crust that is altered. The percentage of new crust that is altered is:

$$\frac{M}{W \cdot T \cdot 10^{-3} (4 \times 10^{16} \text{ g})} \times 100 \quad (9)$$

where  $4 \times 10^{16}$  g of material is estimated to be formed per year at oceanic spreading centers. The percentage of heat lost from axial springs is

$$\frac{M}{T (1 \times 10^{14} \text{ kg/yr})} \times 100 \quad (10)$$

where  $1 \times 10^{14}$  kg/yr of 350°C water is required to remove the total advective heat flux (*e.g.* MOTTLL, 1983).

In Fig. 8, the percentages of advective heat loss and crust alteration associated with high temperature axial hydrothermal activity are related to the mass of hot fluid in the system at any time. If the residence time of this fluid is less than 3 years, then no more than  $9 \times 10^{13}$  kg of seawater can be involved in high temperature rock alteration for the axial heat flux to be less than 30% of the total advective loss. With a water/rock ratio of 2, less than 35% of newly formed crust

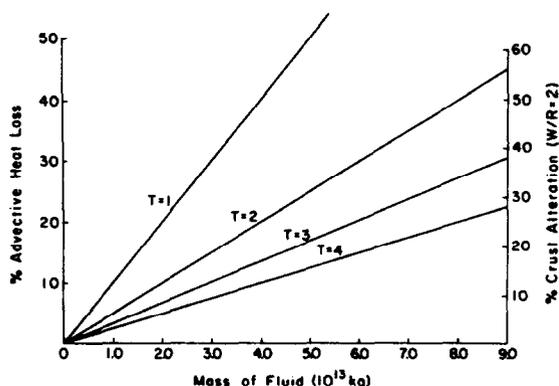


FIG. 8. The % advective heat loss and % alteration of newly formed crust associated with high temperature axial hydrothermal activity as a function of the mass of fluid of interacting with new crust at any one time. The case for several residence times are shown, and a  $w/r = 2$  is used in this example.

would be altered. A higher ratio would result in a proportionally lower degree of basalt alteration. It should be noted that these parameters are inter-related. For example, a decrease in residence time (or increased flow rate) could result in a higher water/rock ratio though the rock alteration rate  $(W \cdot T)^{-1}$  might not change considerably. The heat flux however could increase if  $M$  remained constant (Eqn. 10). Increased heat loss could then ultimately result in cooling of the magma chamber, diminishment of the thermal driving force, and a lower flow rate and longer residence time. These feedback processes are significant when for example, the relationship between hydrothermal fluxes and spreading rate, and the variation with hydrothermal input through time are considered.

### SUMMARY

The  $^{210}\text{Pb}/\text{Pb}$  and  $^{228}\text{Ra}/^{226}\text{Ra}$  ratios measured in fluids and particles venting from the Endeavour Ridge are close to those ratios measured in mid-ocean ridge basalts. Higher  $^{210}\text{Pb}/\text{Pb}$  ratios in some of the particles may in part be due to scavenging of  $^{210}\text{Pb}$  from seawater which is consistent with observations of low  $^{210}\text{Pb}$  concentrations in water over ridge crest locations. Assuming that the use of ratios mitigate the effect of secondary precipitation reactions, then the residence time of the convecting hydrothermal fluid, from the onset of basalt alteration to seafloor venting, is no greater than 3 years. We assume that the radiochemical 'clock' is activated when the pH of the circulating fluid drops in response to  $\text{Mg}^{+2}$  loss to basalt. This may occur early in the convective cycle. This residence time estimate constrains the mass of hot fluid interacting with newly formed material at any one time to be less than  $9 \times 10^{13}$  kg, if the axial heat flux is to be no greater than 30% of the total advective heat loss from the oceanic crust.

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