# RADIONUCLIDE GRADIENTS IN TWO Mn OXIDE DEPOSITS FROM THE MID-ATLANTIC RIDGE: POSSIBLE INFLUENCE OF A HYDROTHERMAL PLUME\*

CLAUDE LALOU AND EVELYNE BRICHET

Centre des Faibles Radioactivités, Laboratoire mixte CNRS-CEA, Domaine du CNRS, 91198 Gif sur Yvette, Cedex, France

## **GEOFFREY THOMPSON**

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, 02543 U.S.A.

#### ABSTRACT

During a 1973 ATLANTIS II oceanographic cruise in the North Atlantic, two Mn-Fe oxide deposits were recovered in the same dredge haul, 135 km west of the Mid-Atlantic Ridge axis at 23°N. One of them is Mn-rich and has mineralogical and chemical characteristics generally attributed to hydrothermal deposits; the other is more comparable to typical hydrogenous ferromanganese deposits. A radiochemical study based on the observed decrease of  $^{230}\mathrm{Th}_\mathrm{excess}$  with depth in the sample suggests a hydrogenous origin for both samples, with growth rates around 20 mm/10<sup>6</sup> years. However, one of the samples consists mainly of well-crystallized todorokite, with a very low U content (1 ppm) and no detectable Th; these features point to a hydrothermal origin for one of the samples. In both samples decreasing gradients with depth for <sup>232</sup>Th and <sup>238</sup>U, as well as the near-constant <sup>230</sup>Th/<sup>232</sup>Th ratios, render questionable the use of the excess <sup>230</sup>Th method to calculate growth rates. To explain the observed gradients with depth, a qualitative model based on the scavenging properties of oxyhydroxides for trace elements is proposed. In this model, the gradients reflect primary chemical rather than radioactive decay gradients, and result from change in the composition of a hydrothermal plume.

*Keywords:* Mn-Fe oxide deposits, hydrothermal, plume scavenging, Mid-Atlantic Ridge, radiochemistry.

#### SOMMAIRE

Au cours d'une mission de l'ATLANTIS II dans l'océan Atlantique en 1973, deux échantillons d'oxydes de manganèse et de fer ont été récoltés dans la même drague, à 135 km à l'ouest de la dorsale medio-Atlantique, à 23°N. L'un des deux présente des caractéristiques minéralogiques et chimiques généralement attribuées aux dépôts hydrothermaux, les caractéristiques de l'autre lui assignant une origine «hydrogénée». L'étude radiochimique permet de montrer qu'en utilisant le gradient d'activité de <sup>230</sup>Th en excès, décroissant avec la profondeur dans les deux échantillons, on pourrait leur attribuer à tous deux une origine hydrogénée avec une vitesse d'accumulation de l'ordre de 20 mm/106 ans. Toutefois, en dehors des caractéristiques minéralogiques et chimiques qui permettent de rejeter l'hypothèse hydrogénée pour l'un des deux (todorokite bien cristallisée, faible teneur en uranium (1 ppm) et totalement dépourvu de thorium 232), d'autres caractéristiques communes aux deux échantillons: gradients décroissants de  $^{232}$ Th et de  $^{238}$ U, rapport  $^{230}$ Th/ $^{232}$ Th constant, permettent de douter de la possibilité d'utilisation de la décroissance de l'excès de  $^{230}$ Th pour calculer un taux de croissance. On propose un modèle qualitatif fondé sur les propriétés qu'ont les hydroxydes d'adsorber les éléments trace. Dans ce cas, les gradients observés seraient des gradients chimiques: un panache hydrothermal décroissant en intensité conduirait à un dépôt dont l'activité spécifique en radionuclides serait de plus en plus élevée, les deux échantillons auraient alors une origine hydrothermale.

Mots-clés: hydrothermalisme, dépôts d'oxydes de Mn-Fe, radiochimie, adsorption, dorsale médio-Atlantique.

### INTRODUCTION

During the ATLANTIS II cruise 78 in the northwestern Atlantic Ocean in 1973, two apparently different Mn oxide deposits were recovered in the same dredge haul on the western flank of the Mid-Atlantic Ridge (MAR). They occur about 135 km from the spreading axis, at 22°53'N, 45°53'W (Fig. 1), on basement about 7 Ma old, and from depths between 2910 and 3860 m (Thompson et al. 1975). One of the samples (AII78-9-21), which is postulated to be of hydrothermal origin, is almost pure todorokite. The other sample (AII78-9-12) is considered to be of hydrogenous derivation. This sample has a Mn/Fe ratio of 0.75, typical of many ferromanganese crusts in the Atlantic, and is composed of  $\delta$ MnO<sub>2</sub> interlayered with amorphous iron oxide and goethite ( $\delta$ MnO<sub>2</sub> is currently used instead of vernadite for deep-sea manganese deposits). Because the genesis and growth rates of marine metallic deposits remain somewhat controversial, and because at this latitude on the MAR, high-temperature hydrothermal vents have recently been recognized (Leg 106 Shipboard Scientific Party 1986, Thompson et al. 1988), we investigated these two apparently different products to establish whether they are genetically independent or part of a continuum.

Mn oxide deposits are generally classified into two groups, depending on chemical composition, location, and growth rates (Bonatti 1975, Cronan 1976). It is generally assumed that hydrothermal deposits

<sup>\*</sup> Contribution 6227 from Woods Hole Oceanographic Institution and 850 from Centre des Faibles Radioactivités.



FIG. 1. Map showing the location of samples (star), ODP Leg 106 hydrothermal site (square) and TAG hydrothermal field in central North Atlantic.





FIG. 2. Schematic cross-section of the two samples showing the sublayers sampled. (A) Sample AII78-9-21 (the thickness of sublayers 1 to 12 has been expanded to show the laminated structure). (B) Sample AII78-9-12.

of Mn form rapidly and contain low concentrations of other trace elements, whereas hydrogenous deposits are formed at very low rates, on the order of a few  $mm/10^6$  years, and are rich in iron and trace elements. Until the discovery during the 1970s of significant hydrothermal activity along the midocean ridges, Mn nodules were the only proof of ore deposition on the ocean floor, except for metalliferous sediments associated with the ridges (Boström & Peterson 1966). After the discovery of strong hydrothermal activity on the ridge crest of the East Pacific Rise (EPR) (CYAMEX 1978, RISE 1980), Bonatti (1983) suggested a classification which related the different kinds of deposits to distance from the hydrothermal source: pre-discharge, syndischarge, and post-discharge deposits, respectively formed within the igneous crust, at vent sites, and from hydrothermally influenced bottom waters away from the ridge itself.

One of the main criteria used to differentiate hydrothermal from hydrogenous deposits is their growth rate, as measured by radiochemical techniques. There is general agreement that hydrothermal Mn oxide deposits are depleted in <sup>230</sup>Th relative to <sup>234</sup>U when they form; the ages calculated from the evolution of the <sup>230</sup>Th/<sup>234</sup>U ratio indicate rapid deposition (Scott et al. 1974, Lalou et al. 1983, Lalou & Brichet 1987). On the contrary, the so-called hydrogenous deposits are characterized by an exponential decrease of <sup>230</sup>Th<sub>excess</sub> toward their interiors; this is generally considered to be due to radioactive decay. In these deposits, <sup>232</sup>Th, owing to its very long half-life, is considered as a radioactively stable element with the same geochemical behavior as <sup>230</sup>Th. The decrease of <sup>230</sup>Th<sub>excess</sub>/<sup>232</sup>Th may be used more effectively than <sup>230</sup>Th<sub>excess</sub> alone to calculate growth rates because this ratio compensates for any variations in the supply of detrital material to the active deposits. Growth rates calculated for hydrogenous deposits using this method are in the order of mm/10<sup>6</sup> years (Bender et al. 1966, Ku & Broecker 1967).

## SAMPLE DESCRIPTION AND ANALYTICAL METHODS

The dredge haul from which the two Mn oxiderich samples were recovered extended from a depth of 3860 to 2910 m, over a distance of at least 5 km. The bottom topography was steep and consisted of a number of fault scarps separated by narrow benches. The bulk of the dredge consisted of weathered basalt. Figure 2A is a schematic crosssection of Mn oxide sample 21 (AII78-9-21). The general shape of the sample is conical; the base of the cone consists of hard plates of well-crystallized todorokite arranged as "sand roses". The rest of the sample is composed of alternating layers of hard, black, metallic-lustered material, and layers with an earthy, softer texture. Such alternations in texture have been described in the hydrothermal Mn oxide deposits drilled by DSDP Leg 70 in the Galapagos hydrothermal-mounds area (Barrett & Friedrichsen 1982, Lalou et al. 1983). Two areas in this sample

100

10

238<sub>U</sub>

232 <sub>Th</sub>

238<sub>U</sub>

were chosen for radiochemical study: the base of the cone, where 5 "petals" of a rose (subsamples 1 to 5, Fig. 2A) were separated, and the upper part where 7 successive layers were removed (subsamples 6 to 12 from exterior to interior). Each layer was represented by an area about 1 cm<sup>2</sup> and was carefully separated with a scalpel to avoid mixing of each structural unit. Layers 12 to 9 are composed of a mixture of birnessite and todorokite, layers 8 and 7 consist of todorokite, and layer 6 is poorly crystalline.

Figure 2B shows a cross-section of sample 12 (AII 78-9-12). Seven mm of ferromanganese oxide crust coat a fragment of very altered basalt. Sublayers 1 to 5 were scraped from the oxide layer: subsample 6 is from the central part of the basalt core. All layers are poorly crystalline, and contain goethite and δMnO<sub>2</sub>.

Radiochemical analyses were done using a method similar to that of Ku & Broecker (1969). About 200 to 400 mg of the powdered sample were dissolved in a HCl-HNO<sub>3</sub>-HClO<sub>4</sub> mixture and spiked with a <sup>232</sup>U-<sup>228</sup>Th tracer. In the exceptional case where an insoluble residue remained, it was separated by centrifugation, dissolved in HF-HNO<sub>3</sub>-HClO<sub>4</sub>, and added to the initial solution. Uranium and thorium were then separated and purified by several precipitations and ion exchanges, and were deposited from organic solution onto stainless-steel planchets. U and Th isotopes were measured by alpha spectrometry using a gridded chamber. For samples with a high activity of <sup>232</sup>Th (especially in the outermost layers), analyses without the tracer were made on aliquots to verify equilibrium between <sup>232</sup>Th and <sup>228</sup>Th. As our spike contains <sup>228</sup>Th, any departure from equilibrium between <sup>232</sup>Th and <sup>228</sup>Th would result in erroneous measurements of the activities of <sup>230</sup>Th and <sup>232</sup>Th. Iron and manganese were measured on the same layers using an energy dispersion X-ray system (EDS).

#### RESULTS

#### Sample 21

### Radiochemical results are given in Table 1 for the

TABLE 1. RADIOCHEMICAL RESULTS FOR SAMPLE 21

Layer N°	Depth in the crus (mm)	2381) t (ppm)	234U (dpm/g)	2340/2380	232Th 2 (ppm)	<sup>30Th</sup> exc (dpm/g)	230Th 232Thexc/ (dpm/dpm)
1 2	Sand rose	1.30±0.19 0.93+0.09	1.28±0.17 0.64+0.06	1.33±0.25 0.93+0.11	*	3.44±1.2	
3 4	8 #	0.95±0.09 1.08+0.07	0.89±0.07 0.87+0.06	1.27±0.15	*	-	
5	<b>u</b>	0,96±0.07	0.81±0.06	1.15±0.10	*		
6 7	0 - 0.5 0.5- 1.5	8.89±0.57 5.77±0.37	7.20±0.46 4.80±0.30	1.10±0.05 1.13±0.07	39.49±4.94 21.63±2.16	4.43±1.5 2.57±0.8	0.47 0.50
8 9	1.5-4.5	2.29±0.13 2.03+0.34	1.97±0.11 1.73±0.27	1.17±0.08 1.16±0.24	6.70±0.41 4.10±0.34	1.66±0.2	1.04
10	6.5- 8.5	1.66±0.13	1.59±0.11	1.30±0.12	3.18±0.35	$0.08 \pm 0.1$	-
12	8.5-10.5 10.5-12.5	1.63±0.29 1.06±0.09	1.12±0.20 0.84±0.07	0.90±0.19 1.08±0.11	1.56±0.17 1.45±0.34	0.28±0.1	5 -

under the detection limit.

Fores quoted are statistical counting errors at 10 level. Subsamples 1 to 5 are sand-rose petals Layers 6 to 12 are successive layers sampled from the surface towards the nter of the sample.

<sup>232</sup>Th 230 : 6/wdp bpm 230<sub>Th</sub> I 2 8 10 12 4 6 mπ DEPTH IN SAMPLE 21

FIG. 3. Chemical variations with depth in sample AII78-9-21. Black circles: <sup>230</sup>Th<sub>excess</sub> (dpm/g); black diamonds: U (ppm); black squares: <sup>232</sup>Th (ppm).

five "sand rose" petals and for layers 6 to 12. The content of radionuclides in the todorokite petals is low: U ~1 ppm, and <sup>232</sup>Th at background levels. This is characteristic of hydrothermal Mn oxide deposits (Lalou 1983). Except for subsample 1, which was located at the base and contained patches of sediment, <sup>230</sup>Th is nearly in equilibrium with <sup>234</sup>U (owing to the very low activity of uranium, a slight excess of <sup>230</sup>Th may be attributed to traces of sedimentary <sup>230</sup>Th). Hence, this part of the sample was formed at least 350,000 years ago. This age is much older than hydrothermal Mn oxide samples from the TAG area on the eastern flank of the rift valley of the MAR (Rona 1980) which have ages of 4,000 to 16,000 years (Lalou et al. 1986). As 350,000 years is a minimum age (the time required for <sup>230</sup>Th to reach radioactive equilibrium with <sup>234</sup>U), the sample could be as old as the 7-Ma-old basement from which it was recovered.

The radiochemical results for layers 6 to 12 from the external part of the sample are plotted against depth in Figure 3. The decrease in <sup>230</sup>Th<sub>excess</sub> activity with depth could be indicative of radioactive decay,

TABLE 2. Mn, Fe CONCENTRATIONS (WT. %) IN

Subsample	Mn	Fe	Mn/Fe		
1		- 2	- 93		
3		.0	-		
4	55	1.8	31		
5	54	1.1	47		
6	14.7	26.3	.56		
7	25.9	16.9	1.5		
8	40.3	6.4	6.3		
9	47	1.8	25.4		
10	49.6	1.3	37		
11	49.3	1.9	25.1		
12	49	2.5	20.2		

the process generally invoked for such trends in manganese nodules. This would yield a growth rate of 18.6 mm/10<sup>6</sup> years, similar to rates found in hydrogenous deposits. Since the total thickness of the layered part of the sample is 25 mm, this would imply that concretion growth began on a hydrothermal base (the Mn petals) about 1.3 Ma ago. However, the mineralogy (well crystallized todorokite and birnessite), the generally very low concentrations of iron (Table 2), and the alternations in texture are not in accordance with hydrogenous growth. The <sup>238</sup>U values (Fig. 3) decrease from about 9 ppm at the surface, consistent with values found in hydrogenous deposits (Ku & Broecker 1969), to about 2 ppm (similar to values found in subsamples 1 to 5 and in pure hydrothermal deposits). <sup>232</sup>Th concentrations are up to 40 ppm in the outer part and, like 230 Th and 238U, show an exponential decrease with depth. The <sup>230</sup>Th<sub>excess</sub>/<sup>232</sup>Th ratio cannot be used to calculate a growth rate because the ratio is near-constant.

#### Sample 12

The radiochemical data for sample 12 are given in Table 3 and are plotted against depth in the Mn crust in Figure 4. The <sup>230</sup>Th<sub>excess</sub> activity decreases from the surface towards the basaltic core (Fig. 4). This decrease vields a calculated growth-rate of about 22.6 mm/10<sup>6</sup> years, similar to that found in the external part of sample 21. The <sup>238</sup>U decreases slightly with depth, but never reaches concentrations as low as those in hydrothermal deposits. The <sup>232</sup>Th concentrations decrease from 75 ppm in the outermost layer to 23 ppm in the innermost one. As in sample 21, the  ${}^{230}\text{Th}_{\text{excess}}/{}^{232}\text{Th}$  ratio is nearconstant, precluding its use in confirming the growth rate. The basalt core contains 5.7 ppm <sup>232</sup>Th. Mn and Fe concentrations (Table 4) are similar to those in many hydrogenous ferromanganese concretions in the Atlantic and have Mn/Fe about 0.5. Hydrothermal deposits are usually characterized by Mn/Fe ratios >10.

Laye N°	r Depth in the crust (mm)	238U (ppm)	234U (dpm/g)	2348/2380	232Th (ppm)	<sup>230Th</sup> exc (dpm/g)	230Th 232Thexc/ (dpm/dpm)
1	0 - 1	11.59±0.62	8.42±0.45	0.99±0.04	75.32±9.10	27:7±4.5	1.54
2	1.0-2.5	11.22±0.76	8.87±0.55	1.07±0.05	69.09±7.69	15.4±2.2	0.94
3	2.5-4.0	10.62±0.49	8.05±0.37	1.03±0.04	34.11±2.99	7.3±1.5	0.90
4	4.0-5.5	9.97±0.74	7.43±0.55	1.01±0.06	27.72±3.31	5.7±1.7	0.86
5	5.5-7.0	9.55±0.78	5.96±0.50	0.85±0.06	23.08±2.44	6.4±1.4	1.17
6	Core	10.19+0.92	6.63±0.61	0.88±0.07	5.70±0.83	- 1	

IABLE 3. RADIOCHEMICAL RESULTS FOR SAMPLE 12

Errors quoted are statistical counting errors at 1  $\sigma$  level Layers 1 to 5 are from the surface towards the core of the sample. Layer 6 has been sampled in the central part of the basaltic core

### DISCUSSION

If  $^{230}$ Th<sub>excess</sub> gradients alone are considered, we would conclude that the two samples are both accumulating slowly as hydrogenous deposits at about 20 mm/10<sup>6</sup> years. Sample 21 apparently accumulated around a previous hydrothermal deposit formed at least 1.3 Ma ago, and sample 12 around a core of altered basalt. However, the structure of sample 21, together with its mineralogical and chemical composition, do not favor a hydrogenous origin. Furthermore, the gradients shown by the other radionuclides, U and Th, cannot be due to radioactive decay and require a different explanation.

Gradients in <sup>232</sup>Th commonly have been observed in Mn nodules (Bhat *et al.* 1973, Burnett & Morgenstein 1976, Lalou *et al.* 1979, Moore *et al.* 1981, Huh & Ku 1984, Kusakabe & Ku 1984). Diffusional models have been established to explain these gradients through postdepositional outward migration of thorium 232 (Huh & Ku 1984). Such diagenetic complications can be circumvented if the <sup>230</sup>Th<sub>excess</sub>/<sup>232</sup>Th ratio is used instead (Kusukabe & Ku 1984). As noted earlier, the <sup>230</sup>Th<sub>excess</sub>/<sup>232</sup>Th ratio in our samples is nearly constant (Tables 1, 3), and therefore this explanation does not explain the decrease of all measured radionuclides with depth. Other possible alternatives which may be invoked

to explain these gradients are: i) Variations in the degree of contamination by sediment. If the radionuclides are linked to the oxyhydroxide phase, a sedimentary (detrital) component may have acted as a diluent. To obtain the observed profiles, a systematic decrease of this component with time would be required because the detrital component is poorer in <sup>232</sup>Th and <sup>238</sup>U than are oxyhydroxides. Such a component was not observed during X-ray diffraction and microscopic examination. ii) Presence of two distinct non-detrital components. Finney et al. (1984) have shown that the manganeserich nodules from MANOP site H are formed with two distinct non-detrital components, one Mn-Urich, the other Fe-Th-rich. These authors were able to separate the effect of dilution by one component on radioactive decay of the other component. However, as shown by the original data in Huh (1982), U and Th do not exponentially decrease inwards as in the case of our samples; thus, we cannot invoke the presence of two such non-detrital components.

iii) Input from the basaltic core. Previous studies have shown that the inner layers of nodules generally have a framework originating from the core (Lalou & Brichet 1976). The basaltic core could be a source of some radionuclide components. For sample 12,  $^{232}$ Th is lower in the core than in the enveloping Mn crust, so core influence could partly explain the  $^{232}$ Th gradient in the crust. For sample 21, however, the possibility can be discarded because there is no core.

iv) Changes in the growth rate. Variations in the supply rate of the main component of the concretions (Mn–Fe oxides) can cause apparent changes in the fluxes of  $^{230}$ Th and  $^{232}$ Th and growth rates. However, normalization of  $^{230}$ Th to  $^{232}$ Th eliminates this effect (Ku 1976). As the  $^{230}$ Th/ $^{232}$ Th ratio in our samples is near-constant, changes in growth rate of the concretions could not have been important in producing the radionuclide trends.

None of these hypotheses accounts for all the observed characteristics of the two samples. Consequently, we present another explanation for our observations, following models of Bonatti (1983), Lalou (1983), and Fleet (1983), wherein some Mnrich seafloor deposits fill a compositional gap thought to exist between hydrogenous and hydrothermal end-members. These models invoke both the scavenging properties of Mn-Fe oxyhydroxide precipitates and the residence time of various elements in seawater to account for the enrichment in trace elements of the so-called "hydrogenous" deposits.

Recent studies have shown that hydrothermal plumes issuing from vents on the axes of mid-oceanic ridges may extend tens to hundreds of km from a ridge crest (Lupton & Craig 1981, Klinkhammer & Hudson 1986). The scavenging efficiency of oxyhydroxides, particularly iron oxyhydroxides, is well known (Goldberg 1954, Craig 1974, Weiss 1977). Scavenging of <sup>210</sup>Po and <sup>210</sup>Pb by a hydrothermal plume has been demonstrated (Kadko et al. 1987). Evidence presented above suggests that the wellcrystallized todorokite, which forms the apparent core of sample 21, is of hydrothermal origin. Whether this core was formed around 7 Ma ago in the median valley of the MAR, or later on the flank of the MAR, cannot be ascertained; the only constraint is its minimum age of about 350,000 years. The pristine appearance and lustrous sheen suggest that the core may be much younger than 7 Ma. We suggest that this was a "syn-discharge" deposit formed at or close to a hydrothermal vent, but certainly in a Mn-enriched plume chemically distinct from seawater. This core was precipitated rapidly



FIG. 4. Chemical variations with depth in sample AII 78-9-12. Symbols as in Figure 3.

without scavenging other elements, *i.e.*, similar to the Mn-rich deposits found at 26°N (TAG) on the MAR (Thompson *et al.* 1985, Lalou *et al.* 1986). This formation was followed by "post-discharge" deposition (layers 12-6) from a hydrothermal plume that was relatively enriched in iron precipitates (*cf.* Trefry *et al.* 1985). These precipitates scavenged U and Th (both <sup>232</sup>Th and <sup>230</sup>Th). Changes in the plume composition over time with respect to Fe/Mn ratio and increased relative scavenging efficiency due to increased dilution with bottom seawater (and hence greater concentration of radionuclides to be scavenged) could account for the observed iron, manganese, and radionuclide profiles in sample 21 (Fig. 5).

In sample 12, U, <sup>232</sup>Th and <sup>230</sup>Th contents increase towards the external layer (Fig. 5), indicative that the same process is operative as observed in the outer layers of sample 21. However, the relatively constant Fe and Mn contents suggest that the plume has now waned considerably, and the Fe/Mn ratio has stabilized but is increasingly diluted with seawater. The outermost layer is probably very close to normal hydrogenous precipitation. Unlike sample 21 there is no syn-discharge core to sample 12. Thus the gradients observed in the two concretions would then be chemical gradients rather than radioactive gradients and would reflect changing hydrothermal-plume compositions. A study is in progress on this same and other North Atlantic Mn

TABLE 4. Mn, Fe CONCENTRATIONS (WT. %) IN

	5760 LL 1	6	
Subsample	Mn	Fe	Mn/Fe
1 2 3 4 5	15.2 14.2 11.9 13.6 12.8	27.6 28.9 33.2 32.5 31.6	.5 .5 .4 .4 .4
6 (core)	.7	22.4	.03

deposits to determine if this model applies to other trace elements. In any case, it would seem that  $^{230}$ Th<sub>excess</sub> profiles should not be used to deduce growth rates without additional chemical data.

It is also possible that the profiles could reflect increasing distance of the concretions from a hydrothermal source as a result of seafloor spreading. For sample 21 we favor the first hypothesis (waning of a hydrothermal plume) for three reasons: i) the apparent freshness of this sample; ii) the unlikelihood that hydrothermal activity was continuous for 7 Ma; and iii) the near-constancy of the  $^{230}$ Th/ $^{232}$ Th ratio, which seems to indicate that hydrothermal activity was active relatively recently.

For comparative purposes Figure 5 shows Fe, Mn, and radionuclide data for layers 1 to 5 of sample 12, and the outer 7 layers of sample 21. The two thorium gradients almost overlay; <sup>232</sup>Th increases from 1.5 ppm in the inner part of sample 21, to 74 ppm in the outer part of sample 12. <sup>230</sup>Th<sub>excess</sub> displays a similar trend from <1 to 27 dpm/g across the same



FIG. 5. Variation with depth in the concentrations of Mn, Fe, Th and U in samples 12 and 21, assuming that they represent a continuum from a hydrothermal end member (inner layers in sample 21) to a "hydrogenous" end member (outer layer of sample 12). Note the relatively near overlap in trends in the two samples.

layers, whereas U varies from 1 ppm to 9 ppm in sample 21, but only from 9 to 11 ppm in sample 12 (a value of about 10 ppm is a high concentration for deep-sea Mn deposits; Cochran 1982). Fe and Mn contents across sample 12 show no obvious trends; concentrations are similar to those in the outermost layer of sample 21. Together with the nearly unbroken Th gradients which result when samples 12 and 21 are "put together", all these data suggest that the two samples form part of a continuum recording of the changes in plume activity. Sample 12 corresponds to the waning and final stages of the post-discharge process, and sample 21 records the initial and waning stages of hydrothermal activity. For an unknown reason, this last part of the process was not registered in sample 21, except perhaps in the outermost layer 6, which has strong textural and chemical similarities with sample 12. The absence of a strong hydrothermal signal in sample 12, similar to that observed in the core of sample 21, is also surprising. However, given the range in seafloor elevation covered by the dredge (almost 1000 m), it is probable that the crusts came from different areas and were differentially exposed to the hydrothermal plume.

#### **CONCLUSIONS**

We have determined variations in the contents of Th, U, Fe and Mn in two Mn oxide-rich samples retrieved by a dredge haul taken 135 km west of the axis of the MAR. The data suggest that the two samples represent between them a continuum from true hydrothermal deposits to so-called "hydrogenous" deposits such as manganese nodules. Even the latter type of deposit seems to have hydrothermal activity as the primary source for the manganese. We suggest that the decrease of radioactive nuclides, including <sup>230</sup>Th activity, with depth in Mn oxide crusts may not always be due to radioactive decay, but rather may arise from primary chemical gradients that reflect differentiation and contribution from waning hydrothermal plumes.

#### **ACKNOWLEDGEMENTS**

We thank the officers and crew of R/V ATLANTIS II for their help during the cruise. Financial support was provided to G. Thompson by the National Science Foundation through Grant #0CE85-10847, and to Claude Lalou and Evelyne Brichet by CNRS and CEA grants. Two anonymous reviewers are acknowledged for helpful comments.

#### REFERENCES

BARRETT, T.J. & FRIEDRICHSEN, H. (1982): Elemental and isotopic compositions of some metalliferous and pelagic sediments from the Galapagos mounds area, DSDP Leg 70. Chem. Geol. 36, 275-298.

- BENDER, M.J., KU, T.L. & BROECKER, W.S. (1966): Manganese nodules, their evolution. *Science* 151, 325-328.
- BHAT, S.G., KRISHNASWAMI, S., LAL, D., RAMA, D. & SOMAYAJULU, B.L.K. (1973): Radiometric and trace elemental studies of ferromanganese nodules. *Proc. Symp. on Hydrogeochem. Biogeochem.* (I. Clarke, ed.). Washington, D.C., 443-482.
- BONATTI, E. (1975): Metallogenesis at oceanic spreading centers. Ann. Rev. Earth Planet. Sci. 3, 401-431.
  - (1983): Hydrothermal deposits from the oceanic rifts: a classification. *In* Hydrothermal Processes at Sea Floor Spreading Centers (P.A. Rona, K. Boström, L. Laubier & K.L. Smith, eds.). Plenum Press, New York, 401-502.
- BOSTRÖM, K. & PETERSON, M.N.A. (1966): Precipitates from hydrothermal exhalations on the East Pacific Rise. *Econ. Geol.* 61, 1258-1265.
- BURNETT, W.C. & MORGENSTEIN, M. (1976): Growth rates of Pacific nodules as deduced by uranium series and hydration rind dating techniques. *Earth Planet*. *Sci. Lett.* 33, 208-218.
- COCHRAN, J.K. (1982): The oceanic chemistry of the U and Th series nuclides. *In* Uranium Series Disequilibrium. Applications to Environmental Problems (M. Ivanovich & R. S. Harmon, eds.). Clarendon Press, Oxford, England, 384-430.
- CRAIG, H. (1974): A scavenging model for trace elements in the deep sea. *Earth Planet. Sci. Lett.* 23, 149-159.
- CRONAN, D.S. (1976): Manganese nodules and other ferromanganese deposits. *In* Chemical Oceanography, 5 (J.P. Riley & R. Chester, eds.). Academic Press, New York, 217-263.
- CYAMEX, ÉQUIPE SCIENTIFIQUE (1978): Découverte par submersibles de sulfures polymétalliques massifs sur la dorsale du Pacifique Oriental par 21°N (Projet RITA). C. R. Acad. Sc. Paris. 287D, 1365-1368.
- FINNEY, B., HEATH, G.R. & LYLE, M. (1984): Growth rates of manganese-rich nodules at MANOP site H (Eastern North Pacific). *Geochim. Cosmochim. Acta* 48, 911-919.
- FLEET, A.J. (1983): Hydrothermal and hydrogenous ferro-manganese deposits: do they form a continuum? The rare earth element evidence. *In* Hydrothermal Processes at Seafloor Spreading Centers (P.A. Rona, K. Boström, L. Laubier & K.L. Smith, eds.). Plenum Press, New York, 535-555.
- GOLDBERG, E.D. (1954): Marine geochemistry. I. Chemical scavengers of the sea. J. Geol. 62, 249-265.

HUH, C.A. (1982): Radiochemical and Chemical

Studies of Manganese Nodules from Three Sedimentary Regimes in the North Pacific. Ph.D. thesis, Univ. Southern California, Los Angeles, Calif.

- & KU, T.L. (1984): Radiochemical observations on manganese nodules from three sedimentary environments in the North Pacific. Geochim. Cosmochim. Acta 48, 951-963.
- KADKO, D., BACON, M. & HUDSON, A. (1987): Enhanced scavenging of <sup>210</sup>Pb and <sup>210</sup>Po by processes associated with the East Pacific Rise near 8°45' N. *Earth Planet. Sci. Lett.* 81, 349-357.
- KLINKHAMMER, G. & HUDSON, A. (1986): Dispersal patterns for hydrothermal plumes in the South Pacific using manganese as a tracer. *Earth Planet. Sci. Lett.* 79, 241-249.
- KU, T.L. (1976): The uranium series methods of age determination. Ann. Rev. Earth Planet. Sci. 4, 347-379.
- & BROECKER, W.S. (1976): Uranium, thorium and protactinium in a manganese nodule. *Earth Planet. Sci. Lett.* 2, 317-320.
- <u>& (1969):</u> Radiochemical studies of manganese nodules of deep-sea origin. *Deep-Sea Res.* **16**, 625-637.
- KUSAKABE, M. & KU, T.L. (1984): Incorporation of Be and other trace metals into ferromanganese deposits. *Geochim. Cosmochim. Acta* 48, 2187-2193.
- LALOU, C. (1983): Genesis of ferromanganese deposits: hydrothermal origin. *In* Hydrothermal Processes at Seafloor Spreading Centers (P.A. Rona, K. Boström, L. Laubier & K.L. Smith, eds.). Plenum Press, New York, 503-534.
- \_\_\_\_\_ & BRICHET, E. (1976): On some relationships between the oxide layers and the cores of deep-sea manganese nodules. *Mineral. Deposita* 11, 267-277.
- <u>4</u> (1987): On the isotopic chronology of submarine hydrothermal deposits. *Chem. Geol.* (Isotope Geosc. section) **65**, 197-207.
- \_\_\_\_\_, \_\_\_\_, JEHANNO, C. & LECLAIRE, H. (1983): Hydrothermal manganese deposits from Galapagos mounds, DSDP Leg LXX, Hole 509B, and Alvin dives 729 and 721. *Earth Planet. Sci. Lett.* 63, 63-75.
- \_\_\_\_, KU, T.L., BRICHET, E., POUPEAU, G. & ROMARY, P. (1979): TECHNO encrustation. I. Radiometric studies. *In* La Génèse des Nodules de Manganèse (C. Lalou, ed.). Colloque Intern. CNRS N° 289, 25-30.
- \_\_\_\_\_, THOMPSON, G., RONA, P.A., BRICHET, E. & JEHANNO, C. (1986): Chronology of selected hydrothermal Mn oxide deposits from the Trans-Atlantic geotraverse "TAG" area, Mid-Atlantic Ridge 26°N. Geochim. Cosmochim. Acta 50, 1737-1743.

- LEG 106 SHIPBOARD SCIENTIFIC PARTY (1986): Mid-Atlantic Ridge bare-rock drilling and hydrothermal vents. *Nature* 321, 14-15.
- LUPTON, J.E. & CRAIG, H. (1981): A major helium-3 source at 15°S on the East Pacific Rise. *Science* 214, 13-18.
- MOORE, W.S., KU, T.L., MACDOUGALL, J.D., BURNS, V.M., BURNS, R., DYMOND, J., LYLE, M. & PIPER, D.Z. (1981): Fluxes of metals to a manganese nodule: radiochemical, structural and mineralogical studies. *Earth Planet. Sci. Lett.* 52, 151-171.
- RISE PROJECT GROUP (1980): East Pacific Rise: hot springs and geophysical experiments. *Science* 207, 1421-1442.
- RONA, P.A. (1980): TAG hydrothermal field: MAR crest at latitude 26°N. J. Geol. Soc. London 137, 385-402.
- SCOTT, M.R., SCOTT, R.B., RONA, P.A., BUTLER, P.A. & NALWALK, A.J. (1974): Rapidly accumulating manganese deposit from the median valley of the Mid-Atlantic Ridge. *Geophys. Res. Lett.* 1, 355-358.

THOMPSON, G., HUMPHRIS, S.E., SCHROEDER, B.,

SULANOWSKA, M. & RONA, P.A. (1988): Active vents and massive sulfides at 26°N (TAG) and 23°N (Snakepit) on the Mid-Atlantic Ridge. *Can. Mineral.* 26, 697-711.

- \_\_\_\_\_, MOTTL, M.J. & RONA, P.A. (1985): Morphology, mineralogy and chemistry of hydrothermal deposits from the TAG area, 26°N, Mid-Atlantic Ridge. *Chem. Geol.* **49**, 243-247.
- \_\_\_\_\_, Woo, C.C. & Song, W. (1975): Metalliferous deposits on the Mid-Atlantic Ridge. Geol. Soc. Amer. Program Abstr. 7, 1297.
- TREFRY, J.H., TROCINE, R.P., KLINKHAMMER, G.P. & RONA, P.A. (1985): Iron and copper enrichment of suspended particles in dispersed hydrothermal plumes along the Mid-Atlantic Ridge. *Geophy. Res. Lett.* 12, 506-509.
- WEISS, R.F. (1977): Hydrothermal manganese in the deep sea: scavenging residence time and Mn/<sup>3</sup>He relationships. *Earth Planet. Sci. Lett.* 37, 257-262.
- Received May 22, 1987; revised manuscript accepted March 3, 1988.