Galapagos
Hydrothermalism
Chronology
Isotope stratigraphy
Radiochemistry

Galapagos
Hydrothermalisme
Chronologie
Stratigraphie isotopique
Radiochimie

The Galapagos hydrothermal mounds: history from about 600,000 years to Present

Claude Lalou, Évelyne Brichet, Héloïse Pérez-Leclaire
Centre des faibles radioactivités, Laboratoire mixte CNRS-CEA, Domaine du CNRS, 91190 Gif-sur-Yvette, France.

Received 8/7/83, in revised form 20/2/84, accepted 20/2/84.

ABSTRACT

Using uranium series disequilibrium and oxygen isotope stratigraphy, a chronology has been established for the different events which led to the formation of the hydrothermal mounds south of the Galapagos Spreading Center.
From the presence of an important uranium enrichment older than 350,000 years, in the deepest part of the sedimentary column of cores drilled from the mounds, it is concluded that hydrothermal activity is well localized under the mounds and began 400,000 to 350,000 years ago. The uranium enrichment event was followed by the formation of nontronitic clay, which represents a transformation of the settling pelagic sediment and which took place from 300,000 to 90,000 years ago. In some mounds, nontronite formation was followed, from 90,000 to 20,000 years ago, by the precipitation of plates of pure todorokite alternating with sediment deeply impregnated with a Mn-rich solution. The formation of nontronite as well as of todorokite shows the pulsed character of the hydrothermal events. Overlying recent pelagic sediments are characterized by a uranium enrichment, dated at 35,000, 18,000 or Recent in different mounds, marking the end or a major interruption of the hydrothermal phenomenon.

Oceanol. Acta, 1984, **7**, 3, 261-270.

RÉSUMÉ

Chronologie des dépôts hydrothermaux des Galapagos

En utilisant diverses possibilités de datation, comme les déséquilibres dans la famille de l'uranium ou l'échelle stratigraphique donnée par les isotopes de l'oxygène dans les tests de foraminifères, on a pu établir la succession des événements dans la zone des monticules hydrothermaux (mounds), au sud de l'axe de dérive des Galapagos.
On a mis en évidence un fort enrichissement en uranium dans les sédiments pélagiques profonds des carottes prélevées dans ces monticules, et montré que cet uranium avait plus de 350 000 ans. La localisation préférentielle de cet uranium dans les carottes forées dans les monticules montre que l'apport hydrothermal est très localisé et a commencé il y a 400 000 à 350 000 ans. Ceci a été suivi par la formation du dépôt de nontronite, qui représente une transformation du sédiment au fur et à mesure qu'il sédimente, entre 300 000 et 90 000 ans. Dans certains monticules, la formation de nontronite a été suivie de celle d'un dépôt de manganèse. Ce dépôt de manganèse, consistant en une alternance de plaques de todorokite pure séparées par un sédiment totalement imprégné de manganèse, montre que le système hydrothermal a été pulsé. Les plaquettes correspondent aux périodes de plus forte activité et un suintement de la solution riche en manganèse, a imbibé le sédiment au fur et à mesure de sa sédimentation lors des périodes de moindre activité.
La sédimentation pélagique récente qui fait suite est caractérisée par un enrichissement en uranium qui permet de dater la fin du phénomène ou une importante interruption dans chaque monticule étudié à 35 000 ans, 18 000 ans ou récemment.

Oceanol. Acta, 1984, **7**, 3, 261-270.

INTRODUCTION

Following its discovery in 1974 (Klitgord, Mudie, 1974), and the description of the associated high heat flows (Williams *et al.*, 1974), the Galapagos Hydrothermal Mounds area (between 00°30 - 00°40 N and 86°05-86°15 W), situated some 20 km south of the Galapagos Spreading Center, has received much attention, especially because comparable features have not yet been found elsewhere.

The first detailed description is due to Lonsdale (1977) who, using the deep-tow instrument package, produced precise data on the shape, size and topographic arrangements of the mounds, and photographed bands of mineralization; these findings led him to the firm conclusion that active hydrothermal circulation must be invoked to explain their formation.

Subsequently, some dredging, Alvin's dives and coring established that the mounds consist essentially of two components: Mn oxide crust (todorokite and birnessite), and well crystallized nontronitic smectite (Corliss *et al.*, 1978). Glomar Challenger drilled 4 holes in the mounds area during Leg 54 of the Deep-Sea Drilling Project (Hékinian *et al.*, 1978; Natland *et al.*, 1979), and returned to the site during Leg 70. On the latter occasion, drilling capability was greatly enhanced by the use of the newly developed hydraulic piston corer, which allows a nearly total recovery of the sedimentary sequence with a good preservation of the stratigraphy (Honorez *et al.*, 1981).

The first rough description of the internal structure of the mounds is due to Hékinian *et al.* (1978). Honnorez *et al.* later (1981) proposed a more precise description of the mounds, based on the results of DSDP Leg 70. Recently, more detailed papers have been published on the physical properties of sediments (Karato, Becker, 1983), on the heat transfer through the sediments (Becker, Von Herzen, 1983), on pore water chemistry (Maris, Bender, 1982; Bender, 1983) and on the geochemistry of the hydrothermal sediments (Moorby, 1983), all endeavouring to establish models for the formation of the mounds.

One major series of measurements was missing: a quantitative chronology of the deposits. Such a chronology, if established, would create constraints which could be used for choosing between the different models: for example, the chemistry of the solution would certainly not be the same if the hydrothermal event is fast or slow, continuous or pulsed. In this paper, we shall attempt to provide such a chronological scale.

MATERIAL AND METHODS

The best stratigraphic description of the mounds is that presented by Honnorez *et al.* (1981) using the 32 holes (including cores, heat flow holes and pore water chemistry) at 5 sites studied during Deep Sea Drilling Project (DSDP) Leg 70 (November-December 1979). This description may be summarized as follows:

The mounds present a succession of pelagic and hydrothermal sediments. The latter are represented by manganese oxide crusts and a green nontronitic clay. The pelagic sediment is composed of a calcareous component containing nannofossils and foraminifera and a siliceous component containing diatoms, radiolaria and silicoflagellates. The hydrothermal components, Mn and nontronite, are not present in all cores; their presence depends on the position of the core with respect to a mound.

Site 508, hole 508, south of the 26.5 km south fault, is the southermost hole, the age of the underlying crust is 0.85 m.y. and there is no apparent hydrothermal modification of the pelagic sediments, which are represented from top to bottom by a siliceous foraminifera nannofossil ooze.

In the mounds area, sites 506, 507 and 509 contain sediments which have been hydrothermally altered to different extents. The northermost, site 510, is located on 3 myr-old crust north of the Galapagos rift, and contains neither hydrothermal sediments nor any visible evidence of alteration.

The sites selected for the present study are indicated in Figure 1, and the principal characteristics of the different holes are given in Table 1.

Our purpose being to try to establish the dates and duration of each of the different sequences, it was first necessary to obtain a rough estimation of the time span covered, so that the appropriate dating method could be selected.

All cores contain at least 10 to 20 m of pelagic ooze resting on the basement, regardless of their location on or off mounds. From the half spreading rate (35 mm/year) and the thickness of the sediment in the area, the mean sedimentation rate is calculated to be

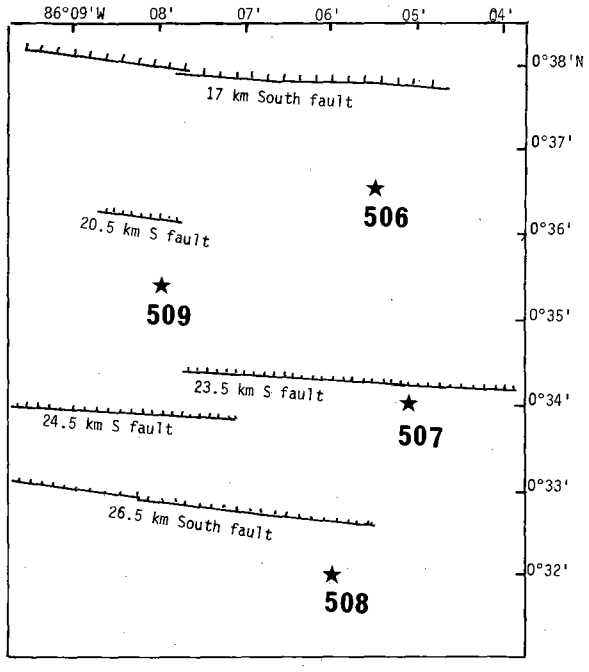


Figure 1
Location of the studied sites.
Emplacement des sites étudiés.

Table 1
Characteristics of the studied cores.
Caractéristiques des carottes étudiées.

Site	Hole	Position	Depth (m)	Length (m)	Localization
506	506C	0°36.46'N 86°05.48'W	2710	31.3	On mound
	506D	0°36.42'N 86°05.48'W	2707	31.9	Off mound 50 m south from 506C
507	507D	0°34.00'N 86°05.04'W	2689	38.7	On mound
	507F	0°34.00'N 86°05.04'W	2695	31.3	On mound
	507H	0°34.00'N 86°05.04'W	2692	32.9	Off mound 200 m south from 507F
508	508	0°32.00'N 86°06.00'W	2782	35.3	Out of mound area
509	509	0°35.34'N 86°07.89'W	2677	32.3	Off mound 50 m south from 509B
	509B	0°35.33'N 86°07.93'W	2687	33.8	On mound

about 5 cm/10^3 years (Klitgord, Mudie, 1974). As the mound area is located some 20-30 km south of the Galapagos spreading axis, the basement is some 500 000-800 000 years old. The 10-20 m of apparently undisturbed sediments represent a time interval of 200 000 to 400 000 years; the main hydrothermal process thus probably occurred between 400 000 years and the present day. This time scale is well suited to the uranium series disequilibrium method of dating. Preliminary results so obtained on a few cores (Lalou *et al.*, 1983 *a*) have effectively shown that the method is applicable; this lead us to make the study more precise and to extend it over the whole area.

The radiochemical procedure used is that of Ku (1966). Some 500 mg to 1 g of sample is dissolved in a HCl-HNO_3 mixture with addition of a spike containing ^{228}Th in secular equilibrium with ^{232}U. Any refractory silicate residue is dissolved by a HF-HNO_3-$HClO_4$ mixture. Uranium and thorium are separated on ion exchange resins, purified and, after a final extraction into 1-(2'-thenoyl)-3,3,3 trifluoroacetone, deposited by evaporation on stainless steel planchets. The alpha activity of the planchets is measured spectrometrically, either with a solid state detector or in a ionization chamber. Blanks are always far below the statistical counting error.

The entire hydrothermal sequence being best preserved in hole 509B, we choose to establish our chronology at site 509, and to check it on the other sites.

From ca 600 000 to ca 300 000 years

Site 509 is located on a basement situated slightly north of the Matuyama-Brunhes reversal, indicating an age of about 600 000 years. This is in agreement with the absence of reversed polarity in the sediments (Levi, 1983).

Two holes, 509B and 509, lying respectively on the edge of and off a mound, have been studied. Hole 509 presents a somewhat regular pelagic sedimentation, while hole 509B contains four different units: pelagic sediments in the bottommost 16 m, overlaid by a nontronite deposit, then a manganese oxide deposit and finally pelagic sediment.

The lower 16 m of sediments in the two cores differ in that the siliceous component is absent from the mound hole (509B) but present in the off-mound one, except for the lower 1.5 m.

Radiochemical investigation of the basal sediments in hole 509B (Table 2) shows that these sediments are greatly enriched in uranium (a common value for a normal calcareous ooze with 70% of carbonates would be about 1 ppm). Even for the most enriched level (sample 509B.7.3.75-76), uranium is in secular equi-

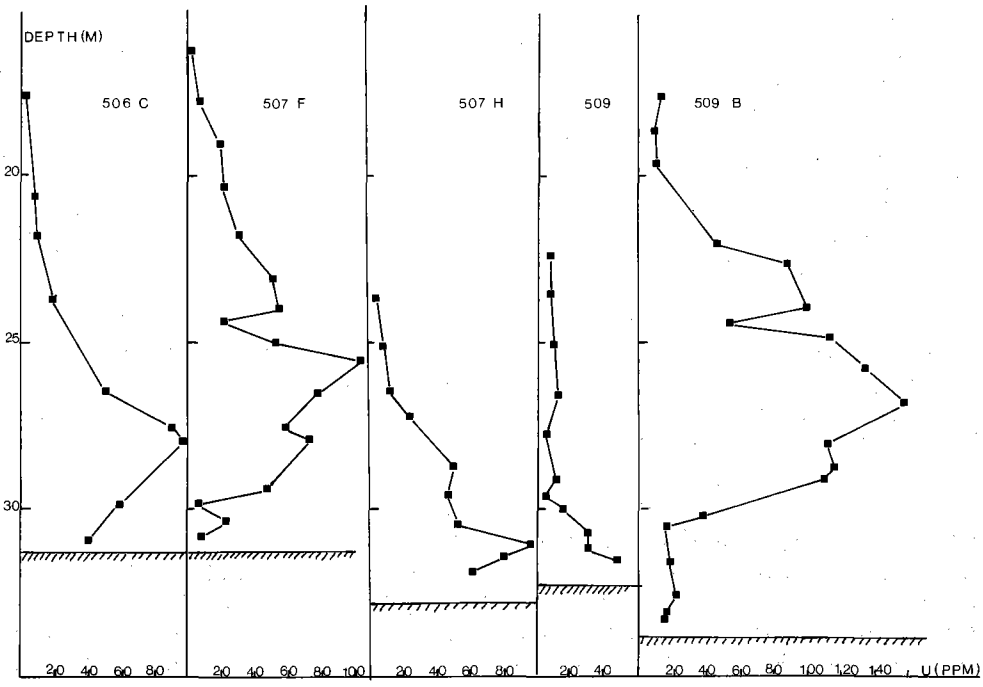


Figure 2
Uranium content (on a $CaCO_3$-free basis) versus depth in the basal sediment of corse 506C, 507F, 507H, 509 and 509B.
Teneurs en uranium des sédiments décarbonatés en fonction de la profondeur dans les sédiments pélagiques de la base des carottes 506C, 507F, 507H, 509 et 509B.

Table 2

Results of radiochemical analyses in the basal sediments.

** In all tables, DSDP nomenclature is used. With the hydraulic piston corer used during Leg 70, the length of cores is 4.50 m, separated in three 1.50 m sections. The depth of the sample is taken respective to the top of each section. So, sample 8-3-80-81 means that it has been taken in the 8th core, at 80-81 cm depth in the third section.*

Résultats des mesures radiochimiques dans les sédiments inférieurs.

* Dans tous les tableaux, la nomenclature DSDP est utilisée. Avec le carottier hydraulique, la longueur des carottes est 4,50 m. Elles sont coupées en trois sections de 1,50 m. La profondeur de l'échantillon est donnée par rapport au sommet de chaque tronçon. Par exemple, l'échantillon 8-3-80-81 indique qu'il a été prélevé dans la 8e carotte, à 80-81 cm du sommet du 3e tronçon.

Sample*	% $CaCO_3$	^{238}U (ppm $CaCO_3$ free)	^{234}U (dpm/g)	^{230}Th (dpm/g)	$^{234}U/^{238}U$ (activity ratio)
509B					
8-3- 80-81	63.5	14.0 ± 0.5	4.4 ± 0.1	4.1 ± 0.2	1.162 ± 0.030
8-3- 49-50	62.8	14.2 ± 0.5	4.4 ± 0.2	4.5 ± 0.1	1.143 ± 0.035
7-3-100-101	82.2	111.8 ± 5.6	14.9 ± 0.8	15.6 ± 0.6	1.017 ± 0.046
7-3- 75-76	78.5	115.8 ± 3.7	18.8 ± 0.6	20.2 ± 0.8	1.023 ± 0.025
6-3- 75-76	75.9	53.5 ± 2.9	11.2 ± 0.6	11.9 ± 0.5	1.173 ± 0.037
6-3- 25-26	79.4	99.0 ± 2.9	15.8 ± 0.45	17.6 ± 0.5	1.051 ± 0.027
6-1-125-126	76.7	42.0 ± 1.7	8.4 ± 0.4	11.2 ± 0.5	1.173 ± 0.055
5-2- 75-76	79.6	9.5 ± 0.5	1.5 ± 0.07	1.4 ± 0.1	1.097 ± 0.063
509					
8-3- 29-30	72.8	31.2 ± 0.7	6.6 ± 0.2	5.9 ± 0.2	1.055 ± 0.026
6-3- 75-76	79.9	6.9 ± 0.3	1.1 ± 0.04	1.1 ± 0.05	1.045 ± 0.050
507F					
7-2- 50-51	72.9	77.8 ± 2.9	17.3 ± 0.7	18.5 ± 0.6	1.114 ± 0.039
7-1- 50-51	64.4	48.3 ± 1.7	14.3 ± 0.5	14.7 ± 0.4	1.127 ± 0.036
506C					
8-2-136-137	79.5	41.7 ± 2.8	6.5 ± 0.4	6.4 ± 0.3	1.026 ± 0.051
8-2- 30-31	76.1	58.1 ± 3.0	10.7 ± 0.6	9.9 ± 0.6	1.049 ± 0.034
7-2-100-101	73.7	98.1 ± 4.8	19.9 ± 1.0	20.0 ± 1.0	1.051 ± 0.025
7-2- 38-39	72.7	90.6 ± 2.7	18.7 ± 0.6	17.2 ± 0.6	1.026 ± 0.021
7-1-100-101	79.4	50.0 ± 1.6	8.3 ± 0.3	9.6 ± 0.2	1.094 ± 0.030
6-2- 52-53	79.7	17.5 ± 0.5	2.7 ± 0.1	2.7 ± 0.1	1.019 ± 0.035
6-1- 52-53	79.5	8.8 ± 0.4	1.3 ± 0.07	1.3 ± 0.06	0.978 ± 0.057
5-1- 82-83	72.6	7.8 ± 0.3	1.6 ± 0.06	1.8 ± 0.07	1.045 ± 0.043
3-3- 53-54	45.0	1.6 ± 0.1	0.8 ± 0.5	1.2 ± 0.07	1.260 ± 0.100

librium with ^{230}Th, indicating that enrichment occurred before ca 300 000 years BP. This phenomenon has previously been established for site 424 which was drilled during Leg 54 in the same mound row (Lalou, Brichet, 1980).

Hole 509, which did not penetrate a mound and was drilled about 60 m from hole 509B, contains no uranium enrichment, except in the lowermost metre. As alpha spectrometric measurements are relatively slow and necessitate the dissolution of the samples, we measured uranium by total alpha activity counting of thick sources in holes other than 509B. Since the ^{232}Th content is very low compared to uranium, and ^{230}Th is in equilibrium with uranium, the alpha counting rates must be directly proportional to the uranium content. This has been verified on some samples, and, in our counting conditions, a quite constant factor of $0.75 \pm .07$ must be applied to total alpha counts to obtain uranium concentrations. Table 3 indicates the uranium content measured either radiochemically or by total alpha counting for all holes studied. Variations of uranium content with depth in the different holes are summarized in Figure 2.

At site 507, measurements were carried out in two holes. In hole 507F, on the edge of the mound, there is a significant U enrichment up to some 12 m above the basement, while in hole 507H, outside the mound, enrichment is limited to the lower 5 m.

At site 506, only 7 samples have been analyzed in the on mound hole (506C), which contains a uranium enrichment in the lower 9 m.

Such uranium enrichments have already been found at the Mid-Atlantic Ridge by Turekian and Bertine (1971, core A 180-74, 00°03'S; 24°10'W), who ascribed them to reducing conditions prevailing in transient basins formed along the ridge; at the East Pacific Rise, at 15°S, by Rydell *et al.* (1974) who ascribed them to postdepositional injection of hydrothermal fluids; and close to the East Pacific Rise, at 8°45'N, in metalliferous hemipelagic sediments, by Kadko (1980) who concluded that the source of the uranium peak is not obvious, but suggested that the correlation between uranium and Fe, Cu and Hg may be due to a redox mechanism.

In the case of the Galapagos mounds sediments, the first argument in favour of a hydrothermal origin is the high $^{234}U/^{238}U$ ratio, calculated by correcting the observed ratio back to the time of deposition (> 300 000 years). This argument is equivocal, however, because preferential migration of ^{234}U after deposition cannot be totaly excluded. Secondly, the location of the enrichment is well limited to the on-mound holes: if an anoxic basin had existed before the formation of the mounds, the sediment would be uniformly enriched throughout the area. Thirdly, the uranium enrichment is quite well correlated with the absence of biogenic silica in the sediments, due to the passage through the sediments of a hot solution.

Recently, Michard *et al.* (1983) have shown that the water from black smokers at 13°N on the East Pacific Rise is considerably depleted in uranium with respect to the original seawater content. This might argue against a hydrothermal origin for the enrichments we found; it should, however, be noted that the Galapagos hydrothermal system, in the mounds area, is very different from that on the EPR in that:

1) the water flux is much lower, 30 cm/yr. as currently established by Becker *et al.* (1983) from geothermal measurements, or between 15 and 30 cm/yr. from pore water measurements (Bender, 1983) instead of 0.5 to 2 m/sec. (Hekinian *et al.*, 1983); it cannot have been very much higher since no important perturbation of the basal sediment exists.

2) it is less acidic, since the only important change in the overlaying sediment is the dissolution of silica which is better explained by a hot basic solution;

3) the temperature of the fluid issuing from the basaltic basement was probably lower; the only indication of high temperature in the area is the isotopic composition of oxygen of recrystallized foraminifera in the sediment at the contact with basalt at hole 508, which gives a temperature around 80°C instead of 350°C at 13°N (Duplessy, pers. comm.);

4) no significant amounts of sulphide minerals are found in the overlaying sedimentary column.

So, the original hydrothermal fluids, if similar to the 13°N ones, have had time to interact with rocks and sediments, leading to changes in their chemical composition, and a direct or indirect hydrothermal origin for the uranium cannot be discounted.

In the three on-mound holes, uranium enrichment is greatest at about the same depth in sediment having ages between about 500 000 and 550 000 years. The enrichment decreases as age decreases, and is absent in sediment younger than 350 000 years. This uranium injection, if of hydrothermal origin, may mark the onset of the hydrothermal activity, which would necessarily have begun at least 300 000 years ago. Injection may

Table 3
Uranium content of basal sediments.
Teneurs en uranium des sédiments inférieurs.

Sample	Subbottom depth (m)	U^+ (ppm)	Mode
506C			
8-2-136-137	30.86	41.7	R*
8-2- 30- 31	29.3	58.1	R
7-2-100-101	28.0	98.1	R
7-2- 38- 39	27.38	90.6	R
7-1-100-101	26.5	50	R
6-2- 52- 53	23.6	17.5	R
6-1- 52- 53	21.52	8.8	R
5-1- 82- 83	17.52	7.8	R
3-3- 50- 54	11.40	1.6	R
507F			
9-1- 47- 48	30.77	8.3	A*
9-1- 14- 15	30.44	24.9	A
8-1-100-101	29.80	7.6	A
8-1- 58- 59	29.38	45.2	A
7-3- 50- 51	27.90	73.1	A
7-3- 0- 1	27.40	57.7	A
7-2- 50- 51	26.40	77.8	R+A
7-1-100-101	25.40	105	A
7-1- 50- 51	24.90	48.3	R+A
7-1- 3- 4	24.43	18.6	A
6-3-100-101	24.00	56.2	A
6-3- 10- 11	23.10	55.3	A
6-2- 25- 26	21.75	30.5	A
6-1- 25- 26	20.25	21.4	A
5-3- 50- 51	19.10	19.8	A
5-2- 50- 51	17.60	6.2	A
5-1- 50- 51	16.10	2.5	A
5-1- 10- 11	15.70	3.5	A
507H			
8-2- 50- 51	31.90	62.4	A
8-2- 5- 6	31.45	81.8	A
8-1-100-101	30.90	99.2	A
8-1- 50- 51	29.50	53.6	A
7-3-100-101	28.75	47.6	A
7-3- 25- 26	28.75	50	A
7-2- 25- 26	27.25	24.2	A
7-1-100-101	26.50	13.4	A
6-3-100-101	25.10	9.2	A
6-2-100-101	23.60	5.7	A
509			
8-3-105-106	31.45	49	A
8-3- 70- 71	31.10	31.1	A
8-3- 29- 30	30.70	31.2	R+A
8-2-105-106	29.95	15.2	A
8-2- 75- 76	29.65	6.3	A
8-2- 29- 30	29.20	11.6	A
8-1- 29- 30	27.70	8.2	A
7-3- 50- 51	26.50	13.7	A
7-2- 50- 51	25.00	10.3	A
7-1- 50- 51	23.50	7.3	A
6-3- 75- 76	22.35	6.9	R+A
509B			
8-3- 80- 81	33.20	14	R+A
8-3- 49- 50	32.90	14.2	R+A
8-3- 10- 11	32.50	20.8	A
8-2- 60- 61	31.50	17	A
8-1- 92- 93	30.32	15.6	A
8-1- 79- 80	30.20	37.2	A
7-3-100-101	29.00	111.8	R+A
7-3- 75- 76	28.75	115.8	R+A
7-2-125-126	27.75	112	A
7-2- 25- 26	26.75	160	A
7-1- 75- 76	25.75	136	A
6-3-125-126	24.85	114.5	A
6-3- 75- 76	24.35	53.5	R+A
6-3- 25- 26	23.85	99.0	R+A
6-2- 50- 51	22.60	87.7	A
6-1-125-126	21.85	42.0	R+A
5-3- 25- 26	19.45	8.8	A
5-2- 75- 76	18.45	9.5	R+A
5-1-125-126	17.45	12.6	A

* R = radiochemistry. * A = total alpha counting. U^+: on a $CaCO_3$ free basis.

have occurred in a single short event, between 350 000 and 400 000 years BP (as it reaches sediments as young as 350 000 yr.), the majority of the uranium being deposited in the more reducing part of the sedimentary column, with the peak in the sediment around 500 000 years old and the tailing-off in the younger sediments. Alternatively, uranium may have been injected more continuously from about 600 000 to 350 000 years BP, with a maximum input rate around 500 000 years ago. We favour the first hypothesis, since there is no reason for an ascending uranium-rich solution to retain its uranium in the reducing zone, and to release it merely at the oxidized sediment-water interface.

From ca 300 000 to ca 90 000 years

At site 509, hole 509B, nontronite is first found at a depth corresponding to an age of about 300 000 years, and is directly overlaid by a manganese oxide layer in which the oldest sample is dated at 65 500 years (Lalou *et al.*, 1983 *b*).

Nontronite is depleted in uranium and contains a slight excess of ^{230}Th, as measured in hole 424B and—at the same position—in hole 509B (Lalou *et al.*, 1983 *a*). However, it is not possible to calculate a sedimentation (or formation) rate, since no normalization to a constantly accumulating sedimentary phase is possible. We therefore attempted to use another chronometer to understand the chronology and mechanism of nontronite formation. At the end of the Quaternary period, the oxygen isotope record in foraminifera may be used as a time scale. This scale has been divided by Emiliani (1955) into stages which are now well dated (Broecker, Ku, 1969; Broecker, Van Donk, 1970; Shackleton, Opdyke, 1976) and which are recognized in sediments throughout the world's oceans (Shackleton, Opdyke, 1973; 1976; Duplessy, 1978). Use of this time scale requires a reference curve; we choose a core apparently undisturbed by the hydrothermal event, slightly out of the mounds area: hole 508, site 508. We shall compare this curve to that obtained at site 506, hole 506D, which contains a well defined layer of nontronite. Oxygen analyses were performed on the planktonic species *Globigerinoides ruber*, using a Micromass 602 C mass spectrometer and following the procedure described by Duplessy (1978).

The curves thus obtained are given in Figure 3. That for hole 508 is typical of isotope records for the last 150 000 years. The curve obtained for the sediments of core 506D, on both sides of the nontronite, fits well with the reference curve, nontronite being in place of isotopic stages 5B, 5C and 5D, which are dated between 90 000 and 110 000 years. This shows:

1) that in this off-mound core, nontronite has been formed *in situ*, and is not due to slumping from the nearby mound (if slumping had occurred stages 5B, 5C and 5D would have been found on both sides of the nontronite deposit);

2) that the nontronite episode is of shorter duration than in the on-mound cores, where it began some 300 000 years ago;

3) that the episode probably ends 90 000 years ago;

4) that the nontronite involves replacement of the pre-existing sediment.

These conclusions are partly in accordance with the conclusions obtained by Moorby (1983) who, from the geochemistry of the nontronite, concluded that the process of nontronite formation occurs within preexisting sediment. Our data, in contrast, argue against a significant volume change. A 25% volume change, as found by Morby, would lead to a 25 cm shift in the isotopic curve, and the two parts of the isotopic record would not fit the reference curve so well.

From 90 000 to present

The Mn oxide deposit

In hole 509B, during this time span, the precipitation of manganese oxide occurred. A thick layer of Mn deposit is formed between 270 and 110 cm depth. This manganese sequence has been studied in great detail

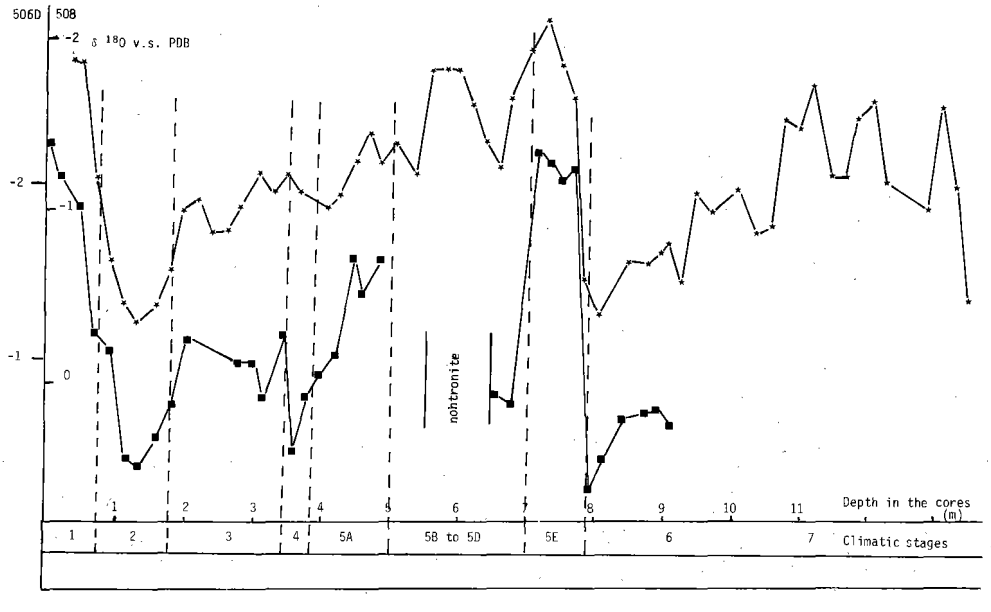


Figure 3

Isotopic composition of the oxygen of the planctonic species Globigerinoides ruber *versus depth in core* 508 *(stars) and in core* 506D *(squares).*

Variations de la composition isotopique de l'oxygène du foraminifère planctonique *Globigerinoides ruber* en fonction de la profondeur dans la carotte 508 (étoiles) et dans la carotte 506D (carrés).

and dated using the $^{230}Th/^{234}U$ ratio method (Lalou *et al.*, 1983 *b*).

The results of this work are given in Figure 4. The deposit comprises a succession of thin, hard plates of pure Mn oxide (todorokite) which exhibit ages in good chronological sequences and in good agreement with the sedimentation rate for the area. These plates are separated by a black, powdery material which, in contrast, contains an excess of ^{230}Th. The succession shows that the deposit was formed through pulsed injections of a Mn-rich solution alternating with periods of diminished hydrothermal activity during which the settling pelagic sediment was impregnated with Mn oxide (Lalou *et al.*, 1983 *b*).

Such a thick manganese layer was absent from the other cores, even from core 509 which was taken only 60 m from core 509B. In these other cores we have studied the post-hydrothermal sedimentation.

The upper pelagic sediments

Uranium series nuclides have been measured in the upper pelagic sediments of four cores. One is an on-mound core (506C), two (507H and 509) are near a mound (respectively 200 m and 60 m from the mound top) and the fourth (508) is out of the mound area, south of the 26.5 km south fault.

The ^{234}U and ^{230}Th activities normalized to 100% clay minerals are given in Table 4, as well as $^{234}U/^{238}U$ activity ratios; Figure 5 gives the variations of uranium content with depth in the four cores. We prefer normalizing to clay minerals, using Al content of the samples (Turekian, Wedepohl, 1961) instead of using $CaCO_3$ free values, as biogenic silica and sometimes nontronite act as diluting agents in these samples.

Very high uranium enrichments are found in all cores. This prevents the direct use of the ^{230}Th decrease to calculate a sedimentation rate.

Such uranium profiles are not uncommon, and three hypotheses may be advanced in explanation:

1) U has been incorporated recently, has penetrated at depth, but has had no time to produce ^{230}Th;

2) U has been incorporated during sedimentation, and ^{230}Th has subsequently formed continuously in a closed system;

3) U was incorporated during an event which was of short duration, but occurring sufficiently long ago to permit a significant proportion of ^{230}Th to accumulate.

To select the most appropriate hypothesis, knowledge of the age of the uranium injection is of interest.

For this, we require an independent method to calculate the sedimentation rate. Due to possible local or temporal variations in such rates over long periods, we cannot use the mean value calculated as 5 cm/10^3 years from the age of the basement and the thickness of sediments; but we have seen previously that the end of the nontronite formation occurred 90 000 years BP. Taking this value, we calculate a sedimentation rate of 4.9 cm/10^3 years for core 506C, in which the end of the nontronitic event is at 440 cm depth. At site 509, hole 509B, the boundary between nontronite and the Mn sequence is at 420 cm depth, so that the apparent sedimentation rate is 4.7 cm/10^3 years; we will use this value for the nearby hole 509. At site 507, hole 507F, the limit between the nontronite and pelagic sediment is at 370 cm depth, giving a sedimentation rate of

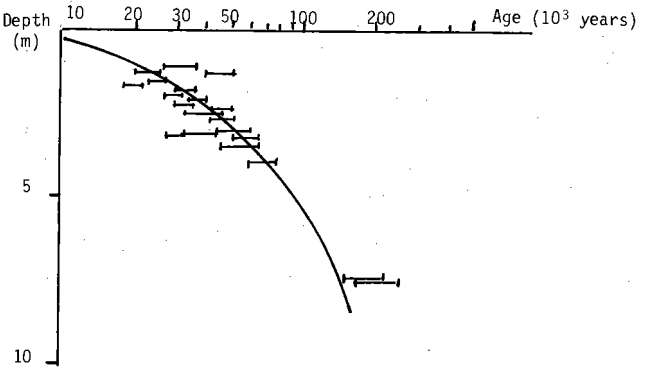


Figure 4

Ages of the todorokite plates versus depth in core 509B (after Lalou et al., 1983 b) *as measured by $^{230}Th/^{234}U$ ratio.*

Ages des plaquettes de todorokite en fonction de la profondeur dans la carotte 509B (d'après Lalou *et al.*, 1983 *b*) mesurés par le rapport $^{230}Th/^{234}U$.

Table 4

Radiochemical results in the upper pelagic sediments.

Résultats des mesures radiochimiques dans les sédiments pélagiques supérieurs.

Sample	Subbottom depth (cm)	^{234}U (dpm/g)*	^{230}Th (dpm/g)*	$^{234}U/^{238}U$	^{230}Th —1.7 dpm U
506C					
1-1- 19- 20	20	1.59	29.10	1.07	27.53
1-1- 34- 35	35	4.08	33.77	1.11	32.20
1-1- 44- 45	45	20.32	32.33	1.16	30.76
1-1- 60- 61	60	22.09	28.71	1.23	27.14
1-1- 85- 86	85	71.19	36.04	1.13	34.47
1-1-110-111	110	30.23	24.74	1.08	23.17
1-1-147-148	148	28.74	27.43	1.06	25.86
1-2- 48- 49	199	12.61	21.85	1.06	20.28
1-2- 99-100	250	9.96	20.0	1.14	18.43
2-1- 15- 16	365	11.49	14.54	1.07	12.97
507H					
1-1- 10- 11	10	1.70	26.51	1.28	24.94
1-1- 30- 31	30	10.71	29.34	1.09	27.77
1-1- 50- 51	50	13.81	32.65	1.13	31.08
1-1- 70- 71	70	23.05	28.86	1.14	27.29
1-1- 90- 91	90	25.24	26.34	1.13	24.77
1-1-110-111	110	23.22	29.89	1.13	28.32
1-1-130-131	130	14.63	24.44	1.11	22.87
1-2- 10- 11	160	16.30	25.05	1.06	23.48
509					
1-1- 30- 31	30	3.29	42.05	1.02	40.48
1-1- 50- 51	50	1.79	33.21	1.01	31.64
1-1- 70- 71	70	16.09	30.36	1.01	28.79
1-1- 90- 91	90	22.30	28.51	1.36	26.94
1-1-110-111	110	24.97	32.29	1.11	30.72
1-1-130-131	130	24.29	25.31	1.12	23.74
1-2- 10- 11	160	12.27	26.89	0.99	25.32
508					
1-1- 20- 21	20	14.25	39.28	1.10	37.71
1-1- 50- 51	50	40.08	43.02	1.13	41.45
1-1- 70- 71	70	44.76	34.97	1.08	33.40
1-1-130-131	130	42.27	33.08	1.12	31.51
1-1-148-149	148	39.46	32.20	1.13	30.63
1-2- 50- 51	200	30.41	26.63	1.19	25.06

* Normalized to 100% clays.

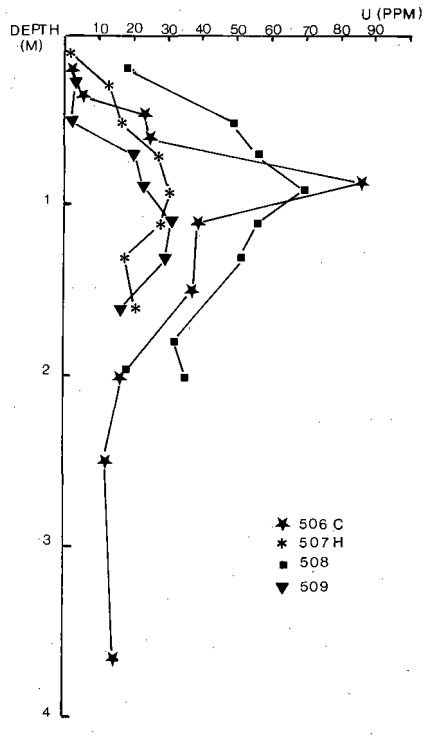


Figure 5

Uranium content (normalized to 100% clay) in the upper pelagic sediment versus depth in cores 506C, 507H, 508 and 509.

Teneurs en uranium (normalisées à 100% d'argile) dans le sédiment pélagique supérieur en fonction de la profondeur dans les carottes 506C, 507H, 508 et 509.

4.2 cm/10^3 years, which will be used for hole 507H. For site 508, out of the mounds area, we cannot use this approach as no nontronite is present, but the isotopic curve (Fig. 3) is identical to that of site 506D, showing that the sedimentation rate is similar at both places (4.9 cm/10^3 years).

Let us first consider hole 506C. If excess uranium has been incorporated very recently, it has had no time to give any ^{230}Th (first hypothesis), so we can try to fit the sedimentation rate, using a constant common value of 2 ppm (1.57 dpm ^{234}U with a ^{234}U/^{238}U ratio of 1.07 as measured in the first sample) uranium for the detrital component and subtract it from the total ^{230}Th value (curve A Fig. 6). The best fit line gives an apparent sedimentation rate of 4 cm/10^3 years (r=.86), too slow compared to the 4.9 cm/10^3 years calculated previously.

With similar uranium enrichments, Kadko (1980) calculated the growth of ^{230}Th from this uranium excess $U_z^{ex}(1\text{-}\exp(-\lambda z/s))$, considering that the injection of uranium is contemporaneous with sedimentation at each level (hypothesis 2), so:

$$^{230}Th_{exc} = {}^{230}Th_{z(total)} - [U_z^{ex}(1-e^{-\lambda z/S})]\text{-}1.6$$

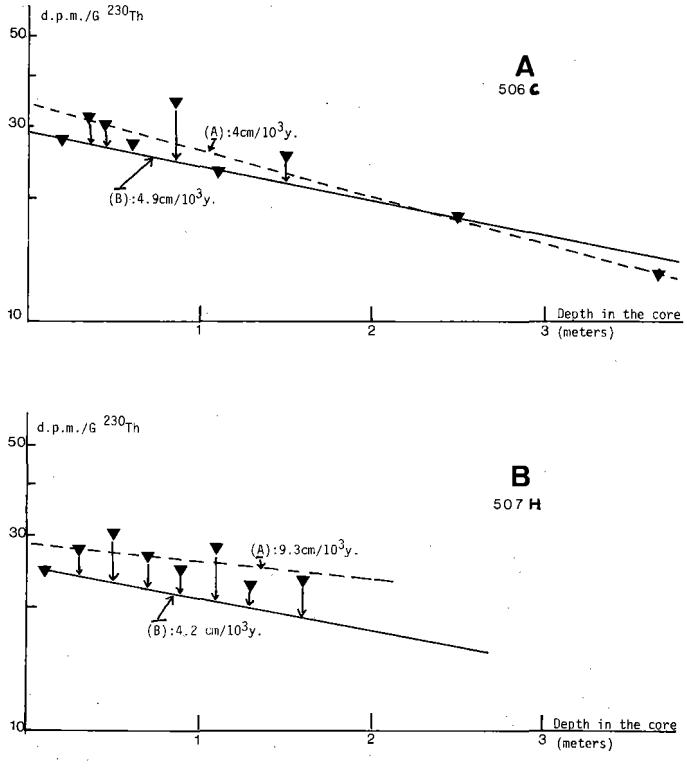
where λ is the ^{230}Th decay constant,

S is the sedimentation rate in cm/10^3 years,

z is the depth in cm,

and U_z^{ex} is $U_{total\ z}$-1.6.

The use of this equation for hole 506C leads to a very slow sedimentation rate (2.1 cm/10^3 yr.) incompatible with what is known in the area. Therefore we conclude that the uranium injection is not contemporaneous with sedimentation.



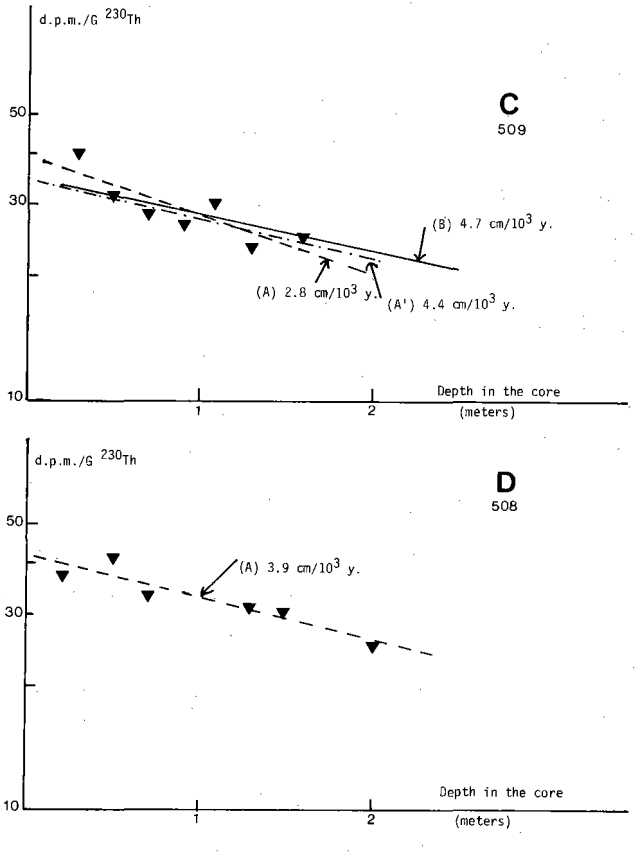


Figure 6

Variations of the ^{230}Th excess (calculated for a mean uranium concentration of 2 ppm; triangles) versus depth in the studied cores. The dashed line is the best fit line for the measured values; the full line is the line corresponding to the sedimentation rate calculated assuming that the nontronite formation ended 90 000 years ago. The arrows indicate the excess of ^{230}Th built from the uranium excess.

Variation de l'excès de thorium 230 (calculé pour une teneur moyenne en uranium de 2 ppm; triangles) en fonction de la profondeur dans les différentes carottes. La ligne en tireté représente la meilleure exponentielle pour les points de mesure, le trait plein, la droite correspondant au taux de sédimentation calculé en admettant que l'épisode de nontronite s'est terminé il y a 90 000 ans. Les flèches indiquent l'excès de thorium 230 formé à partir de l'uranium en excès.

The third hypothesis is that uranium is introduced at a well defined time, sufficiently old to allow some accumulation of ^{230}Th. To evaluate the age of this uranium, we assume that the first point (at 20 cm depth), with 2 ppm U content, has not been affected by the injection and, from this point, we draw the line 4.9 cm/10^3yr., as calculated from the age of nontronite formation (curve B, Fig. 6A). Points 2, 3, 4, 5, 7, 8 and 9 are higher than the line, showing an excess of ^{230}Th relative to the value on the line. Except for point 2, the ratio of this ^{230}Th excess, due to the radioactive decay of $U_{exc.}$, to the uranium excess at each point, is quite constant, and a mean value of 0.13 is found, leading to an age of about 15000 years for this uranium.

For hole 507H, where the most probable sedimentation rate is 4.2 cm/10^3 years, the hypothesis of a recent injection is not valid (curve A, Fig. 6B, r=0.25, v=9.3 cm/10^3 yr.) since it implies an unreasonably high sedimentation rate. The second hypothesis, using Kadko's equation, is best fitted for a sedimentation rate of 3 cm/10^3 yr. (r=.71), which is clearly too slow. With the third hypothesis, using point 1 as a reference point, and drawing the line 4.2 cm/10^3 yr. (curve B, Fig. 6B), neglecting point 2 which is too high, the other points fit fairly well with a uranium age of about 35000 years ($^{230}Th_{exc.}/^{234}U_{exc.}$ = 0.30).

For hole 509, where the most probable sedimentation rate is 4.7 cm/10^3 yr., the situation is less clear. Curve A, figure 6C, representing the hypothesis of a recent injection, gives a sedimentation rate of 2.8 cm/10^3 yr., which is too slow. The value for point 1 seems too high compared to the other values of the area for sediment 30 cm deep. If we do not take into account this point (curve A'), it gives a sedimentation rate of 4.4 cm/10^3 yr., but with a bad correlation factor (.54). The use of Kadko's equation would give a sedimentation rate of 1 cm/10^3 yr. which is unrealistic. The use of point 2 (1.79 dpm/g ^{234}U) which seems the least affected by the uranium injection, and a sedimentation rate of 4.7 cm/10^3 yr., leads to curve B which does not fit with the measured points very well. However these points are not, as in the preceeding examples, systematically too high, so no correction is possible. A recent injection of uranium is probably the best explanation.

At hole 508, the sedimentation rate is 4.9 cm/10^3 yr. Curve A Figure 6D gives a sedimentation rate of 3.9 cm/10^3 yr. For this core, we have no point with a normal low uranium content, so we have no starting point for the line 4.9 cm/10^3 yr. and we cannot constrain the age of the uranium injection.

Table 5 summarizes the different results.

The $^{234}U/^{238}U$ ratio of this recent uranium is the same as the present seawater one. There is no possibility or evidence that the uranium comes from below, as it could not have passed through the entire sedimentary column without precipitating. Thus we need to find a mechanism allowing the seawater to have entered the system recently. This does not seem possible when the

Table 5

Sedimentation rates in the upper pelagic sediments using different hypotheses.

Taux de sédimentation dans les sédiments pélagiques supérieurs calculés en utilisant diverses hypothèses.

Core	Sedimentation rate calculated from the end of nontronite (cm/10^3 yr.)	Sedimentation rate assuming a recent U injection (cm/10^3 yr.)	Sedimentation rate using Kadko hypothesis (cm/10^3 yr.)	Estimated time of U injection (10^3 yr.)
506C	4.9	4	2.1	15
507H	4.2	9.3	3	35
509	4.7	2.8 4.4	1	recent (?)
508	4.9	?	?	?

mounds are active, as they present an outgoing flux (Becker, Von Herzen, 1983; Bender, 1983). The best explanation would thus be that the age of this uranium gives the time when the mounds ceased for a period to be active and were sufficiently cooled to allow the penetration of seawater, which precipitated its uranium when reaching the reducing sediments some cm below the sediment-water interface. This event must have been very localized in time, since no recent uranium excess is present in the system, and the pore water results (Bender, 1983) show that at present there is an outflow in all studied holes.

CONCLUSION

From the above results and if the studied cores are representative of the mounds area, we can draw some conclusions about the chronology and the mechanisms of the hydrothermal events.

The hydrothermal phenomenon began some 350000 years ago, at very localized points (where mounds are now found) as indicated by the uranium injection in the pelagic sediments at the base of the mounds. This was probably due to the existence of small faults in the basement, which served as channels for the outpouring of hydrothermal fluids which are not representative of the 350°C end-member of hydrothermal fluids since it is colder, less acid and less reducing. Soon after, the hydrothermal solution, debouching slowly at the sediment-water interface, transformed the sediment into nontronite. This transformation occurred as sedimentation proceeded, but probably in pulses, resulting in some interfingering of normal calcareous ooze (Honnorez *et al.*, 1981). In some mounds, the hydrothermal event then ceased, and pelagic sedimentation blanketed the mounds. In others, on the contrary, the chemistry of the fluid changed and the same phenomenon of slow transformation of the sediment continued, but with a Mn-rich solution giving rise to successive layers of pure todorokite during the active part of a pulse, followed by impregnation of the sediment by the seeping fluid during inactive periods.

Depending on the time when the hydrothermal event slows down at each mound, transient cooling of the

mound permits a reversal of the circulation of the interstitial waters; seawater may penetrate the mounds and may deposit its uranium. This appears to have happened 35 000 years ago at hole 507, about 15 000 years ago at site 506 and much more recently at site 509 (which is the only one where hydrothermal activity has taken place after the end of nontronite formation), and possibly at site 508.

Acknowledgements

Samples were supplied with assistance from the National Science Foundation, which is gratefully acknowledged. We thank Dr. J. C. Duplessy for discussion of the oxygen isotope results; B. Le Coat and J. Antignac for oxygen measurements and the preparation of the samples; Drs. J. Labeyrie. L. Labeyrie and C. Jehanno for stimulating discussions and criticisms; and finally, M. L. Bender who agreed to review this paper, to improve the language and to discuss with us the points on which we are not in accordance. This study received financial support from the Centre National de la Recherche Scientifique (CNRS) and the Commissariat à l'Énergie Atomique (CEA) and from an ATP Chemical Oceanography grant.

REFERENCES

Becker K., Von Herzen R. P., 1983. Heat transfer through the sediments of the mounds hydrothermal area. Galapagos spreading center at 86°W, *J. Geophys. Res.*, **88,** B2, 995-1008.

Bender M. L., 1983. Pore water chemistry of the mound hydrothermal field, Galapagos Spreading Center. Results from Glomar Challenger piston coring, *J. Geophys. Res.*, **88,** B2, 1049-1056.

Broecker W. S., Ku T. L., 1969. Carribean cores P 6304-8, P 6304-9, new analysis and absolute chronology, *Science*, **166,** 404-406.

Broecker W. S., Van Donk J., 1970. Insolation changes, ice volumes and the 0-18 record in deep sea cores, *Rev. Geophys. Space Phys.*, 169-196.

Corliss J. B., Lyle M., Dymond J., 1978. The chemistry of hydrothermal mounds near the Galapagos rift, *Earth Planetary Sci. Lett.*, **40,** 12-24.

Duplessy J. C., 1978. Isotope studies, in: *Climatic changes*, edited by J. B. Gribbin, Cambridge Univ. Press, 46-67.

Emiliani C., 1955. Pleistocene temperatures, *J. Geol.*, **63,** 538-578.

Hékinian R., Rosendhal B. R., Cronan D. S., Dmitriev Y., Fodor R. V., Goll R. M., Hoffert M., Humphris M., Mattey D. P., Natland J., Petersen N., Roggenthen W., Schrader E. L., Srivastava R. R., Warren N., 1978. Hydrothermal deposits and associated basement rocks from the Galapagos Spreading Center, *Oceanol. Acta*, **1,** 4, 473-482.

Hékinian R., Francheteau J., Renard V., Ballard R. D., Choukroune P., Cheminée J.-L., Albarède F., Minster J.-F., Charlou J.-L., Marty J.-C., Boulègue J., 1983. Intense hydrothermal activity at the axis of the East Pacific Rise near 13°N: submarine witnesses the growth of sulfide chimney, *Mar. Geophys. Res.*, **6,** 1-14.

Honnorez J., Von Herzen R. P., Barret T. J., Becker K., Bender M. L., Borella P. J., Hubberten H. N., Jones S. C., Karato S., Laverne S., Levi S., Migdison A. A., Moorby S. A., Schrader E. L., 1981. Hydrothermal mounds and young ocean crust of the Galapagos, preliminary deep-sea drilling results Leg LXX, *Geol. Soc. Am. Bull.*, **92,** 457-472.

Kadko D., 1980. A detailed study of some uranium series nuclides at an abyssal hill area near the East Pacific Rise at 8°45'N, *Earth Planetary Sci. Lett.*, **51,** 115-131.

Karato S. I., Becker K., 1983. Porosity and hydraulic properties of sediments from the Galapagos Spreading center and their relations to hydrothermal circulation in the oceanic crust, *J. Geophys. Res.*, **88,** B2, 1009-1017.

Klitgord M. D., Mudie J. D., 1974. The Galapagos spreading center, a near bottom geophysical survey, *Geophys. J. R. Astron. Soc.*, **38,** 563-586.

Ku T. L., 1966. Uranium series disequilibrium in deep sea sediments, *Ph. D. Dissert., Columbia Univ., N.Y.*

Lalou C., Brichet É., 1980. Anomalously high uranium content in the sediments under Galapagos hydrothermal mounds, *Nature*, **284,** 251-253.

Lalou C., Brichet É., Leclaire H., Duplessy J. C., 1983*a*. Uranium series disequilibrium and isotope stratigraphy in hydrothermal mounds samples from DSDP sites 506-509, leg 70 and site 424, leg 54; an attempt at chronology, *Initial Rep. DSDP*, **vol. 70,** edited by J. Honnorez, R. P. Von Herzen *et al.*, Washington D. C., US Gov. Printing Office, 303-314.

Lalou C., Brichet É., Jehanno C., Pérez-Leclaire H., 1983*b*. Hydrothermal manganese oxide deposits from Galapagos mounds. DSDP leg 70, Hole 509B and Alvin dives 729 and 721, *Earth Planetary Sci. Lett.*, **63,** 63-75.

Levi S., 1983. Paleomagnetism and rock magnetism of submarine basalts from the Galapagos Spreading Center near 86°W, *Initial Rep. DSDP*, **vol. 70,** edited by J. Honnorez, R. P. Von Herzen *et al.*, Washington D. C., US Gov. Printing Office, 429-436.

Lonsdale P., 1977. Deep tow observations at the mounds abyssal hydrothermal field, Galapagos rift, *Earth. Planetary Sci. Lett.*, **36,** 92-110.

Maris C. R. P., Bender M. L., 1982. Upwelling of hydrothermal solutions through ridge flank sediments shown by pore water profiles, *Science*, **216,** 623-626.

Michard A., Albarède F., Michard G., Minster J.-F., Charlou H.-L., 1983. Rare Earth elements and uranium in high-temperature solutions from East Pacific Rise hydrothermal vent field (13°N), *Nature*, **303,** 795-797.

Moorby S. A., 1983. The geochemistry of transitional sediments recovered from the Galapagos hydrothermal mounds field during DSDP leg 70. Implications for mound formation, *Earth Planetary Sci. Lett.*, **62,** 367-376.

Natland J. H., Rosendhal B. R., Hékinian R., Dmitriev Y., Fodor R. V., Goll R. M., Hoffert M., Humphris S. E., Mattey D. P., Petersen N., Roggenthen W., Schrader E. L., Srivastava R. K., Warren N., 1979. Galapagos hydrothermal mounds: stratigraphy and chemistry revealed by Deep-Sea Drilling, *Science*, **204,** 613-616.

Rydell H., Kraemer T., Bostrom K., Joensuu O., 1974. Postdepositional injections of uranium-rich solutions into East Pacific Rise sediments, *Mar. Geol.*, **17,** 151-164.

Shackleton N. J., Opdyke N. D., 1973. Oxygen isotopes and paleomagnetic stratigraphy of Equatorial Pacific core V 28-238: oxygen isotope temperatures and ice volumes on a 10^5 year time scale, *Quat. res.*, **3,** 39-55.

Shackleton N. J., Opdyke N. D., 1976. Oxygen isotope and paleomagnetic stratigraphy of Pacific core V 28-239, late pliocene to latest pleistocene, *Geol. Soc. Am. Mem.*, **145,** 449-464.

Turekian K. K., Wedepohl K. H., 1961. Distribution of the elements in some major units of the Earth's crust, *Geol. Soc. Am. Bull.*, **72,** 175-192.

Turekian K. K., Bertine K. K., 1971. Deposition of molybdenum and uranium along the major ocean ridge system, *Nature*, **229,** 250.

Williams D. L., Von Herzen R. P., Sclater J. G., Anderson R. N., 1974. The Galapagos Spreading center: lithospheric cooling and hydrothermal circulation, *Geophys. J. R. Astron. Soc.*, **38,** 587-608.