

# Preliminary study of uranium and thorium redistribution in *Callichirus lauræ* burrows, Gulf of Aqaba (Red Sea)

Uranium  
Thorium  
Burrow  
Crustacea  
Red Sea  
  
Uranium  
Thorium  
Terrier  
Crustacé  
Mer Rouge

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## ABSTRACT

A limited number of samples from superficial sediments and burrows of a callianassid shrimp from the Gulf of Aqaba (Red Sea), were analyzed for uranium and thorium isotopes. The preliminary results showed that uranium and thorium isotopes are redistributed by *Callichirus lauræ* Saint Laurent, 1984 (Crustacea: Thalassinidea), and a significant increase of their concentration was observed in the mucus and humic acid rich burrow lining as well as in the intestinal content of the shrimp. The mud-shrimp organs did not show these high values.

It is hypothesized that the concentration of uranium and thorium isotopes in sediment, lining and intestine content results from fixation on humic substances. In the burrow lining  $^{234}\text{U}/^{238}\text{U}$  ratios were as high as 1.36, while only 0.9 to 1.1 in the surface sand, which is probably due to the adsorption of uranium with those ratios from the pore water nearby, as it passes through the lining. These findings demonstrate a significant redistribution of uranium by the shrimp, but as an indirect consequence of the creation of a burrow lining.

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## RÉSUMÉ

Étude préliminaire de la redistribution de l'uranium et du thorium dans le terrier de *Callichirus lauræ*, Golfe d'Aqaba, Mer Rouge

Une étude préliminaire de la distribution de  $^{230+228}\text{Th}$  et  $^{238+234}\text{U}$  a été effectuée à partir d'un nombre limité d'échantillons de sédiment superficiel et de parois de terriers du crustacé fouisseur *Callichirus lauræ* Saint Laurent, 1984 (Thalassinidea). Les résultats ont montré que ces isotopes sont redistribués par *C. lauræ*: une augmentation significative de la concentration a pu être mise en évidence au niveau des parois muqueuses du terrier ainsi que dans le contenu intestinal de la crevette. Cette augmentation de concentration pourrait résulter de la fixation des radionucléides sur les matières humiques. Le rapport  $^{234}\text{U}/^{238}\text{U}$  est de 1.36 dans la paroi et de 0.9 à 1.1 dans le sédiment superficiel. Cette différence pourrait s'expliquer par un enrichissement de la paroi par de l'uranium transitant de l'eau interstitielle vers l'eau du terrier.

Ces résultats montrent que la redistribution de l'uranium dans le terrier de *C. lauræ* est directement liée aux propriétés de la paroi muqueuse, celle-ci se comportant comme une interface réactive entre le sédiment environnant et l'eau circulant dans le terrier. La crevette elle-même ne montre pas d'accumulation sensible de radionucléides dans les organes analysés.

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## INTRODUCTION

Mound and funnel fields produced by the sediment reworking activity of *Callichirus laurae* Saint Laurent, 1984 (Crustacea: Thalassinidea: Callianassidae) are conspicuous features of the sedimentary environment of the Gulf of Aqaba-Eilat in the Red Sea (Reiss, Hottinger, 1984; Vaugelas, 1984).

As Thalassinid populations cover enough of the bottom to be considered an effective means of bioturbation, their activities lead to the redistribution of nutrients (Aller *et al.*, 1983; Waslenchuk *et al.*, 1983), organic matter (Suchanek *et al.*, 1986; Buscail, Vaugelas, submitted) and trace elements (Pemberton *et al.*, 1976; Ahsanullah *et al.*, 1981; Aller *et al.*, 1983; Abu-Hilal *et al.*, submitted). Data on radionuclides redistribution by callianassid mud-shrimps are somewhat scarce: Suchanek *et al.* (1986), in their study on actinide redistribution by callianassid shrimps in Enewetak lagoon, clearly demonstrated the biological control of  $^{90}\text{Sr}$ ,  $^{239+240}\text{Pu}$  and  $^{60}\text{Co}$  distribution, but did not specify the extent of binding with the burrow lining, although some of the highest concentrations of radionuclides were found at depths where burrows were most abundant. Nevertheless, in the same set of studies, McMurry *et al.* (1986, p. 42) made the hypothesis that a peak of radioactivity observed in core 5D-3 could result from bioaccumulation, possibly in the mucus lining of a callianassid burrow sampled inadvertently.

Most work on radionuclides redistribution in the marine environment considers either accumulation in the bulk sediment or in the organisms themselves (Davis, Foster, 1958). However, recent work shows an increasing interest for the study of element fixation on biogenic substrates such as fecal pellets or mucous linings (Kershaw *et al.*, 1983 and 1984; Juniper *et al.*, in press). The aim of the present study was therefore to clarify the possibility for *C. laurae* burrow lining to be a place of radionuclide fixation.

Another set of results on the same crustacean burrows demonstrated the presence of high levels of humic matter in *C. laurae* lining (Buscail, Vaugelas, submitted). Since humic substances are known to complex radionuclides (Rashid, 1985), we thought it interesting to study the extent of this relation through the redistribution of uranium and thorium isotopes.

## MATERIALS AND METHODS

Study area and *Callichirus laurae* behaviour

Samples were taken in the Jordanian Gulf of Aqaba (29° 29' N; 34° 58' E), in the bay bordering the Marine Science Station (Fig. 1).

A general description of the Gulf of Aqaba-Eilat can be found in Reiss and Hottinger (1984) and Jordanian sandy substrates were described in Gabrié and Montagnoni (1982). Three types of substrates were sampled. At a depth of 10 m in the bay, a fine terrigenous sand

with admixed carbonate particles is either covered by a *Halophila stipulacea* seagrass bed (seagrass sand: Md=125 µm; So=1.63, well sorted; ca. 18% carbonates) or devoided of seagrasses (bare sand: Md=200 µm; So=1.91, well sorted; 20 to 30% carbonates). On the northern side of the bay, at 3 m deep, a medium to coarse coral sand was sampled in the upper part of the fore reef zone (Md=400 µm; So=1.78, well sorted; 80 to 95% carbonates).

In bare sand, Eh profiles decreased from +300 mV at the surface to 0 mV at ca. 3.5 cm deep (RPD layer at 3 cm deep) and -150 mV at a depth >6 cm. In the more reduced seagrass sand, we measured 0 mV at 2 cm (RPD at 1 cm) and -150 mV at a depth >3 cm. In the coarse coral sand, the 0 mV level was between 4 and 5 cm deep (RPD at 3 to 4 cm) (Vaugelas *et al.*, 1983 and unpublished data).

*Callichirus laurae*, a micro-detritus consumer, feeds by sorting up to 10 kg shrimp<sup>-1</sup> week<sup>-1</sup> of surface sand sliding into the burrow by gravity (Vaugelas, 1984). It was demonstrated that the concentration of organic carbon and humic substances is ca. 30 times higher in the gut compared to the 0-2 cm layer of surface sediment (Buscail, Vaugelas, submitted). In order to consolidate its permanent burrow, *C. laurae* builds a 5 to 15 mm thick cohesive burrow lining in which fine particles (Md=100 to 150 µm; So=1.3, very well sorted; 40 to 80% carbonates) are soaked in a mucus: the concentrations in organic carbon and humic substances are 4 to 6 times higher in the burrow lining than in the surrounding sediment (Buscail, Vaugelas, submitted). It was observed that the incurrent tunnel was always

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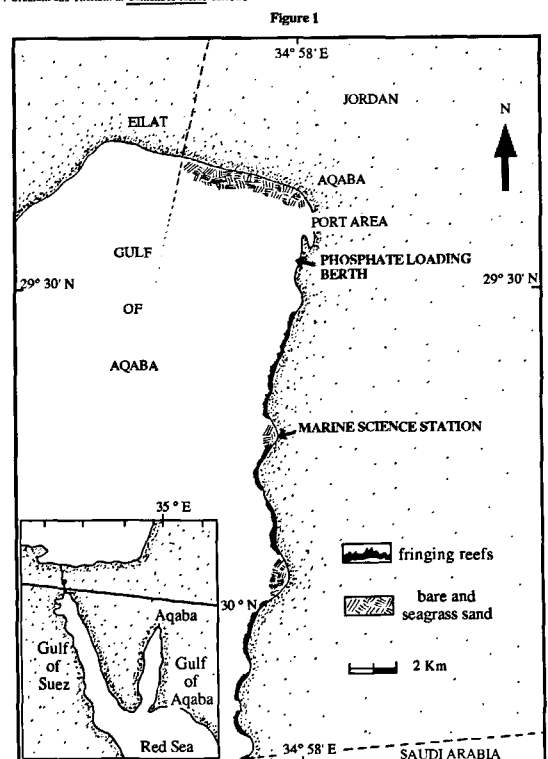
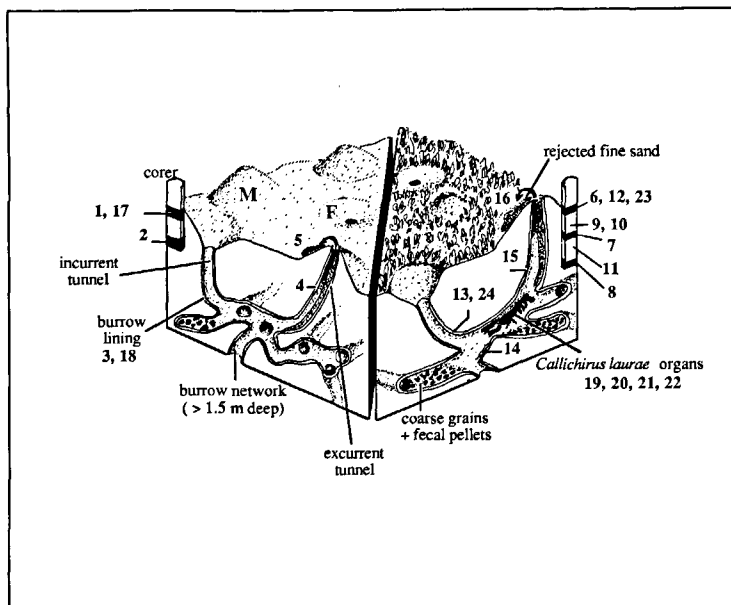


Figure 1  
Location of the study area (Marine Science Station), about 8 km south of the phosphate loading berth, a source of uranium contamination in the Gulf of Aqaba.  
Localisation de la zone d'étude.

Figure 2

Location of samples on a diagram of *Callichirus laurae* burrow structure. Key: M=mound; F=funnel; 1 to 5=bare sand samples; 6 to 16=seagrass sand samples; 17 and 18=coral sand samples; 23 and 24=phosphate mud samples.

Localisation des échantillons sur un bloc diagramme schématique représentant l'organisation des terriers de *Callichirus laurae*. Légende : M=cône; F=entonnoir; échantillons 1 à 5=sédiment nu; 6 à 16=sédiment avec herbier; 17 et 18=sédiment corallien; 23 et 24=boue phosphatée.



slimy—i.e. with freshly incorporated mucus—and displayed colour evidence of oxidation of the smooth inner lining when compared with the excurrent tunnel (Fig. 2). The latter was 3/4 full of fine sand and except for the narrow passage through which the fluidized sediment was ejected by the shrimp after feeding (Fig. 2), the wall of this tunnel had the same dark grey colour as the surrounding sediment.

### Sampling and analysis

All samples were taken by hand with plastic corers while scuba-diving and deep-frozen immediately until subsequent analysis. Before sampling, burrows were prepared according to the "archaeological" method described in Vaugelas (1984). An adult specimen of *Callichirus laurae* was collected in a bare sand area with a "weighted line", as described in Vaugelas (1985); its length from rostrum to telson was 120 mm.

After drying and ashing 0.5 g of sediment in a muffle furnace at 700-800°C overnight, the subsequent analysis of uranium and thorium isotopes was similar to those described by Bojanowski *et al.* (1983). Acid dissolution was followed by ion exchange separation of uranium and thorium on Biorad AG 50 WX 12. After elution of uranium with other elements using 5 M HCl, the thorium was eluted with 0.5 M Oxalic acid. The uranium fraction was separated from other elements except iron on a Biorad AG 1 X 8 column, by eluting with 0.5 M HCl, and purified from iron on another Biorad AG 1 X 8 column in sulphate form, from which the iron was eluted with 1 M ammonium sulphate at pH 1.5, and the uranium finally eluted with 0.5 M HCl after reconversion of the column to chloride form. Both uranium and thorium fractions were electroplated onto stainless steel disks.

$^{229}\text{Th}$  and  $^{232}\text{U}$  were used as yields determinants. All results were individually corrected for yields less than 100%. Yields for thorium had a mean and standard deviation of  $40 \pm 27\%$  while the corresponding figures for uranium were  $63 \pm 26\%$ . Counting errors on  $^{232}\text{Th}$  results were about  $\pm 20\%$  and are not included in the

tables. The adult mud-shrimp was analyzed (carapace, intestinal content, digestive gland and muscles) but the weights of the organs were all less than 300 mg and the yields for thorium were very low: these results are therefore given only in terms of minima (Tab. 1).

Organic carbon content of the dry sediment was obtained by combustion in a LECO analyzer. Total humic matter (HM) of sediments, burrows and intestine content was extracted with a base (Debyser, Gadel, 1983); Humic acids (HA) were precipitated after acidification to pH 2 and separated from fulvic acids (FA). Organic carbon was then measured with a COULOMAT 702 (Strohlein Instruments; Buscail, Vaugelas, submitted).

Determination of grain size distribution of the sand and the burrow lining was carried out using an AFNOR sieve column. Cumulative grain size curves were used to calculate mean diameter (Md) and Trask sorting index (So). Redox potentials were measured using a thin wire platinum electrode.

### RESULTS

The number of samples being limited, great care was taken in the analysis of the data and only the most obvious relations were outlined. The highest values for uranium and, to a lesser extent, for thorium were found in *Callichirus laurae* intestinal content and in its burrow lining (Tab. 1).

The results from gallery walls were compared statistically (*t* test) with all other sediment samples to see if there was a significant enhancement of U and Th contents. For the seagrass sand area, the gallery walls were significantly higher in U ( $p < 0.01$ ) but not so for Th ( $p = 0.06$ ). For the bare sand area, the gallery walls were also significantly higher in U ( $p < 0.05$ ) and Th ( $p < 0.05$ ). The differences were not significant however in the coral sand area. In a polluted area near the port where an uranium-rich phosphate powder is dumped from a loading berth (Hulings, 1982; Abu-Hilal, 1985), U bound to the lining was 3 to 5 times more abundant (U=15 ppm) than linings sampled in the unpolluted

Table 1

Thorium and uranium isotopes ( $Bq\ Kg^{-1}$ ) distribution in bare sand, seagrass sand, coral sand and *Callichirus lauræ* organs. Errors (%) are counting errors only and represent the coefficient of variation. Key: I=incurrent tunnel; E=excurrent tunnel. Location of samples in Figure 2.

Distribution des isotopes de l'uranium et du thorium dans des sédiments nus ou recouverts par un herbier, dans des sédiments coralliens et dans les organes de *Callichirus lauræ*. L'erreur de comptage, ou coefficient de variation, est exprimée en pourcentage. Légende: I=galerie d'entrée; E=galerie de rejet de l'eau et du sédiment. Localisation des échantillons: voir figure 2.

Sample n°	Sample	230 Th ( $Bq\ Kg^{-1} \pm \%$ )	228 Th ( $Bq\ Kg^{-1} \pm \%$ )	228 Th/ 230 Th	238 U ( $Bq\ Kg^{-1} \pm \%$ )	234 U ( $Bq\ Kg^{-1} \pm \%$ )	234 U/ 238 U
<b>Bare sand area</b>							
1	surface	10.2±6.4	24.0±3.7	2.4	15.3±4.4	15.3±4.5	1.00
2	-10 cm	9.8±5.0	21.8±3.2	2.2	27.7±6.6	28.3±6.5	1.02
3	burrow lining I	23.0±11	29.0±10	1.3	50.0±1.9	66.0±1.7	1.32
4	burrow lining E	20.8±6.4	45.3±4.5	2.2	42.0±1.9	43.3±1.8	1.03
5	rejected sediment	16.5±7.4	35.3±4.9	2.1	20.2±3.7	21.3±3.6	1.05
<b>Seagrass sand area</b>							
6	core 1: surface	43.8±3.7	113.0±2.3	2.6	22.5±4.3	24.0±4.2	1.06
7	core 1: -10 cm	33.3±6.7	68.7±4.5	2.1	18.7±4.6	19.3±4.5	1.03
8	core 1: -20 cm	28.1±7.4	35.7±6.6	1.3	29.5±4.3	33.3±4.1	1.05
9	core 2: 0-5 cm	29.8±6.4	35.3±5.8	1.2	33.7±3.9	34.5±3.8	1.02
10	core 2: 5-10 cm	26.8±6.6	28.2±6.2	1.1	32.2±3.4	32.0±3.4	0.99
11	core 2: 10-15 cm	17.3±7.5	17.7±7.1	1.0	28.0±5.0	26.8±5.2	0.96
12	core 3: surface	36.2±4.9	44.2±4.4	1.2	29.8±2.9	28.5±3.0	0.96
13	burrow lining I	50.8±4.8	57.1±4.5	1.1	61.0±3.1	82.8±2.6	1.36
14	burrow lining	42.5±5.1	39.5±5.2	0.9	41.3±2.3	56.3±2.0	1.36
15	burrow lining E	32.5±5.0	33.2±4.8	1.0	44.3±1.8	44.7±1.8	1.01
16	rejected sediment	18.8±3.8	23.5±3.3	1.3	42.0±10	36.0±10	0.86
<b>Coral sand area</b>							
17	surface	9.2±17	13.3±14	1.4	25.3±2.3	28.2±2.2	1.11
18	burrow lining E	7.7±8.3	24.2±4.6	3.1	39.0±2.9	42.8±2.7	1.10
<b><i>Callichirus lauræ</i> (collected in bare sand)</b>							
19	carapace	>3.7±16	>0.5±11	0.1	11.0±16	8.2±19	0.7
20	muscles	>23.8±3.2	>1.4±13	0.1	2.8±19	2.0±24	0.7
21	digestive gland	>8.3±10	>2.2±30	0.3	14.3±9	13.1±10	0.9
22	intestinal content	>37.5±8.5	>33.1±8.8	0.9	82.0±10	70.0±12	0.9

Table 2

Distribution of total uranium (U), organic carbon (OC), humic matter (HM), fulvic acids (FA), humic acids (HA) and mean diameter (Md). Except for coral sand and phosphate mud samples, OC, HM, FA and HA values are reprinted from Buscaill and Vaugelas (submitted). Location of samples in Figure 2. — = no data.

Distribution de l'uranium total (U), du carbone organique (OC), de la matière humique (HM), des acides fulviques (FA), des acides humiques (HA) et de la médiane granulométrique (Md). A l'exception des données sur le sédiment corallien et la zone des phosphates, les valeurs de OC, HM, FA et HA sont tirées de Buscaill et Vaugelas (soumis pour publication). Localisation des échantillons: voir figure 2. — = Absence de données.

Sample n°	Sample	U (ppm)	OC (%)	HM (%)	FA (%)	HA (%)	Md ( $\mu m$ )
<b>Bare sand area</b>							
1	surface	1.2	0.18	0.033	0.019	0.013	200
2	-10 cm	2.2	0.09	0.017	0.010	0.007	200
3	burrow lining I	4.0	1.12	0.164	0.080	0.085	150
4	burrow lining E	3.4	1.56	0.113	0.053	0.060	150
5	rejected sediment	1.6	0.07	0.013	0.012	traces	200
<b>Seagrass sand area</b>							
6	core 1: surface	2.4	0.32	0.107	0.045	0.062	125
7	core 1: -10 cm	1.5	0.06	0.055	0.011	0.044	125
13	burrow lining I	4.9	1.03	0.320	0.140	0.180	100
15	burrow lining E	3.6	0.69	0.128	0.063	0.065	100
16	rejected sediment	3.4	0.12	0.028	0.020	0.008	125
<b>Coral sand area</b>							
17	surface	2.0	0.28*	0.045*	0.001*	0.044*	400
18	burrow lining E	3.1	0.63*	0.155*	0.021*	0.134*	150
<b><i>Callichirus lauræ</i> (collected in bare sand)</b>							
22	intestinal content	6.6	3.37	1.012	0.225	0.782	10
<b>Phosphate mud area</b>							
23	surface	—	0.60**	—	—	—	80
24	burrow lining I	15.0 (°)	1.58**	—	—	—	100

\* Buscaill and Vaugelas, unpublished.

\*\* Abu-Hilal *et al.*, in press.

(°) measured by D. Calmet, Commissariat Énergie Atomique, France.

bay near the Marine Science Station (U=3.4 to 4.9 ppm; Fig. 1 and Tab. 2). We also noted that levels of U and Th were consistently lower in burrow lining samples from excurrent tunnels than from incurrent tunnels and that the sediment rejected after feeding displayed higher values than the nearby surface sand (Fig. 2 and Tab. 1).

Organic analyses of the burrow walls from bare and seagrass sand showed levels of organic carbon and humic matter that were significantly higher than those in the nearby sediment (Tab. 2 and Buscail, Vaugelas, submitted). Correlation coefficients were calculated between each value of  $^{238}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{228}\text{Th}$  and each value of total organic carbon, humic matter, fulvic acids, humic acids contents, and the mean granulometric diameter (Tab. 3).

For uranium there were correlations significant at  $0.01 < p < 0.05$  for all parameters except mean diameter (Md). Correlations for thorium isotopes were not significant though the correlations between  $^{230}\text{Th}$  and fulvic acids and Md were close to the significance level  $p = 0.05$ . There is, therefore, a much better correlation with organic matter for uranium than for thorium isotopes. Hulings (1982) did not find a similar statistical correlation, but noted that low values of uranium were associated with the organic-poor terrigenous bare sand while high levels were associated to the organic-rich, uranium-rich, phosphate mud, the content in seagrass sand being intermediate.

## DISCUSSION

The main purpose of this study was to check if the redistribution of radionuclides by callianassid bioturbation could be related to the fact that these burrowing crustaceans consolidate their tunnels with a mucus-rich, humic matter-rich, lining.

Our study area, located at the Marine Science Station (MSS; Fig. 1), was 8 km south of a source of uranium contamination—i.e. the phosphate loading berth (Hulings, 1982). The uranium values we measured are in the same range than those found by Hulings in 1982 for unpolluted sediments, which confirm his conclusion that uranium pollution via phosphate dust is localized. Therefore, the results obtained at MSS can be considered as representative of natural conditions for the Gulf of Aqaba.

Uranium concentration at the water/sediment interface was 1.2 ppm in bare sand and 1.8 to 2.7 ppm in seagrass sand, which is similar to previously published values for the same types of sediments. Hulings (1982) gives a mean of 1.2 ppm for bare sand and 2.4 ppm for seagrass sand. However, our only data for surface coral sand, 2 ppm, is lower than Hulings' mean value of 2.8 ppm. This could arise from differences in sampling stations, the microdistribution of coral sand being a function of the dominant reef materials in the area considered (Swart, Hubbard, 1982). In Hulings' work

Table 3

Correlation coefficients between radioactive components, organic matter and the mean diameter. All  $r$  are statistically different from 0 ( $0.01 < p < 0.05$ ), except when followed by n.s. (not significant,  $p > 0.05$ ). All correlation coefficients in the table have a standard deviation of 0.35.

Tableau de corrélations entre les radionucléides, la matière organique et la médiane granulométrique. Toutes les valeurs de  $r$  sont statistiquement différentes de 0 au seuil  $0.01 < p < 0.05$ . n.s. = non significatif ( $p > 0.05$ ). Tous les coefficients de corrélation ont une erreur standard de 0.35.

	Organic carbon	Humic matter	Fulvic acids	Humic acids	Mean grain size
238 U	0.86	0.87	0.92	0.83	-0.42 n.s.
230 Th	0.43 n.s.	0.47 n.s.	0.66 n.s.	0.40 n.s.	-0.64 n.s.
228 Th	0.16 n.s.	0.15 n.s.	0.40 n.s.	0.08 n.s.	-0.36 n.s.

and our study, values of uranium and thorium isotopes were consistently higher in the seagrass sand than both in bare and coral sand, suggesting a control due to the presence of the seagrass itself, or conceivably, a preference of the seagrass for a sediment type which also happens to contain slightly higher values of uranium and thorium. The fact that the surface sand values compare well with those obtained by Hulings in 1982 indirectly indicates that the observed increase from the surface sediment to the intestinal content of the mud-shrimp and/or to its burrow lining, are not fortuitous.

The following discussion considers firstly, the chemical and biological processes which may govern fixation of the radionuclides to the lining and, secondly, the fixation routes.

### Factors governing fixation to the intestine content and the lining

When feeding, *Callinectes lauræ* tends to select and concentrate organic elements from the small size fraction of the sand, which results in an increase of radioactivity (especially noticeable for [U]) in their intestinal content, of which the animal itself shows no signs. The mud-shrimp intestinal content is rich in humic matter (HM) and a significant correlation was observed with the concentration of uranium, while the correlation between fulvic acids and thorium was at the limit of the significance level (Tab. 3). This suggests that at least uranium is bound to the humic substances of the organic matter, in agreement with what is currently known about binding properties of HM towards radionuclides (Nash *et al.*, 1981; Rashid, 1985). The intestinal content being enriched in U and Th, it is probable that fecal pellets are also (Davis, Foster, 1958). Most of these are permanently buried (Buscail, Vaugelas, submitted). This has implications for the inventory of radionuclides in callianassid-reworked sediments. However, the concentration of uranium and thorium may not change significantly in the burrow storage chambers since large quantities of shell, gravel and other diluent material are stored along with fecal pellets.

Statistical analysis showed that except for the coral sand sample,  $^{238}\text{U}$  is significantly enhanced in burrow linings compared with other sediment samples. The main biogenic material added to the gallery wall is the mucus secreted by the shrimp. Uranium enrichment of mucus consolidated substrates has also been reported for the "Palm worm" *Paralvinella* sp. from deep sea hydrothermal chimneys (Juniper *et al.*, in press). Other species may also incorporate fecal pellets in their lining, as it was observed for the echinuran *Maxmulleria lankesteri* (Kershaw *et al.*, 1983 and 1984), but Buscail and Vaugelas (submitted), using intestinal propionate as a tracer, did not find any incorporation of fecal material in *C. laurae* lining. The mechanism by which radionuclides are incorporated in *C. laurae* lining is therefore different from a consolidation of the walls with radionuclide-rich fecal pellets. It could be explained in three ways, not mutually exclusive: the secretion of a radionuclide-rich mucus by the shrimp, the incorporation of finer mineral fractions and a higher concentration of reactive organic matter.

a) The secretion of a radionuclide-rich mucus by the shrimp seems unlikely since the results show little bioaccumulation in body parts. However we do not have specific data on the content of radioelements in the mucus prior to its secretion, so this possibility cannot be disregarded entirely.

b) When lining their burrows, callianassid shrimps select fine particles. Since Sackett (1978) showed that thorium was strongly associated with the finer particles, higher levels of Th in linings may be accounted for. However, since most of the observed variation for uranium is explained by the relationship with organic matter, explanation of enrichment in the gallery walls by a process of grain size sorting is not supported for uranium.

c) The burrow lining is enriched in humic matter and this could also cause adsorption of radionuclides (Nash *et al.*, 1981; Rashid, 1985). On the basis of the correlations reported therein, we suggest that the binding properties of humic substances is a tentative explanation for the observed redistribution of uranium in callianassid mud-shrimps burrows, but to a lesser extent for thorium since the influence of grain size sorting on its concentration is more accentuated.

#### Fixation routes

The following paragraph tentatively analyses the main routes followed by U and Th prior to their fixation in the lining.

Consideration of the  $^{234}\text{U}/^{238}\text{U}$  ratios seems to indicate that the lining is an interface for the exchange of solutes from the nearby reduced sediment to the oxygenated burrow water irrigating the burrow network. The ratios in the entire set of samples are strongly clustered around 1.0, with three outliers all from freshly made burrow walls, having values of 1.32 (sample 3), 1.36 (sample 13) and 1.36 (sample 14). The remaining three burrow wall ratios (samples 4, 15 and 18) are respectively 1.03, 1.01 and 1.10, but these samples all come from excurrent tunnels, which contain less humic sub-

stances and are more reduced than incurrent tunnels samples. Uranium does not attach strongly to fine particles, hence there should be a tendency for such particles to reflect the isotopic ratio of the original source rock, *i.e.* 1.0 as has been found by Hodge *et al.* (1979) or Anderson (1986). For the ratio in the seawater irrigating the burrow network, one expects a value somewhere in the range 1.15-1.19 (Koide, Goldberg, 1965; Veeh, 1968; Yaron, Frenkel, 1969), which is slightly higher than normal for open ocean but could reflect a peculiarity of the Gulf of Aqaba-Eilat: restricted hydrology and high salinities (Reiss, Hottinger, 1984). Adsorption of seawater uranium on organic material in burrow linings might therefore produce ratios of 1.15-1.19, yet that is still much too low. The origin cannot be the fecal pellets of the shrimp since it was previously shown that they are not incorporated in the lining. Furthermore, the analysis of the shrimp's intestinal content, made of compacted clayish particles, gave a value of 0.9 (Tab. 1), within statistical error of 1.0, the value expected for fine particles.

The remaining possibility is the pore water in the nearby sediments. We did not investigate the uranium in the pore water, but some information is available in the literature. Interstitial pore waters found in marine systems seem sometimes to contain higher than normal amounts of uranium, as much as 40 times those found in seawater, even under reducing conditions (Kolodny, Kaplan, 1973; Barnes, Cochran, 1986). Simultaneously the  $^{234}\text{U}/^{238}\text{U}$  ratio in pore waters is as high as 1.25 and is significantly higher than the ratio in seawater. Enrichment is normally expected in pore waters and may be high in terrestrial environments. Thompson *et al.* (1975) showed seepage water values of 1.3-2.3 in a limestone cave. We do not have porewater carbonate concentrations from the study area, but work on carbonate in pore waters from a similar environment (Skirrow, 1975) showed high carbonate values. One might therefore expect rather high isotope ratios in Aqaba interstitial waters. A high interstitial carbonate content encourages solution of surface uranium from particles, which through the recoil effect is enriched in  $^{234}\text{U}$ . Cochran *et al.* (1986) did not find  $^{234}\text{U}/^{238}\text{U}$  ratios higher than 1.0 but their environment was much less rich in carbonate than ours.

In view of the Eh values of  $-100$  to  $-150$  mV in the pore waters surrounding the burrow, it might be expected the uranium would not be mobile, but precipitated. However the work of Langmuir (1978), although showing that in laboratory systems such reduction from  $\text{U}^{6+}$  to  $\text{U}^{4+}$  might be expected, also gives an Eh/pH diagram including carbonate at low concentrations typical of terrestrial aquifers. The diagram shows that  $\text{U}^{6+}$  complexed by the carbonate will exist as the tricarbonate complex at pH 8 (typical for marine pore waters) and be stable to reduction down to  $-200$  mV. In the present case the concentration of carbonate is similar (Skirrow, 1975) and one expects stability. Even though these sediments are reduced, the uranium will keep the same oxidized form. In some anoxic marine waters whose carbonate concentration is not so high, Ander-

son (1986) has been able to experimentally confirm that uranium does exist in the  $U^{6+}$  valency form.

One therefore anticipates that a likely origin of the uranium in the burrow lining is the surrounding pore water. This water would be pumped through the lining as a result of the permanent stream of water maintained in the burrow network by the shrimp for irrigation purposes. During this phase of percolation, fixation of uranium occurs in the lining, due to its strong affinities with humic substances.

Thorium isotopes, on the other hand, have not been reliably reported in significant quantities in pore water and their weak concentration in the burrow wall is more likely to be from inside the burrow system and the associated movement of water and particles, when adsorption/desorption processes occur at the burrow interface. Translocated elements adsorbed on particles are pumped out to the surface with the sifted sand. In Enewetak Atoll lagoon, material resuspended through callianassid pumping had generally higher gross  $\alpha$  plus  $\beta$  activity per unit weight than controls (Colin *et al.*, 1986). These authors demonstrated that callianassid pumping activity in Enewetak Atoll is a very significant route of radionuclide transfer from the sand to the overlying waters. In our study, uranium and, to a lower extent, thorium levels are higher in the ejected sand than in the surface sand before it enters the burrow, something which could result from a contamination of the sand during its transit in the burrow, when in contact with the isotope-enriched walls. This regular release of radionuclides in the ejected sand may be an effective means for limiting isotope concentration in the lining.

Our findings are similar to the results obtained by Kershaw *et al.* (1983 and 1984), who demonstrated the biological control of Pu, Am and Cm by the echiuran

*Maxmulleria lankesteri*. Consolidated burrows such as those of callianassids or echiuroids being abundant in most soft-bottoms, including the huge expanses of abyssal plains (Heezen, Hollister, 1971), these microenvironments deserve specific attention when sampling for radionuclides. Conventional methods tend to provide samples of the bulk superficial sediment, without considering biogenic structures extending far below the 0-30 cm layer. Consideration of such biogenic structures could be ultimately included in oceanic uranium mass balance (Cochran, 1982), though more studies are needed to assess the persistence of radionuclide fixation to biogenic microenvironments through geological time.

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## REFERENCES

- Abu-Hilal A., 1985. Phosphate pollution in the Jordan Gulf of Aqaba, *Mar. Pollut. Bull.*, **16**, 281-285.
- Abu-Hilal A., Badran M., Vaugelas J. de, Distribution of trace elements in *Callinectes laurae* burrows and nearby sediments in the Gulf of Aqaba, Jordan (Red Sea), *Mar. Environ. Res.*, in press.
- Ahsanullah M., Negilski D. S., Mobley M. C., 1981. Toxicity of zinc, cadmium and copper to the shrimp *Callinectes australiensis*. I: Effects of individual metals, *Mar. Biol.*, **64**, 299-304.
- Aller R. C., Yings J. Y., Ullman W. J., 1983. Comparative biogeochemistry of water in intertidal *Onuphis* (Polychaeta) and *Upogebia* (Crustacea) burrows: temporal patterns and causes, *J. Mar. Res.*, **41**, 571-604.
- Anderson R. F., 1986. Uranium geochemistry in the Black Sea, *EOS AGU*, **67**, 1069.
- Barnes C. J., Cochran K., 1986. Porewater uranium profiles in reducing marine sediments, *EOS AGU*, **67**, 1008.
- Bojanowski R., Fukai R., Ballestra S., Asari H., 1983. Determination of natural radioactive elements in marine environmental materials by ion-exchange and alpha-spectrometry, *Proc. 4th Symposium on the Determination of Radionuclides in Environmental and Biological Materials*, Lab. Government Chemists, London, **9**, 1-15.
- Buscaill R., Vaugelas J. de, Humic substances distribution in burrows of the thalassinid crustacea *Callinectes laurae*, Aqaba (Red Sea), submitted.
- Cochran J. K., 1982. The oceanic chemistry of the U- and Th-series nuclides, in: *Uranium series disequilibrium: applications to environmental problems*, edited by M. Ivanovich and R. S. Harmon, Clarendon Press, Oxford, 384-430.
- Cochran J. K., Carey A. E., Sholkovitz E. R., Surprenant L. D., 1986. The geochemistry of uranium and thorium in coastal marine sediments and sediment pore waters, *Geochim. Cosmochim. Acta*, **50**, 663-680.
- Colin P. L., Suchanek T. H., McMurtry G., 1986. Water pumping and particulate resuspension by callianassids (Crustacea: Thalassinidea) at Enewetak and Bikini Atolls, Marshall Islands, *Bull. Mar. Sci.*, **38**, 19-24.
- Davis J. J., Foster R. F., 1958. Bioaccumulation of radioisotopes through aquatic food chains, *Ecology*, **39**, 530-535.
- Debyser Y., Gadel F., 1983. Géochimie des kérogènes, in: *Géochimie organique des sédiments marins d'ORGON à MISEDOR*, edited by CNRS, Paris, 421-450.
- Gabrié C., Montaggioni L. F., 1982. Sedimentary facies from modern coral reefs, Jordan Gulf of Aqaba, Red Sea, *Coral Reefs*, **1**, 115-124.
- Heezen B. C., Hollister C. D., 1971. *The face of the deep*, Oxford University Press, New York, 250 p.
- Hodge V. F., Koide M., Goldberg E. D., 1979. Particulate uranium, plutonium and polonium in the biogeochemistry of the coastal zone, *Nature*, **277**, 206-210.
- Hulings N. C., 1982. The uranium content of sediments from the Jordan Gulf of Aqaba, *Mar. Pollut. Bull.*, **13**, 47-49.
- Juniper S. K., Thompson J. A. J., Calvert S. E., Accumulation of minerals and trace elements in biogenic mucus at hydrothermal vents, *Deep-Sea Res.*, in press.
- Kershaw P. J., Swift D. J., Pentreath R. J., Lovett M. B., 1983. Plutonium redistribution by biological activity in Irish Sea sediments, *Nature*, **306**, 774-775.
- Kershaw P. J., Swift D. J., Pentreath R. J., Lovett M. B., 1984. The incorporation of plutonium, americium and curium into the Irish Sea seabed by biological activity, *Sci. Total Environ.*, **40**, 61-81.
- Koide M., Goldberg E. D., 1965. Uranium-234/uranium-238 ratios in sea water, *Progr. Oceanogr.*, **3**, 173-177.
- Kolodny Y., Kaplan L. R., 1973. Deposition of U in the sediments and interstitial waters of an anoxic fjord, *Proc. Symp. Hydrogeochemistry and Biogeochemistry, Tokyo*, **1**, 418-442.
- Langmuir D., 1978. Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, *Geochim. Cosmochim. Acta*, **42**, 547-569.
- McMurtry G. M., Schneider R. C., Colin P. L., Buddemeier R. W., Suchanek T. H., 1986. Vertical distribution of fallout radionuclides in Enewetak Atoll lagoon sediments: effects of burial and bioturbation on the radionuclide inventory, *Bull. Mar. Sci.*, **38**, 35-55.
- Nash K., Sherman F., Friedman A. M., Sullivan J. C., 1981. Redox behavior, complexing, and adsorption of hexavalent actinides by humic acid and selected clays, *Environ. Sci. Technol.*, **15**, 834-837.
- Pemberton G. S., Risk M. J., Buckley D. E., 1976. Supershrimp: deep bioturbation in the Strait of Canso, Nova Scotia, *Science*, **192**, 790-791.
- Rashid M. A., 1985. *Geochemistry of marine humic compounds*, Springer-Verlag, Berlin, 291 p.
- Reiss Z., Hottinger L., 1984. *The Gulf of Aqaba. Ecological micropaleontology*, Springer-Verlag, Berlin, 354 p.
- Sackett W. M., 1978. Suspended matter in seawater, *Chem. Oceanogr.*, Wiley, London, **7**, 127-172.
- Skirrow G., 1975. The dissolved gases-Carbon dioxide, in: *Chemical Oceanography, 2nd Ed.*, edited by J. P. Riley and G. Skirrow, Academic Press, London, **2**, 1-192.
- Suchanek T. H., Colin P. L., McMurtry G. M., Suchanek C. S., 1986. Bioturbation and redistribution of sediment radionuclides in Enewetak Atoll lagoon by callianassid shrimp: biological aspects, *Bull. Mar. Sci.*, **38**, 144-154.
- Swart P. K., Hubbard J. A. E. B., 1982. Uranium in scleractinian coral skeletons, *Coral Reefs*, **1**, 13-19.
- Thompson P., Ford D. C., Schwarcz H. P., 1975.  $^{234}\text{U}/^{238}\text{U}$  ratios in limestone cave seepage waters and speleothem from West Virginia, *Geochim. Cosmochim. Acta*, **39**, 661-669.
- Vaugelas J. de., 1984. Preliminary observations on two types of callianassid (Crustacea, Thalassinidea) burrows, Gulf of Aqaba, Red Sea, *Proc. Symp. Coral Reef Environ. Red Sea, Jeddah, January 1984*, 520-539.
- Vaugelas J. de, Madi E., Hashwa F., 1983. Redox potentials, hydrogen sulfide and bacterial activity in sediment cores from the Gulf of Aqaba (Jordan), *Proc. 3rd Int. Symp. Microbial Ecology, Michigan State University* (abstract).
- Veeh H. H., 1968. U-234/U-238 in the East Pacific sector of the Antarctic Ocean and in the Red Sea, *Geochim. Cosmochim. Acta*, **32**, 117-119.
- Waslenchuk D. G., Matson E. A., Zajac R. N., Dobbs F. C., Tramonano J. M., 1983. Geochemistry of burrow waters vented by a bioturbating shrimp in Bermudian sediments, *Mar. Biol.*, **72**, 219-225.
- Yaron F., Frenkel R., 1969. U-234/U-238 ratio in the Red Sea, *Israel J. Earth Sci.*, **18**, 149.