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MANGANESE, METHANE AND HELIUM ANOMALIES IN SEA WATER ABOVE THE MID-ATLANTIC RIDGE : EVIDENCE OF HYDROTHERMAL ACTIVITY

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ABSTRACT — Manganese, helium and methane are highly enriched in hydrothermal effluents and their vertical distributions in sea water are commonly used as chemical tracers of hydrothermal activity. The cruise performed during may 1985 with the RV *Akademik Boris Petrov* (Vernatsky Institut of Geochemistry, Moscow) allowed us to present vertical total dissolved manganese and CH_4 concentration profiles at seven stations : four along the south Middle Atlantic Ridge (13°20'S - 14°64'W ; 14°12'S - 13°58'W ; 21°28'S - 11°37'W ; 19°56'S - 11°52'W) and three along the north MAR (12°24'N - 44°05'W ; 13°47'N - 44°59'W ; 14°05'N - 45°01'W). Some samples in each profile have been analysed for $^3He/^4He$ ratios and ^4He amounts. The hydrographic stations have been set up over the axial ridge valley combined with bathymetric and geochemical rock studies. The results show many hydrothermal tracer anomalies in the water column both in the northern and southern studied areas. Although the amplitude and shape of the anomalies are clearly smaller than those observed at the well documented hydrothermal sites (Galapagos Spreading Center, East Pacific Rise, Juan de Fuca Ridge, TAG), plumes originated by hydrothermal discharge are present in the two southern studied areas as well as in the northern one.

Manganese, Methane, Helium, Mid-Atlantic Ridge, Hydrothermal activity

Anomalies de manganèse, méthane et hélium dans la colonne d'eau de mer au droit de la ride médio-atlantique : des évidences d'activité hydrothermale

RÉSUMÉ — Les eaux hydrothermales sous-marines sont extrêmement enrichies en manganèse, méthane et hélium. Ces composés se trouvent donc notablement enrichis dans la colonne d'eau située au voisinage d'un site actif. La mission effectuée par le NO *Akademik Boris Petrov* du Vernatsky Institut of Geochemistry (Moscou) en mai 1985 nous a permis d'étudier les profils de manganèse et de méthane à sept stations : quatre le long de la ride médio-atlantique sud (13°20'S - 14°64'W ; 14°12'S - 13°58'W ; 21°28'S - 11°37'W ; 19°56'S - 11°52'W) et trois le long d'un segment nord de cette même ride (12°24'N - 44°05'W ; 13°47'N - 44°59'W ; 14°05'N - 45°01'W). Le rapport $^3He/^4He$ a été mesuré sur quelques échantillons de chaque profil, ainsi que les concentrations en ^4He. Toutes les stations ont été effectuées à la verticale de la vallée axiale de la ride et l'étude des eaux, de la bathymétrie et de la géochimie des roches ont été effectuées simultanément. Des anomalies de concentrations des traceurs de l'hydrothermalisme sont mises en évidence dans les zones nord et sud, bien que l'intensité des panaches détectés soit significativement plus faible que dans le cas des zones précédemment étudiées (Centre d'expansion des Galapagos, Ride du Pacifique Est, Dorsale Juan de Fuca Ridge, Zone TAG)

Manganèse, Méthane, Hélium, Ride médio-atlantique, Activité hydrothermale

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Manganese

Total dissolved manganese (TDM) was determined on board using the leucomalachite green colorimetric method which has been applied to direct sea water measurements by BOULÈGUE and HAMELIN (1983). The sensitivity of this method is close to 0.5 nmol/kg with an accuracy of +/− 10% at 1 nmol/kg concentration level. In order to minimize contamination, water samples without treatment (filtration or acidification) were immediatly transfered from the Niskin bottle into 50 ml volumetric flasks. Manganese concentration profiles were usually known within 5 hours after sampling.

Methane

CH_4 were analysed by J.L. CHARLOU using a gas chromatographic technique which allows to work on small volumes (100 to 250 ml). Methane is stripped from sea water with helium carrier gas, then trapped on activated charcoal at − 80°C and detected using a flame ionization detector. The limit of detection is 0.5 μcc (STP) CH_4 per liter of sea water ; the accuracy is +/− 3% over a 3 to 150 μcc (STP)/l range. Sea water samples were stored in glass bulbs (250 ml) fitted with PTFE stopcocks at both ends. They were slowly filled from the bottom to overflowing and natrium azide was added to avoid bacterial growing. Samples were analysed at the IFREMER laboratory (Brest) except for stations HY2-14 and HY2-15, both performed on board.

Helium

The method used to measure helium concentrations and isotopic compositions is basically that described previously by CLARKE *et al.* (1969) and JENKINS *et al.* (1972). The sea water samples were stored in copper tubes tightly closed at each end by a clamp. Analyses have been performed by P. JEAN-BAPTISTE.

For extracting the dissolved ^3He and ^4He, the copper tube is attached to a vacuum extraction line with an O-ring coupling. Then helium as well as other dissolved gases are transferred to a glass bulb containing charcoal at liquid N_2 temperature were the major degassed species are adsorbed on the charcoal. Water vapour is frozen onto the glass surface. This water vapour flux acts as a diffusion pump for transferring helium which is not quantitatively absorbed on charcoal. When the extraction is completed, the bulb is sealed off with a flame. The extraction efficiency is about 99.6%.

Helium isotopes are measured with a specially designed 90° magnetic sector single focusing VG Micromass 3000 spectrometer operated at 3.0 KV. He ions are collected on a Faraday cup. The ^3He ion beam, typically 2000 ions/sec for a 40 cc sea water sample, is collected on a 20 stage electron multiplier operated in pulse mode. The analysis consist of 50 five-seconds integrations on the ^3He and ^4He peaks simultaneously and 20 five-seconds integrations on the baseline. The statistical error on the excess ^3He (δ %), defined as the percentage deviation of the ^3He ^4He isotopic ratio of the water from the standard ratio in air, is equal to +/− 0.15%. The sample reproducibility is estimated from the average scatter of the standard ratios over one day. This gives a reproducibility of about +/−0.2% on δ % ^3He. The overall reproducibility of the method has been tested by measuring ten samples from the same water tank (Mediterranean surface water). The result for these ten measurements is $\delta^3He = -1.5\% +/- 0.4\%$.

Station HY2-21 (fig. 3 a)

Two evident anomalies in the manganese profile were found : one is located around 1850 m (800 m above the bottom of the axial valley) with a maximum concentration of 7.5 nmol/kg and another one between 2200–2270 m with TDM = 3.2 nmol/kg in the deepest water sample. The first strong anomaly is correlated with a temperature anomaly (+0.06°C) and carbonate alkalinity increasing (δAlk = $+1.10^{-5}$ eq/kg). Neither methane nor helium anomaly is noticeable at this depth. The second smaller anomaly is supported by a slight increase of the CH_4 concentrations (up to 12 μcc (STP)/l) at depth lower than 2100 m. Helium results are characterized by an anomalous δ^3He value (+8.5 %) at 2030 m. These results suggest the occurrence of one or several hydrothermal fluid inputs in the vicinity of this station.

Tab. 1 – *Analytical results of sea water samples from southern stations HY2-14, HY2-15, HY2-21, HY2-22 (* in situ temperature ; ^{4}He = helium excess).* Résultats analytiques des échantillons d'eau de mer des stations sud HY2-14, HY2-15, HY2-21 et HY2-22 (* température *in situ* ; ^{4}He = hélium en excès)

Depth m	Temp.* °C	Salinity g/kg	Mn nmol/kg	CH_4 μcc STP	$\delta\,^3$He %	^{4}He %
Station HY2-14 (13°20'S - 14°64'W)						
10	25.979	37.127	6.0			
100	21.617	36.623	4.6	34		
300	10.203	34.946	4.9	23		
800	4.727	34.482	3.9	10		
1500	3.847	34.893		4		
2880	2.640	34.894	5.6	7		
2963	2.635	34.897	5.3	5		
3027	2.615	34.896		5		
3087	2.608	34.897	4.2	5		
3150	2.609	34.903	4.2	5		
3220	2.587	34.896	4.3	4		
3285	2.592	34.896	4.1	4		
3330	2.596	34.896	5.3	4		
3370	2.596	34.900	5.1	5	2.6	18.30
3395	2.598	34.896	4.5			
3450	2.600	34.896	5.2	5	5.7	16.40
Station HY2-15 (14°12'S - 13°58'W)						
10	25.882	37.114	3.9	35		
100	20.893	36.529	1.3	32		
301	11.037	35.037	0.7	24		
800	4.411	34.457	1.5	7		
2201	2.861	34.906	0.9	9		
2798	2.652	34.917	1.8	8		
2825	2.632	34.910	1.0	8		
2856	2.615	34.908	1.2	8		
2885	2.616	34.967		8		
2912	2.575	34.920	1.0	10		
2940	2.570	34.907	1.9			
2975	2.556	34.917	2.2	10		
3021	2.544	34.904		10		
3065	2.528	34.882	1.9	11	2.1	7.01
3095	2.516	34.905	2.6			
3155	2.497	34.880	3.7	12	3.4	8.82

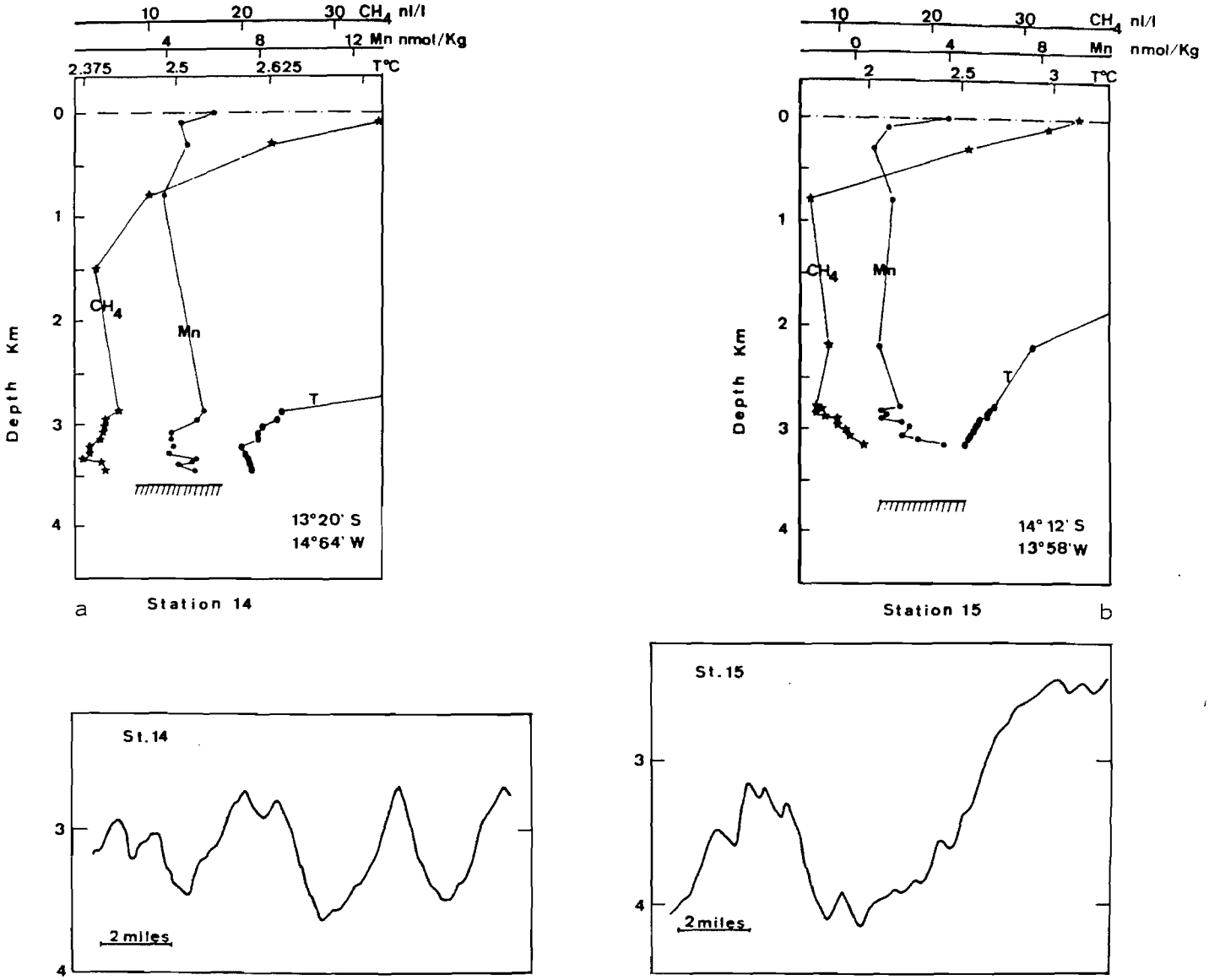

Fig.2 – *Manganese, methane and temperature profiles and bathymetric cross-sections with station locations for (a) station HY2-14 and (b) station HY2-15. The hached lines indicate the bottom depth.* Profils de manganèse, méthane et température, et coupe bathymétrique avec localisation des stations HY2-14 (a) et HY2-15 (b). Les droites hachurées indiquent la profondeur du plancher océanique

KLINKHAMMER (1985a, 1985b) for manganese at the TAG site. Recently, higher amounts of TDM (360 nmol/kg : KLINKHAMMER *et al.*, 1986) and of methane (2400 μcc (STP)/l : CHARLOU *et al.*, 1987) were published in this area with samples taken near the vents, at about 10 meters.

We often observe several anomalies along the same profile. These anomalies must originate from hydrothermal discharges and we may have sampled several different plumes coming from distinct venting sites. This conclusion fit in with TDM and CH_4 concentration profiles, as well as δ^3He values which are consistent with nearby hydrothermal activity. However, our data cannot estimate quantitatively either the importance or the exact location of the hydrothermal inputs.

Tab. 2 – *Analytical results of sea water samples from northern stations HY2-36, HY2-38, HY2-39 (* in situ temperature ; ^4He = helium excess).* Résultats analytiques des échantillons d'eau de mer des stations nord HY2-36, HY2-38 et HY2-39 (* température *in situ* ; ^4He = hélium en excès)

Depth m	Temp.* °C	Salinity g/kg	Mn nmol/kg	CH_4 µcc STP	$\delta\ ^3He$ %	^4He %
Station HY2-36 (12°24'N - 44°05'W)						
1000			1.0	10		
2000			1.8		-2.5	61.00
2159	3.117	35.323	0.7	10	3.1	
2320	2.910	35.316	0.1	16		
2493	2.779	35.314		15	2.8	
2636	2.671	35.314	1.0	12	-2.6	
2823	2.547	35.313	0.1			
2996	2.504	35.315	1.2	15		
3287	2.368	35.310	1.2	25		
3541	2.280	35.306	2.0	44		
3835	2.163	35.299	0.6	35		
3917	2.124	35.296	11.4	24	-7.0	27.32
3999	2.121	35.296	6.4	25	2.0	15.75
4086	2.121	35.296	1.8	24		
Station HY2-38 (13°47'N - 44°59'W)						
800	5.946	35.074		8		
1998	3.220	35.326				
2195	2.923	35.316	3.0	17	-7.4	32.14
2297	2.833	35.314	2.8	15	4.4	
2401	2.780	35.313	2.5	17		
2590	2.668	35.312	1.8	17	-5.2	30.70
2690	2.652	35.313	3.0	15	0.3	27.00
2791	2.608	35.312	2.8	10	2.5	17.19
2902	2.548	35.309	2.5	10		
3097	2.484	35.307	1.0	10		
3222	2.460	35.305	2.2	10		
3276	2.456	35.307	2.0	13		
Station HY2-39 (14°05'N - 45°01'W)						
800			0.1	40		
1500	4.277		1.9	9		
1897	3.423	35.333		11		
1998	3.248	35.328	0.1	10		
2080	3.123	35.326	0.1	12		
2175	2.989	35.322				
2264	2.894	35.320	0.1	17	0.8	24.60
2344	2.847	35.318	1.6	20	-1.9	27.79
2442	2.818	35.319	0.1	20		
2534	2.720	35.316	3.5	15	3.6	22.70
2622	2.686	35.314	3.1	17	4.7	26.10
2715	2.568	35.308	2.4	29		

nmol/kg at ten meters over TAG smokers (KLINKHAMMER *et al.*, 1986). Insufficient number of δ^3He data do not permit to clearly describe the shape and the position of the hydrothermal plume. Therefore, the ^{3}He profile yields similar characteristics in shape than that of GEOSECS station 37 (12°N) which is also characterized by low δ values at 2000 m and 4000 m (−0.1 % and 0.8 %) surrounding a maximum up to 2.7 % and then δ^3He values increase towards the bottom.

Station HY2-38 (fig. 4b)

This hydrographic station is located at the rift valley axis where the sea floor is at 3900 m. As we have shown at station HY2-36, there is a small CH_4 anomaly (17 μcc (STP)/l) at the same depth around 2500 m. It is also correlated with a small temperature anomaly (about +0.02°C). There is no deeper significant CH_4 anomaly observed, only a very small increase of methane concentration (13 μcc (STP)/l) in the last sample located 600 m above the bottom. TDM versus depth profile shows a slight increasing in manganese concentration between 2200 m and 3300 m (2–3 nmol/kg). As at station HY2-36 and correlated with the small CH_4 anomaly around 2500 m, two negative δ^3He values are associated with an intermediate positive value. In the deeper part of the profile, a gradual increase of δ^3He up to +4.4 % is observed.

Station HY2-39 (fig. 5a)

This station is located over a zero age topographic high (14°N) where the maximum depth is 3000 m. Two methane positive anomalies where determined : the first one occurs around 2500 m (maximum CH_4 = 20 μcc (STP)/l), the second at 2800 m reaches 28 μcc (STP)/l in concentration (200 m above the sea floor). Between 2500 m and 2800 m, a distinct TDM anomaly with a maximum concentration of 3.5 nmol/kg is associated with the deepest CH_4 anomaly. δ^3He variations are similar to those of stations HY2-36 and HY2-38. As in station HY2-38, δ^3He values increase with depth up to +4.7 %, associated with the increasing of CH_4 and TDM amounts.

Previous evidence of hydrothermal activity at the Mid-Atlantic Ridge from 10°N to 26°N was substantial : photographic evidence of metalliferous sediments and manganese crusts (RONA, 1985) ; manganese concentration anomalies (KLINKHAMMER, 1985a, 1985b) ; temperature anomalies (LOWELL and RONA, 1976) and ^{3}He/^{4}He anomalies in the water column (JENKINS *et al.*, 1980). The existence of active "Black Smokers" was confirmed (July 1985) by photographs of a vent field on the east wall of the rift valley in the TAG hydrothermal field (KLINKHAMMER, 1985b ; RONA, 1985). This was the first observation of active hydrothermal vents on a slowly spreading ridge.

A quantitative comparison between all profiles shows that both CH_4 and TDM are more enriched in the water column at station HY2-36 (42 μcc (STP)/l ; 11.5 nmol/kg) than at station HY3-39 (28 μcc (STP)/l ; 3.5 nmol/kg). The shape of plume at station HY2-36 located at 12°N suggest that larger amounts of tracers are injected in the ocean water by a most important hydrothermal activity than at station HY2-39 at 14°N over the topographic height of the ridge. If we compare with both KLINKHAMMER' studies of manganese plumes (1985a, 1985b), in another way, we can think that station HY2-36 is not as far from an active vent field as station HY2-39.

Some of our helium measurements show puzzling negative δ^3He values. The helium supersaturation of the samples ranges from 8 % to 60 % with a mean value of 20.9 %. When plotting ^{3}He versus ^{4}He absolute amounts (cf. fig. 6), we can calculate the isotopic ratio of the added helium : R = 0.77 * Ra (Ra = atmospheric ratio). However, contamination of samples with ^{4}He enriched air is not possible for the following reasons :

- the negative δ^3He values are found in samples which were analysed during there was no source of non atmospheric helium on board the ship ;
- possible correction of the δ^3He values by subtracting the helium component above solubility equilibrium for each sample leads to high δ^3He values. On the opposite, the non-corrected values are very close to the GEOSECS values.

We must conclude that hydrothermal helium is injected along the MAR with a clear radiogenic ^4He component originating from the oceanic crust which is known to be enriched in radiogenic ^4He with an $^3He/^4He$ isotopic ratio of 0.1 time the atmospheric ratio or even lower (CRAIG and LUPTON, 1981). This idea is supported by the fact that, in spite of the existence of active "Black Smokers" on the MAR, the Atlantic waters are depleted in ^3He relative to the Pacific Ocean. BROECKER (1980) has shown that eastern basin waters are depleted in ^3He relative to what was expected from hydrographic data. LUPTON (1976) suggested that helium with an isotopic ratio lower than the atmospheric ratio could be added to the eastern basin.

Another striking feature is the correlation between the negative anomalies at stations HY2-36 and HY2-39 and the $^4He/^3He$ anomalies measured in the underlying basalts (STAUDACHER *et al.*, 1989) : at these stations, the helium isotopic composition of the basalt samples show an helium-4 enrichment ($^4He/^3He$ = 110.000) relative to the MORB typical value ($^4He/^3He$ around 85.000).

CONCLUSION

The present work remains exploratory, but we might suggest from the TDM and CH_4 plumes discovered, that there are many active hydrothermal fields along the three studied sections of the MAR, in the southern part as well as in the northern part. The sizes and the shapes of the anomalies vary with the latitude along the spreading ridge. These changes may result from different configurations and depth of the axial rift valley. Furthermore, in the absence of strong anomalies, the hydrographic properties in the vicinity of the MAR has to be better understood to allow a more accurate study of our data. Except for station HY2-36, there is no doubt that we have sampled too far from active hydrothermal sites. Nevertheless, all TDM, CH_4 and helium results are consistent with a wide-spread hydrothermal activity on the Mid-Atlantic Ridge involving a significant crustal contribution. When compared with the results of the East Pacific Rise, the differences can be in part explained by a more rapid ventilation of the Atlantic ocean, but may also reflect significant differences in the hydrothermal circulation patterns of the two ridges.

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