The Genesis of the Methane in Lake Kivu (Central Africa)

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With 12 figures and 3 tables

Zusammenfassung

Im Tiefenwasser des Kivusees sind u. a. große Mengen an Methan und Kohlendioxid gelöst. Während über den hauptsächlich magmatischen Ursprung des Kohlendioxids weitgehend Einigkeit besteht, sind die bisherigen Modellvorstellungen zur Genese des Methans widersprüchlich. Sie beruhen auf zu wenigen und zum Teil zu ungenauen Meßdaten.

Mit Hilfe neuer Meßergebnisse an Gas- und Sedimentproben des Kivusees wurden einige der alten Vorstellungen zu einem neuen Modell weiterentwickelt. Danach ist das Methan hauptsächlich bakteriell aus dem organischen Kohlenstoff des Sediments entstanden. Wahrscheinlich enthält es auch geringe Beimengungen thermokatalytischen Methans.

Der organische Kohlenstoff des oberen Sediments stammt zu rd. 70 % aus dem vorwiegend magmatischen Kohlendioxid („alter" Kohlenstoff), das aus dem Tiefenwasser durch turbulenten Austausch in die Biozone des Sees gelangt und dort assimiliert wird. Die restlichen 30 % stammen aus dem in der Biozone assimilierten atmosphärischen Kohlendioxid („junger" Kohlenstoff). Weil jedoch auch Methan aus tieferen Sedimentschichten in den See wandert, beträgt der ^{14}C-Gehalt des im Seewasser gelösten Methans nicht 30 % modern, sondern nur ca. 10 % modern.

Weitere Isotopenuntersuchungen an Plankton-, Methan-, Kohlendioxid- und Sedimentproben sind notwendig, um das Modell abzusichern.

Abstract

Large amounts of methane and carbon dioxide, among other gases, are dissolved in the deep water of Lake Kivu. There is no dispute about the primarily magmatic origin of the carbon dioxide, but models of the genesis of the methane have been contradictory up to now. They have been based on too few and partly too inaccurate data.

On the basis of new measurements obtained from gas and sediment samples, some of the old concepts have been further developed to a new model. According to this model, the methane is generated mainly by bacteria from the organic carbon of the sediment. It probably also contains minor amounts of thermocatalytic methane.

About 70 % of the organic carbon of the upper sediment is derived from mainly magmatic carbon dioxide ("old" carbon), which enters the biozone of the lake from the deep water by eddy diffusion and is assimilated there. The remaining 30 % comes from atmospheric carbon dioxide ("young" carbon) assimilated in the biozone. But because methane also migrates into the lake from deeper sediment, the ^{14}C-content in the methane dissolved in the lake water is not 30 % modern but only ca. 10 % modern.

More isotopic measurements on plankton, methane, carbon dioxide and sediment samples are necessary to support this model.

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Résumé

De grandes quantités de méthane et d'oxyde carbonique sont dissoutes dans les eaux profondes du Lac Kicu. Alors qu'on est en général d'accord sur l'origine surtout magmatique de l'oxyde carbonique, les modèles devant représenter la genése du méthane sont contradictoires. Ils reposent sur des données trop peu nombreuses et en partie trop inexactes.

A l'aide de nouveaux résultats de mesures faites sur des échantillons de gaz et du sédiment, on a développé un nouveau modèle, à partir des anciennes représentations. D'après celui-ci, le méthane provient pour sa plus grande part du carbone organique du sédiment, transformé par des bactéries. Il contient probablement des traces d'un méthane de thermocatalyse.

Le carbone organique du sédiment supérieur provient pour 70 % de l'oxyde carbonique surtout magmatique (carbone »ancien«), des eaux profondes parvenu, par échanges turbulents, dans la biozone du lac, où l'oxyde carbonique est assimilé. Les 30 % restant proviennent de l'oxyde carbonique atmosphérique (carbone »jeune«) assimilé dans la biozone. Le méthane des couches profondes du sédiment migrant dans le lac, la teneur en ^{14}C de méthane dissous dans les eaux du lac n'est pas de 30 % modernes, mais de 10 % modernes.

D'autres recherches sur les isotopes d'échantillons du plancton, du méthane, de l'oxyde carbonique et du sédiment du Lac Kivu seront nécessaires pour confirmer ce modéle.

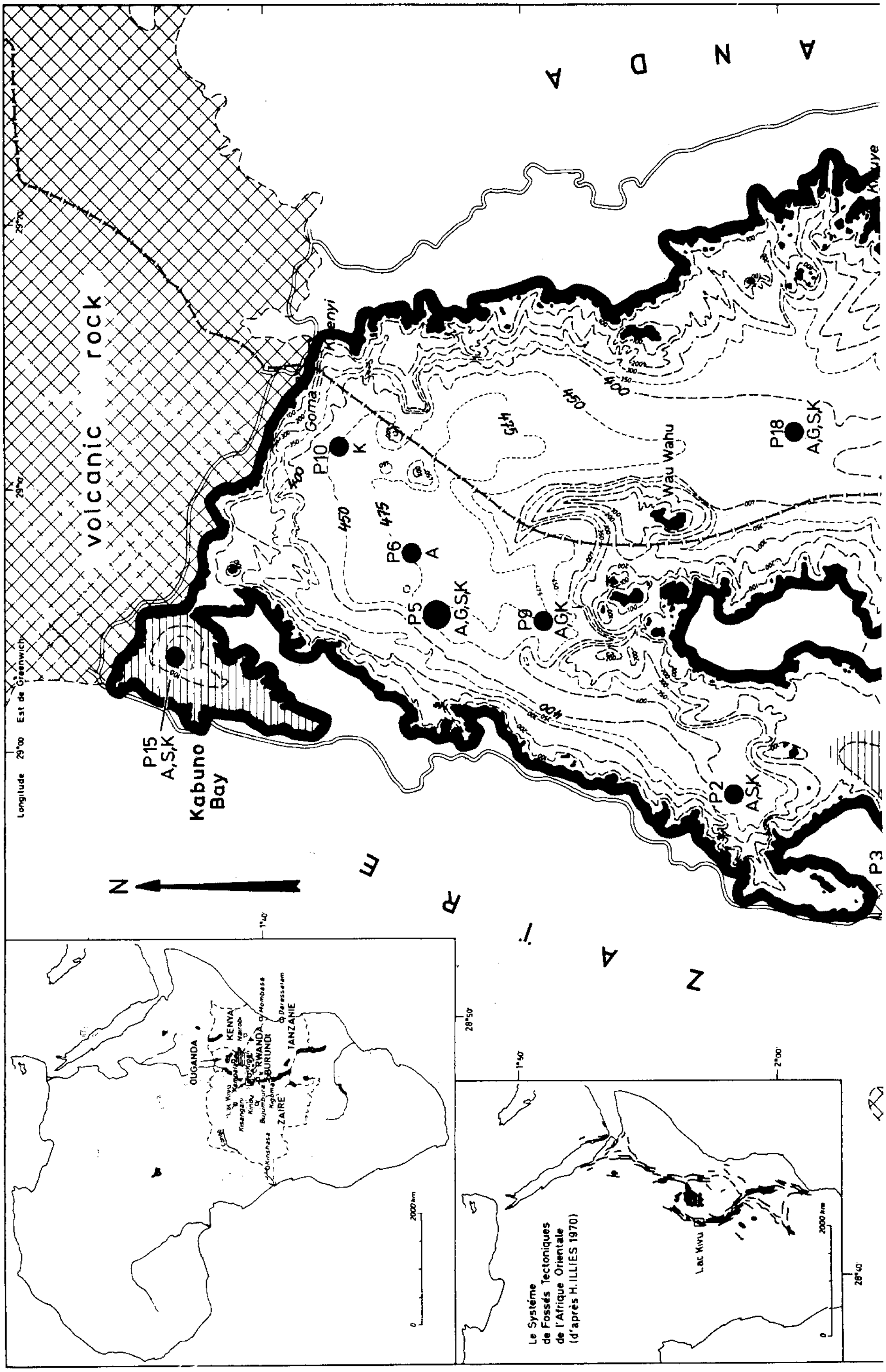
Краткое содержание

В глубинной воде озера Киву растворены между прочим большие количества метана и углекислого газа. В то время как имеется широкое единство мнений о том, что углекислый газ обладает в основном магматическим происхождением, существовавшие до сих пор модельные представления о генезисе метана противоречивы в связи со слишком немногими и частично слишком неточными данными измерений.

При помощи новых резулватов, полученных при измерении образцов газа и осадка озера Киву, некоторые из древних представлений развились дальше к новой модели. Согласно этой модели метан образовался главным образом бактериально из органического углерода осадка. Вероятно он содержит и малые количества примесей метана, образовавшегося путем термического катализа.

Около 70 % органического углерода верхней части осадка происходит от преимущественно магматического углекислого газа („древний" углерод), который турбулентным обменом из глубоинной воды попадает в биозону озера, где он ассимилируется. Остальные 30 % происходит от ассимлированной в биозоне атмосферного углекислого газа („молодой" углерод). Однако, так как и метан из относительно глубоких осадочных слоев мигрирует в озеро, содержание ^{14}C растворенного в озерной воде метана составляет не 30 % modern, но только около 10 % modern.

Для подтверждения модели необходимо произвести дальнейшие изотопные исследования образцов планктона, метана, углекислого газа и осадка.


volcanic rock
Longitude 29°00 Est de Greenwich
Kabuno Bay
P15 A,S,K
Goma
P10 K
P6 A
P5 A,G,S,K
P9 AGK
Wau Wahu
P18 A,G,S,K
P2 A,SK
P3
RWANDA
ZAIRE
N
OUGANDA
KENYA
RWANDA
BURUNDI
TANZANIE
ZAIRE
Le Système de Fossés Tectoniques de l'Afrique Orientale (d'après H. ILLIES 1970)
Lac Kivu

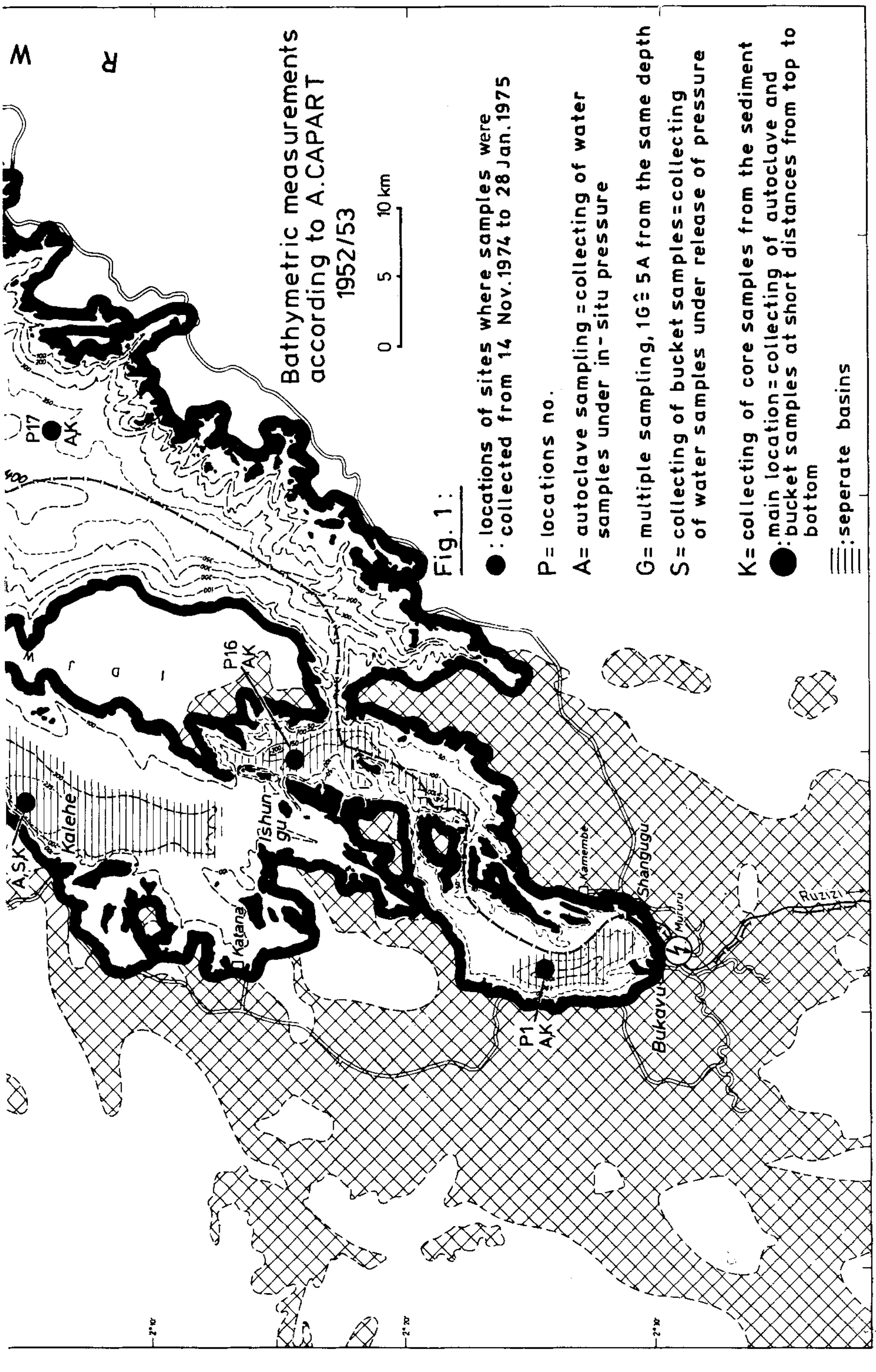


Fig. 1: Lake Kivu with locations of the sites where samples were collected.

Table 1: Models for the Generation of Methane in Lake Kivu.

Origin	Main arguments pro	valid yes	valid no	Main arguments contra	valid yes	valid no
Bacterial; generation from the organic carbon in the sediment; SCHMITZ & KUFFERATH, 1955.	Composition of the gas from mud near the shore;	?		$\delta^{13}C_1$=-45 ^{0}/oo at depths > 250 m in the main basin (DEUSER et al., 1973);		x
	comparison of the proportions of carbon, nitrogen, phosphorous, and sulfur in small organisms in the biozone with the proportions of these elements dissolved in the deep parts of the lake.	?		not enough phosphorous in the water or in the top 12 m of sediment (DEUSER et al.,1973);		x
				not enough organic carbon in the top 30 cm of sediment (≈ 1000 years of sedimentation, DEUSER et al., 1973);		x
				not valid because: the $\delta^{13}C_1$-value for the main basin is in general not -45^0/oo, but -58^0/oo (this paper); the phosphorous can remain mainly in the biomass of the biozone by rapid bacterial decomposition and assimilation from newly dead organisms; the methane could also come from depths greater than 30 cm in the sediment; the organic carbon on the top of the sediment could be rapidly converted to methane and carbon dioxide ;		
Magmatic; BURKE & MUELLER, 1963.	Active volcanoes in the area;		x	The volcanic gases of the neighboring volcanoe Nyiragongo do not contain methane (TAZIEFF, 1963);	x	
	only traces of gas are dissolved in Lake Tanganyika, which is some distance away;		x	thermal water from springs near Lake Kivu does not contain methane (DEUSER et al.,1973);	x	
	the H/C, O/H, and H/C : O/H ratios of the gases are quite similar to those for Thucholithes.		?	the distribution of higher hydrocarbons in the gas as a function of depth corresponds to that of the methane (this paper).	x	

Bacterial; generation to ca. 80% directly from magmatic corbon dioxide and hydrogen; generation of the remaining 20% from organic carbon in the sediment; DEUSER et al., 1973.	$\delta^{13}C_1$ = -45 $^o/oo$ at depths >250 m in the main basin; hydrogen is present in the volcanic gases; hydrogen is released in the formation of heavy metal sulfides.		x ? ?	The $\delta^{13}C_1$ value in the main basin is in general not -45 $^o/oo$, but -58 $^o/oo$ (this paper); only minor traces of H_2 were measured in the gas samples (this paper).	x x	
Thermocatalytic; STAHL, 1975.	$\delta^{13}C_1$ = -45 $^o/oo$ at depths >250 m in the main basin (measured by DEUSER et al., 1973).		x	The $\delta^{13}C_1$ value in the main basin is in general not -45 $^o/oo$, but -58 $^o/oo$ (this paper).	x	
Bacterial with small amounts of thermocatalytic methane; generation from the organic carbon in the sediment. About 70% of the organic carbon of the upper sediment is derived from primarily magmatic carbon dioxide ("old" carbon) which enters the biozone of the lake from the deep water by eddy diffusion and is assimilated there. The remaining 30% comes from atmospheric carbon dioxide ("young" carbon) assimilated in the biozone. But because methane also migrates into the lake from deeper sediment, the ^{14}C-content in the methane dissolved in the lake water is not 30% modern but only ca. 10% modern (this paper).	$\delta^{13}C_1$ = -58 $^o/oo$ in the main basin; the distribution of higher hydrocarbons as a function of depth corresponds to that for methane; the conventional ^{14}C-age of the methane is greater than 17 000 years; the conventional ^{14}C-age of the top layer of the sediment in the main basin is 11 000 years; analysis of the pollen in the same samples yield to a "historical" age of 1 000 years; maximum of the n-alkane distribution curve for the sediment samples is at C_{23}.					

$$\delta^{13}C = \frac{R_{(sample)} - R_{(standard)}}{R_{(standard)}} \cdot 1000\ ^o/oo,$$ where R is the isotope ratio $^{13}C/^{12}C$, $C_1 = CH_4$, $C_2 = C_2H_6$.

standard see CRAIG, 1957.

Introduction

Lake Kivu is situated within the western branch of the East African rift zone. It consists of a main basin and four smaller basins (the Bukavu, Ishungu and Kalehe basins and Kabuno Bay, see Fig. 1), which are separated from the main basin by submarine rises. The total water surface of the lake is about 2400 km^2, the maximum depth is 485 m and the total water volume ca. 580 km^3. *)

A unique phenomenon of great scientific and economic interest are the large quantities of methane and other gases, physically dissolved in the deep water of this lake (discovered by DAMAS, 1937). The total amount of methane available is about $63 \cdot 10^9$ m^3 **) (TIETZE, 1978). The deposit is contained by a stable density stratification of the lake water.

Anaerobic conditions prevail at different depths in the various basins. The biozones in the main basin, the Ishungu and Kalehe basins reach depths of about 50 m. The biozone in Kabuno Bay reaches depths of only ca. 12 m and the water in the Bukavu basin is mixed down to the bottom at depths of about 100 m because there is no permanent stratification in this basin (TIETZE, 1978).

The models of the genesis of the methane (SCHMITZ & KUFFERATH, 1955; BURKE & MÜLLER, 1963; DEUSER et al., 1973; STAHL, 1975) that have been developed are contradictory as they are based on too few and partly too inaccurate data (see Table 1).

New data

At the end of 1974 and beginning of 1975, a measuring campaign was started on Lake Kivu with the major objective to acquire basic data for the development of the methane deposit. Various parameters of the lake water were systematically measured in-situ at 30 locations (41 profile measurements) distributed over the entire lake. These parameters were the density, conductivity, temperature and pressure. Additionally, 185 water and gas samples as well as 12 sediment samples were taken at 11 locations. They were analysed in the laboratory for the concentrations of tritium, deuterium, oxygen-18, and the various gases physically dissolved in the lake. (TIETZE, 1978). Apart from the above-mentioned measurements, a number of investigations were carried out as listed in Table 2.

Table 2: Investigations of the samples.

method	applied to
$\delta^{13}C$-measurements	methane, ethane, carbon dioxide, organic carbon in sediment
^{14}C-age determinations	methane, organic carbon in sediment
palynological investigations	sediment
organic-geochemical analyses	sediment

*) calculated according to a topographic map compiled by IRSAC in 1959; bathymetric measurements by CAPART (1952/53).
**) m^3 at STP (0 °C, 101 325 Pa).

The locations of the sites where the samples were collected are shown in Fig. 1. The new data obtained make it possible to further develop some of the old concepts about the genesis of the methane to a new model.

As it was the main objective of the survey to achieve the basic knowledge necessary for the development of the deposit (TIETZE & MAIER-REIMER, 1977), the problem of the genesis of the methane could not be dealt with as intensively as desired. Therefore, in order to clear up certain important details, very specific follow-up investigations would have to be carried out (see below).

The data from the investigations mentioned in Table 2 are presented in Figs. 4—8 and in Table 3.

The Figs. 2 and 3 show the concentrations of the most important gases dissolved in the water of Lake Kivu as a function of depth. The distribution of ethane, propane, and butane was also measured. The concentrations of these gases amount only to 0.03 to 1 per mill of the methane; it is, however, obvious that their depth distribution correspondes to that of the methane (see TIETZE, 1978). Hydrogen was only found in even smaller traces.

Carbon isotope ratios for methane, ethane and carbon dioxide are presented in Figs. 4—7; Fig. 8 shows the ^{14}C-age data for methane and the upper sediment in the main basin and in Kabuno Bay (see also Table 3).

Table 3: ^{14}C-ages and $\delta^{13}C$-data of the organic carbon from sediment samples.

basin	Location	part of core [cm]	$\delta^{13}C$ [o/oo]	conventional ^{14}C-age [years B.P.]
main basin	5	0-15	-23.0	11 270 ± 280
	9	0-20	-18.6	10 360 ± 260
		50-70	-22.6	11 190 ± 280
	18	0-20	-25.5	9 830 ± 250
		60-70	-17.5	11 810 ± 340
Kabuno Bay	15	0-20	-21.5	3 320 ± 260
		60-85	-19.5	3 440 ± 180

Discussion

The data from the investigations mentioned above are discussed in the following (see also Figs. 9—11):

a) The $\delta^{13}C_1$-values for the main basin (mean value — 58 ‰, see Fig. 4) correspond to the range of bacterially generated gases on the maturation line for natural gases (STAHL, 1975; see Fig. 9).

The lower value from Kabuno Bay (see Fig. 5) is also within the range of bacterially generated gases. The higher value from this basin is — 45 ‰ and no longer on the maturation line. This value becomes explicable if one considers that this sample was taken from the transition zone to the biozone of Kabuno Bay.

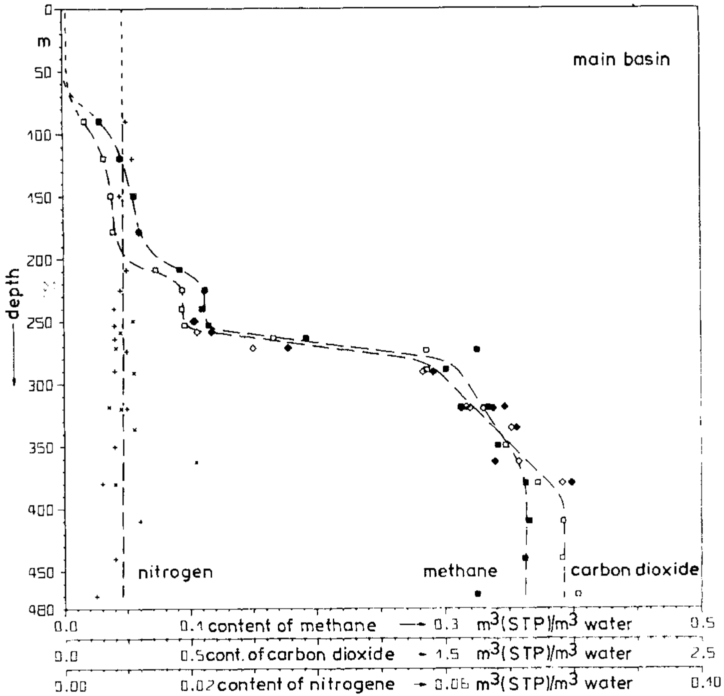


Fig. 2: Quantities of methane [■ ◆], carbon dioxide [□ ◇], and nitrogen [+ ×] contained in physically dissolved gas vs depth in the main basin (location 5 ■ □ +, other locations ◆ ◇ ×, —— best-fit curve, - - - extrapolation of best-fit curve). Samples collected from 14 November 1974 to 28 January 1975

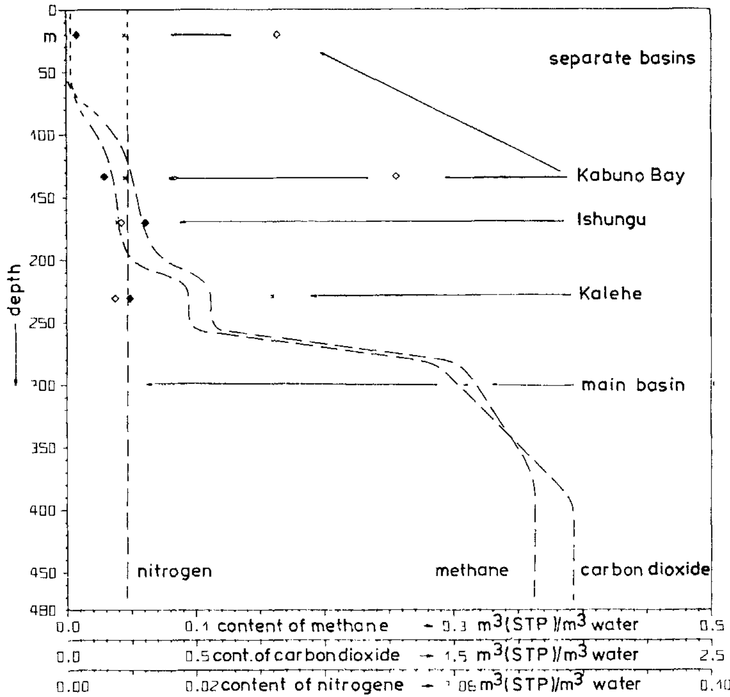


Fig. 3 Quantities of methane [◆], carbon dioxide [◇] and nitrogen [×] contained in physically dissolved gas vs depth in the separate basins of the Kabuno Bay, Ishungu and Kalehe The best-fit curves for the main basin are shown for comparison. Samples collected from 14 November 1974 to 28 January 1975

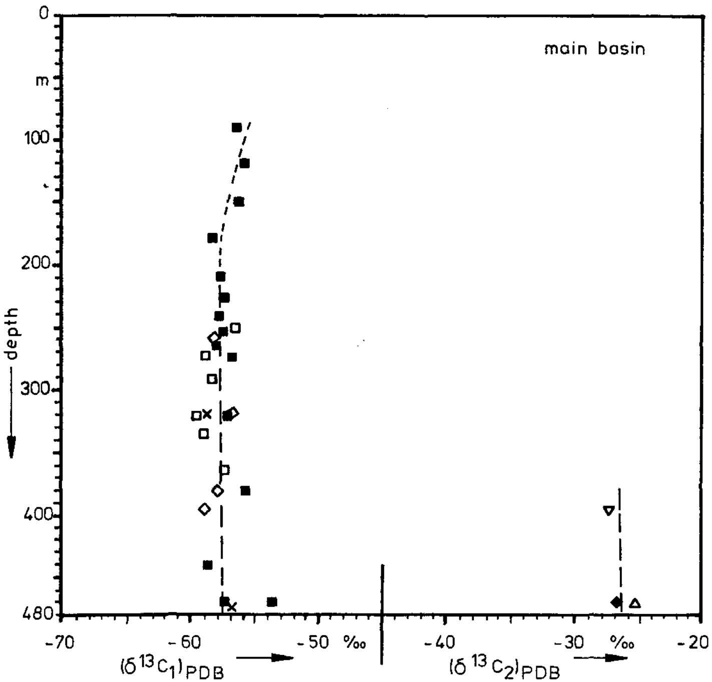


Fig. 4: Carbon-isotope ratios of methane[$(\delta^{13}C_1)_{PDB}$, ■, □, ◇, x] and ethane [$(\delta^{13}C_2)_{PDB}$, ◆, ▽, △] from the main basin vs. depth (■, ◆ = location 5; □, ◇, X, ▽, △ = other locations — — — = best-fit curve, - - - - - = extrapolation of best-fit curve).

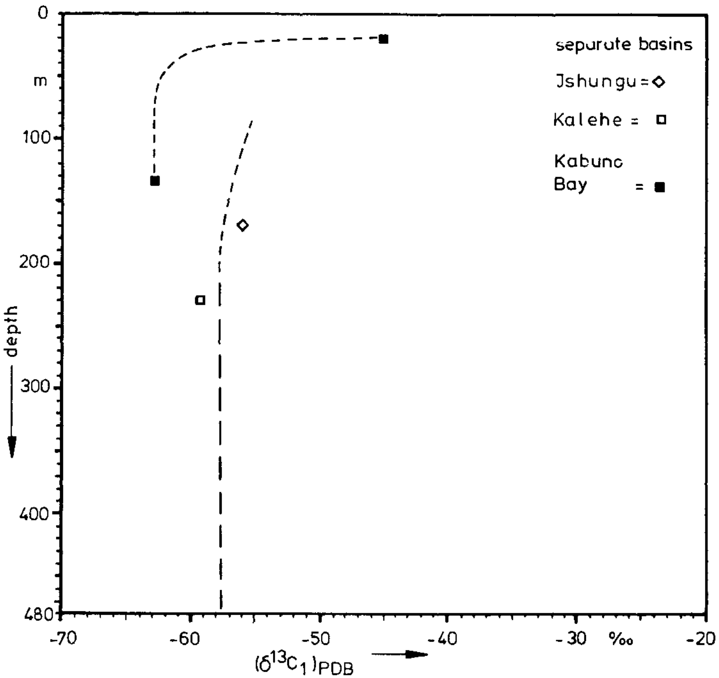


Fig. 5: Carbon-isotope ratios of methane $(\delta^{13}C_1)_{PDB}$ from the separate basins of Ishungu (◇), Kalehe (□), and the Kabuno Bay (■) vs. depth (estimated course of the curve = - - - - -). The best-fit curve from the main basin is shown for comparison (— —, - - -).

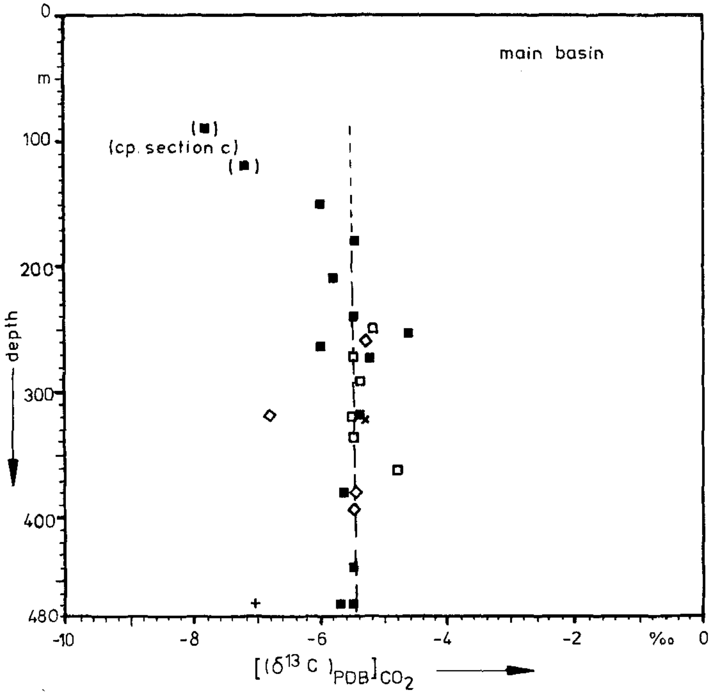


Fig. 6: Carbon-isotope ratios of carbon dioxide from the main basin vs. depth. (■ = location 5; □, ◇, +, × = other locations, — — — = best-fit curve, - - - - = extrapolation curve).

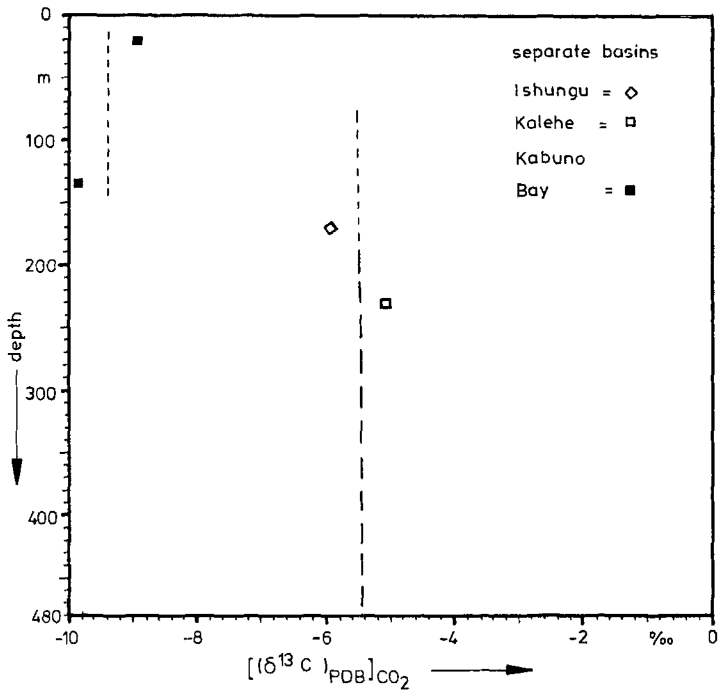


Fig. 7: Carbon-isotope ratios of carbon dioxide from the separate basins of Ishungu (◇), Kalehe (□) and Kabuno Bay (■) vs. depth. The best-fit curve from the main basin is shown for comparison.

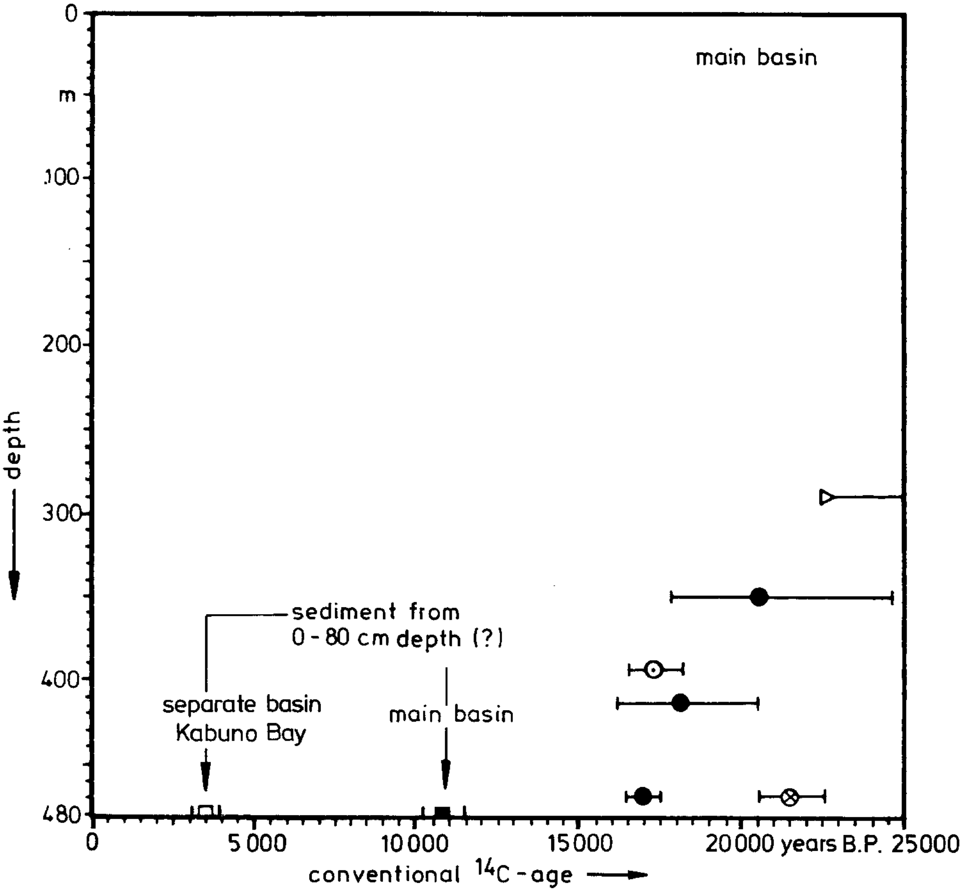


Fig. 8 · Conventional ^{14}C-age (⊢●⊣ ⊢⊙⊣ ⊢⊗⊣)
of methane from the main basin vs. depth
(⊢●⊣ = location 5, ⊢⊗⊣ = location 9, ⊢⊙⊣ = location 18,
▷—— = greater than, ⊢—⊣ = standard deviation) and from
sediment samples from the main basin ⊢■⊣
and the separate basin Kabuno Bay ⊢□⊣.

Here, oxidation processes are to be expected. According to LEBEDEW et al. (1969), $\delta^{13}C_1$-values can be increased by oxidation processes. *)

b) The mean $\delta^{13}C$-value for the organic carbon in the upper sediment (see Table 3) is ca. — 21 ‰. This value is normal for most sediments as is $\delta^{13}C_1$ = — 58 ‰ normal for methane generated bacterially in sediments.

c) Magmatic carbon dioxide is characterised by $\delta^{13}C$-values of about — 4 ‰ to — 10 ‰ (see STAHL, SCHOELL & WENDT, 1973, p. 111). The δ-values for carbon dioxide from Lake Kivu are within the same range (see Fig. 6 and 7). **)

It may be pointed out that the $\delta^{13}C$-values for atmospheric and carbonatic carbon dioxide correspond to those of magmatic carbon dioxide. This is important, because these three types of carbon dioxide are, via assimilation in the biozone, the source for the organic carbon in the sediment of Lake Kivu (see Table 1, column "Origin", point 5).

d) In Lake Kivu, up to 200 ppm of gaseous hydrocarbons higher than methane were found (see TIETZE, 1978). According to FUEX (1977) bacterial gases contain only 20 ppm higher hydrocarbons at a maximum; thermocatalytic gases, however, contain in general considerably more. From this it can be derived that the Lake Kivu gas has small amounts of thermocatalytic ***) methane in addition to the bacterial methane. According to WEBER & MAXIMOV (1976) however, large quantities of higher hydrocarbons can also be generated bacterially in early stages of diagenesis in sediments.

e) The nitrogen content of the lake water is the same at all depths. It corresponds to the nitrogen content at the surface of the lake calculated according to Henry's Law from the partial pressure of nitrogen in the air (saturation value at atmospheric pressure, see Fig. 2). From this it could be concluded that the nitrogen was dissolved at atmospheric pressure in groundwater which later enters the lake warm and mineralised at the bottom (about hydrothermal activity in Lake Kivu see DEGENS & KULBICKI, 1973 and TIETZE, 1978).

f) Organic-geochemical studies on sediment samples reveal a distinct majority of n-alkanes with an odd number of carbon atoms, a phenomenon typical for young non-marine sediments. The maximum of the n-alkane distribution curve is C_{23}. From this it can be concluded that the hydrocarbons are derived primarily from plankton. As these studies showed, a minor part was also contributed by terrestrial plants. According to these investigations, the bacterial transformation of the organic material has not yet made much progress.

g) Palynological studies confirm these results by furnishing evidence of animal

*) In the main basin, there are also indications of such an effect above a depth of 170 m (see Fig. 4, extrapolation of the best-fit curve). There is, however, practically no oxidation below a depth of 50 m in the main basin and below a depth of 12 m in Kabuno Bay. But there may be a zone of intermediate $\delta^{13}C$-values caused by eddy diffusion between deep water and the biozones, which begin at these depths.

**) The $\delta^{13}C$-values in Fig. 6 for depths less than 170 m are below the extrapolated best-fit line. This is probably due to an isotope separation during the degasing (at $8.5 \cdot 10^4$ Pa, 25 °C), since more than half of the carbon dioxide remains dissolved in the water if the samples are taken at depths of less than 200 m and this contains to a large extent the molecules with the heavier isotopes.

***) According to HOW-KIN WONG & VON HERZEN (1974), the maximum sedimentary thickness amounts to about 500 m; due to the proximity of active volcanoes it is possible that the temperatures necessary for thermocatalysis occur here.

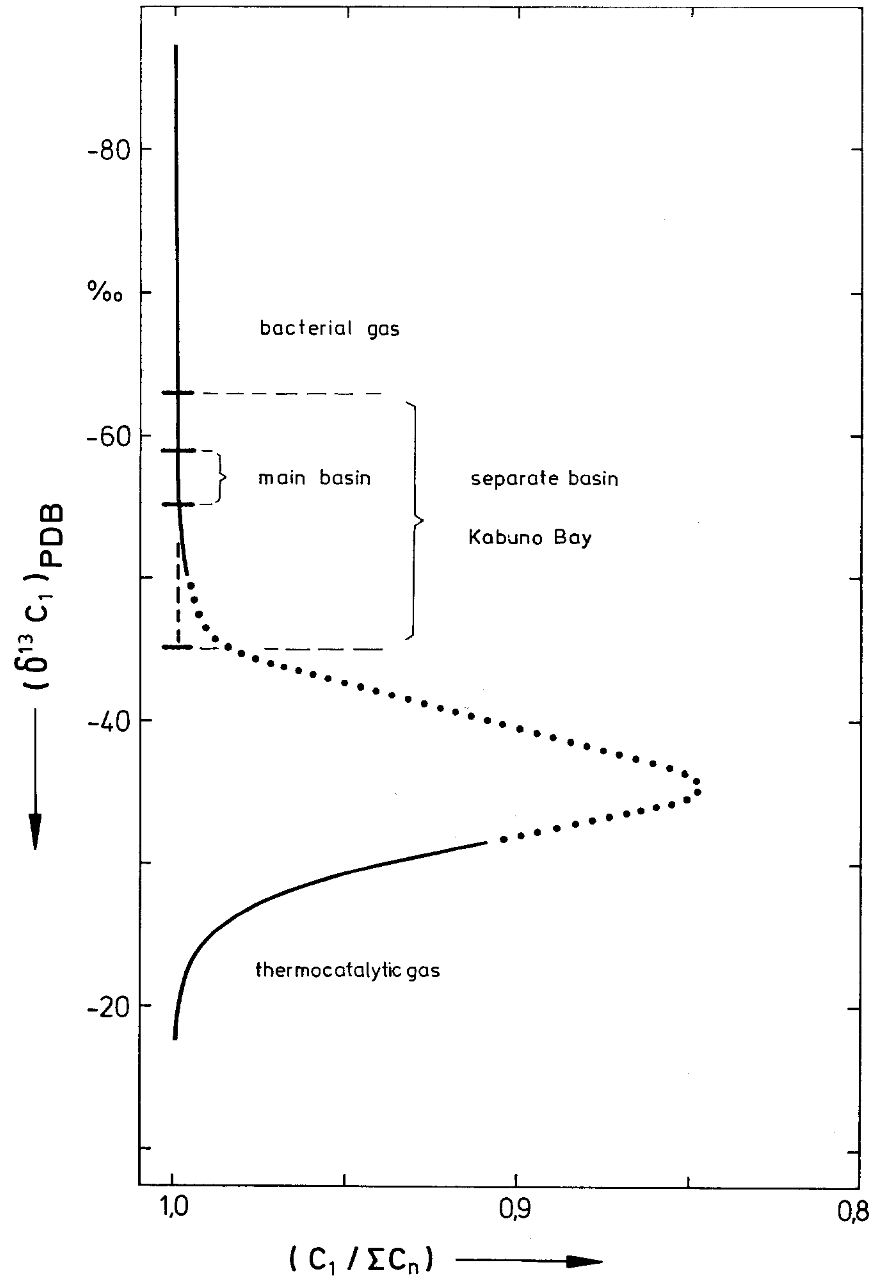


Fig. 9 : Maturation line for natural gases from a terrestrial milieu according to STAHL (1975) with $\delta^{13}C_1$ - values from the main basin and the separate basin Kabuno Bay of Lake Kivu. (The dotted part of the curve has not been verified).

and plant micro-remains. The animal micro-remains consist only of limnic species, predominantly of Cladocera. Some of the samples are rich in planktonic diatoms and volcanic ash particles. The percentage of algal cell walls in the structured microfossil remains is very high, whereas micro-remains of terrestrial plants occur only to an extent of less than one per cent.

h) The conventional ^{14}C-ages of the methane samples are greater than 17 000 years B. P. (see Fig. 8). Whether they decrease with depth as it appears in Fig. 8, cannot be seen from the data; the standard deviations, which are due to insufficient quantities of methane, are too great.

The organic portion of the sediment samples from the main basin yielded conventional ^{14}C-ages of about 11 000 years B. P. (see also Table 3). It is not quite sure whether the samples were collected directly from the sediment surface, as the coring device might have penetrated the sediment more deeply. A disk that was placed around the corer should have prevented this, however.

Analyses of the pollen in the samples have shown a "historical" age of either about 1000 or about 10 000 years. This can be derived from the comparison with pollen spectra from Lake Victoria (KENDALL, 1969).

If the "historical" age of the sediment samples is really 1000 years, the organisms of the biozone which later formed part of the sediment have partly "old" carbon (in terms of its ^{14}C-age) in their cellular material. From the relationship between the "historical" age and the conventional ^{14}C-age, it can be derived that "old" carbon makes up about 70 % of the carbon in the upper sediment. *) The difference between the ^{14}C-age of the methane in the water and that of organic material in the upper sediment could be explained by assuming, that the methane comes not only from the upper sediment, but also from deeper parts.

The "old" carbon in the upper sediment originates from the assimilation of magmatic carbon dioxide which passes from deep water into the biozone of the lake by eddy diffusion and double-diffusive convection (see TIETZE, 1978). The remaining 30 %, which is "young" carbon, originates from the assimilation of atmosheric carbon dioxide. It may be noted that the quantity of physically dissolved carbon dioxide which enters the biozone of the main basin from deep water is about $6 \cdot 10^8$ m³ per year (ca. 5 times the quantity of methane, see JANNASCH, 1975). The total amount of physically dissolved carbon dioxide in the biozone has been estimated to be $1.7 \cdot 10^9$ m³. The comparison of these data show that the mainly magmatic carbon dioxide which enters the biozone from deep water may play an important role as carbon source for the organisms in the biozone.

If the "historical" age of the sediment samples is 10 000 years, this would mean that the coring device collected a sediment sample from several meters depth and that the conventional ^{14}C-age is correct. The same would also have to be true for the ^{14}C-age of the methane (see Fig. 8), which is, however, contradictory to the fact that the residence time of the methane in the water is about 400 years (JANNASCH, 1975).

There is yet another indication for the first interpretation. The conventional

*) This could also explain why HEKY & DEGENS (1973) obtained ^{14}C-ages of 9500—13 500 years B. P. for 13 cores from Lake Kivu (except for one core with an ^{14}C-age of 6200 years B. P.). They interpreted this as due to loss of the top of the cores and set up a ^{14}C-age-scale based on an interpolation of these data.

^{14}C-age of the organic fraction of a sediment sample from Kabuno Bay is ca. 3400 years B. P. and thus considerably less than the conventional ^{14}C-age of about 11 000 years B. P. of the organic fraction of the three sediment samples from the main basin (see Fig. 8 and Table 3). However, all of the sediment samples have almost the same pollen spectrum. Therefore the "historical" age of about 1000 years for the sediment samples is considered to be correct.

The lower conventional ^{14}C-age of the sediment from Kabuno Bay is explainable since the first density gradient below 12 m is 50 times greater in Kabuno Bay than the comparable density gradient in the main basin below 50 m (TIETZE, 1978). Consequently, there is less eddy diffusion and therefore less transport of magmatic carbon dioxide into the biozone of Kabuno Bay than into those of the main basin. Compared with this fact, the concentration of carbon dioxide directly below the biozone in Kabuno Bay, which is 10 times greather than that in the main basin directly below the biozone (see Fig. 2 and 3), does not seem to be so important.

For these reasons the quantity of magmatic CO_2 absorbed by the organisms of the biozone of Kabuno Bay should be lower than in the main basin. Accordingly, the percentage of "old" carbon in the upper sediment of Kabuno Bay is only 25 %, corresponding to the relationship between the "historial" age and the conventional ^{14}C-age.

i) Previous and recent measurements of the methane and the carbon dioxide content are compared in Figs. 10 and 11. DEUSER et al. (1973) assumed that there had been an increase in the methane content in Lake Kivu due to the fact that the measurements from DEGENS et al. (1973) deviated from those made by SCHMITZ & KUFFERATH (1955). However, the new data presented here agree well within the margin of error (± 5 %) with those of SCHMITZ & KUFFERATH (1955). According to the concept developed here, the lake is, with the exception of minor disturbances, in a quasi-stationary stage. Probably as much methane escapes through eddy diffusion and double-diffuse convection into the biozone as passes from the sediment into the water. JANNASCH (1975) investigated the oxidation of methane in the layers above 50 m depth. He estimates the annual loss of methane from the lake to amount to 120 million m³. Accordingly, the methane contained in the lake would be completely replaced within about 400 years.

The bacterial generation of methane does not, of course, apply only to Lake Kivu. Similar processes, except the source of the carbon, can take place in any other lake with anaerobic conditions in deep water. But no methane accumulation comparable to that of Lake Kivu has been found in any other lake.

These large methane quantities have been able to accumulate in Lake Kivu because of the presence of distinct, density layers over a long period of time. On the one hand, the density stratification has prevented an intermixing of the lake water, and on the other hand, it has suppressed the eddy diffusion sufficiently for an accumulation of the methane. In many other lakes, however, an intermixing of the lake water down to the lake bottom takes place in an annual cycle, so that any accumulated gas escapes. In other cases, the density gradients may be large enough to prevent an intermixing down to the bottom of the lake, but not strong enough to sufficiently suppress eddy diffusion through the density layers. If the potential turbulent transport rate of methane is greater than its rate of generation in the sediment, only minor quantities of methane will be present in the deep water.

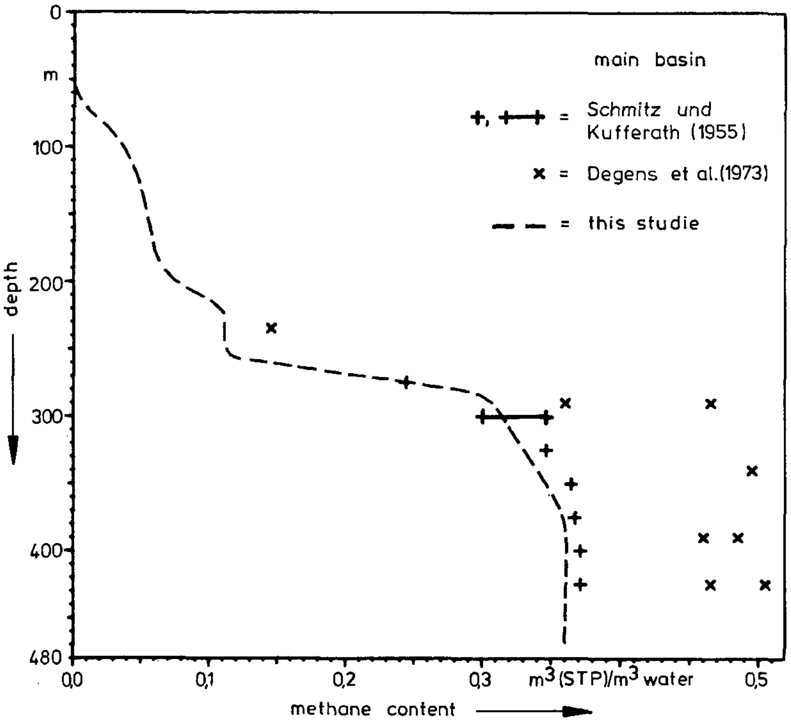


Fig. 10 : Comparison of previous measurements of the methane content in Lake Kívu (+—+ ≙ 10 samples) with those of this study.

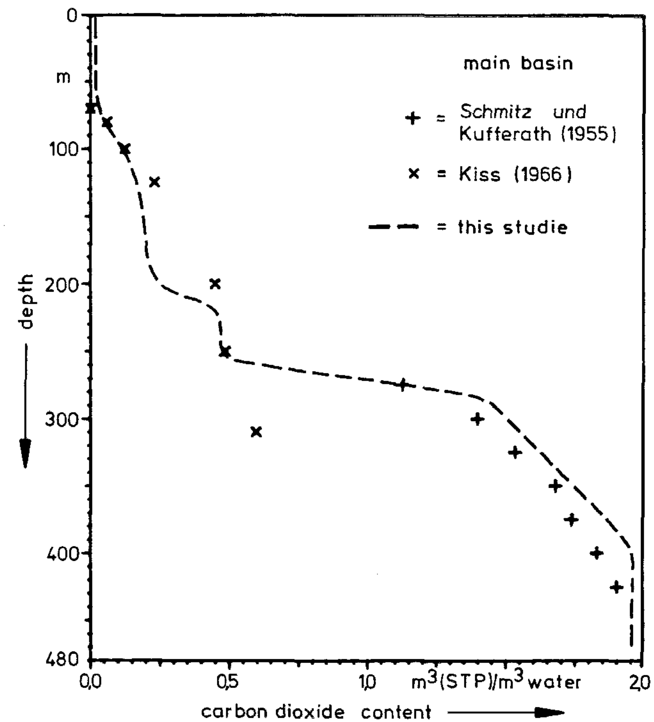


Fig. 11 : Comparison of previous measurements of the physically dissolved quantities of carbon dioxide in Lake Kivu with those of this study (+ =degased amounts corrected to total physically dissolved carbon dioxide).

Conclusion

The overview of the results presented here leads to the assumption that the methane is generated for the most part bacterially from the organic material in the sediment. It probably contains minor amounts of methane of thermocatalytic origin, also from the sediment. The methane is slowly transported through the layers of water by eddy diffusion and double-diffusive convection together with other soluble matter and heat (see TIETZE, 1978). Most of this methane is probably oxidized to carbon dioxide and water in the biozone. The deposit is very likly in a state of dynamic equilibrium, i. e. as much methane passes from the sediment into the water as is oxidized in the biozone.

The carbon dioxide, or at least the carbon of the carbon dioxide, is probably for the most part of magmatic origin. Part of it is assumed to originate from carbonates, and another part generated bacterially from the organic material of the sediment. The nitrogen probably originates from the atmosphere.

The carbon dioxide is transported through the layers of water just like the methane until it also passes into the biozone. There it is available, together with carbon dioxide from the atmosphere and from the oxidation of methane for incorporation by the organisms of the biozone. After dying, the organisms sink to the bottom of the lake. There, they are decomposed primarily bacterially to methane and carbon dioxide via various chains of reactions. Apart from the organic material produced in the lake, carbon compounds from terrestrial plants blown in by wind or washed in by streams are also transformed to methane (less than 1 %); their carbon content is also from atmospheric carbon dioxide.

The carbon of the methane has, therefore, a conventional ^{14}C-age which depends on the mixing ratio of "old" carbon, originating from magmatic and carbonatic carbon dioxide, with "young" carbon, originating from atmospheric carbon dioxide. According to the model presented here, in the main basin the portion of "old" carbon in the upper part of the sediment is about 70 % and that of "young" carbon is ca. 30 % (about 25 % and 75 % respectively in Kabuno Bay). Due to the difference between the ^{14}C-ages of the upper sediment and the methane (see Fig. 8), it is assumed that the methane comes not only from the upper part of the sediment, but also from deeper parts. Therefore, the ^{14}C-content in the methane is not 30 % modern but only ca. 10 % modern.

This concept (see Fig. 12) has been confirmed to a large extent by the above-mentioned data. The follow-up investigations listed below on samples to be taken from profiles would be required to finally clarify the process:

determinations of ^{14}C-age of

— plankton from the biozone,
— carbon dioxide, especially from the biozone, and
— methane, using large quantities of methane in order to keep the margin of error small;

determinations of $\delta^{13}C$ for

— plankton from the biozone and
— methane and carbon dioxide at depths of less than 90 m, especially from the biozone;

determinations of δD for methane, and

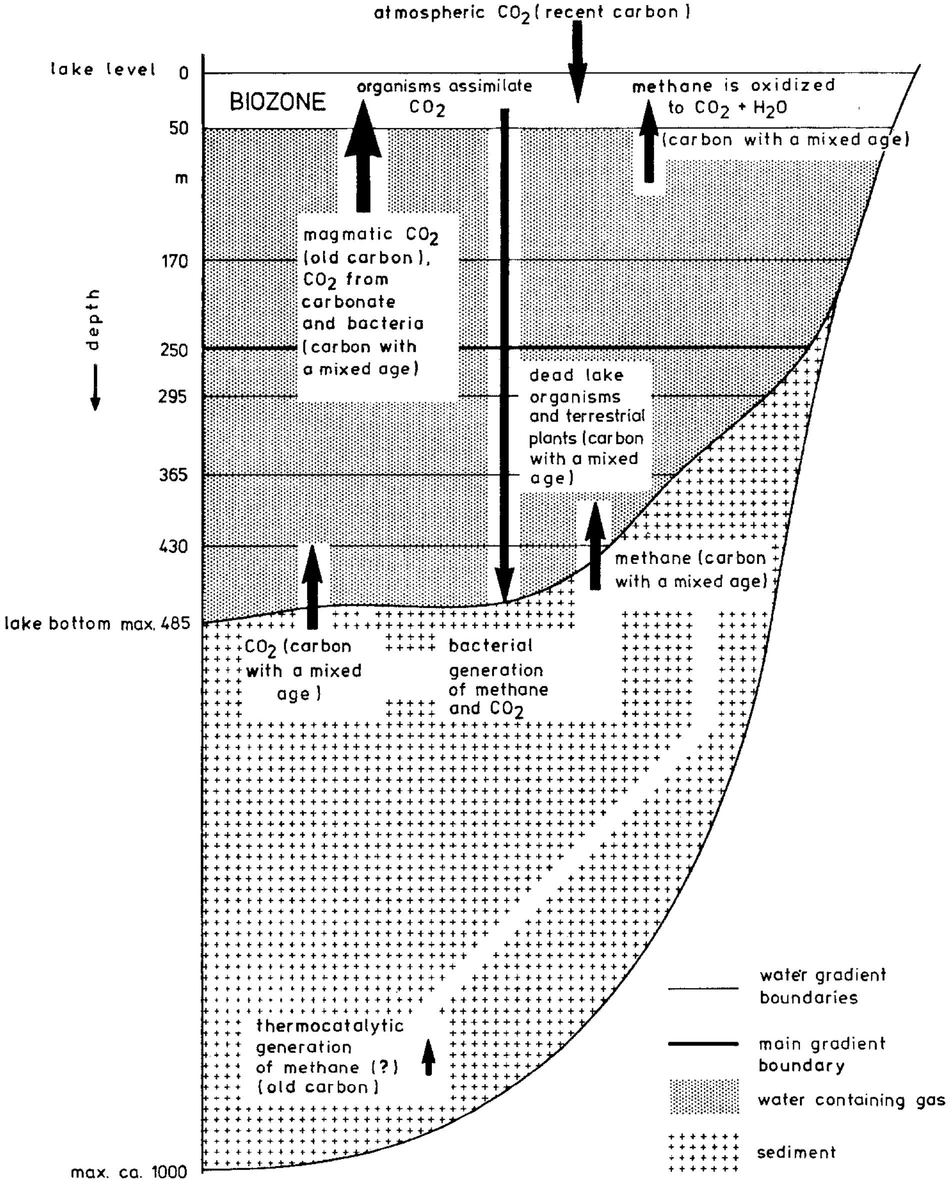


Fig. 12: Model for methane generation in Lake Kivu

determinations of ^{14}C-age and $\delta^{13}C$ for sediment samples for which there is no doubt that they were collected at the sediment surface. Additionally these determinations should be made on long cores which reach as deep as possible from the sediment surface.

These investigations must be carried out before the development of the methane deposit begins. There may be little time left.

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