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ORIGIN OF METHANE IN LAKE KIVU (EAST-CENTRAL AFRICA)

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Abstract

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The isotopic composition of Lake Kivu methane ($\delta^{13}C = -58‰$, $\delta D = -218‰$) and its ^{14}C activity can be explained by the simultaneous formation of methane through fermentation and CO_2 reduction. Culture experiments with Lake Kivu sediments were only successful for acetic acid fermenting *Sarcina*-type bacteria. The methane produced in deuterated water equivalent to Lake Kivu water had a $\delta^{13}C$- and δD-value of $-45‰$ and $-316‰$, respectively. Using the culture data as being representative for the fermentation-derived methane, it can be calculated that approximately one-third of the methane in Lake Kivu is derived from an acetate fermentation process and two-thirds from a CO_2-reducing bacterial process which uses the dissolved CO_2 in the lake water as a source. This dual bacterial origin satisfactorily explains the lower ^{14}C activity in the methane compared to the sediment. He enriched in ^3He and CO_2 which are also found in the dissolved gases are most likely of magmatic origin. Lake Kivu is, therefore an excellent example how gases of very different origin (i.e. bacterial and magmatic) can become mixed in the same system.

1. Introduction

The discussion on the origin of the dissolved gases in Lake Kivu (Fig. 1) has been revived since the report of excess ^3He in the gases (H. Craig, pers. commun., 1988), because ^3He indicates a mantle origin of the He. Several years ago Gold and Soter (1980) invoked a mantle origin of the methane in Lake Kivu. The location of Lake Kivu in the East African rift system with its roots in the upper mantle (Wohlenberg, 1975) provides undoubtedly a favorable environment for mantle degassing. However, a review of all geochemical data as well as experimental evidence contradict the hypothesis of a mantle origin of methane in Lake Kivu.

2. Statement of the problem

Lake Kivu is one of the lakes within the western branch of the East African rift system and is situated immediately adjacent to the active volcano Nyiragongo (Fig. 1). The waters, reaching a maximum depth of 485 m, are permanently stratified and contain $\sim 63 \cdot 10^9$ m^3 of dissolved methane and about five times as much dissolved carbon dioxide (Tietze, 1978; Tietze et al., 1980).

Various research groups have advanced vastly

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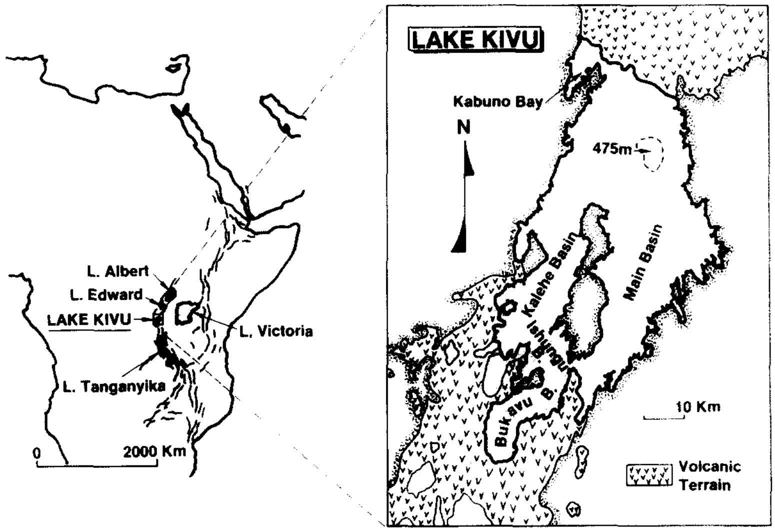

Fig. 1. Geographic location of Lake Kivu in the western branch of the East African rift system. The lake covers an area of ~2400 km^2 and contains $63 \cdot 10^3$ m^3 of methane and 5 times as much CO_2.

different hypotheses to explain the origin of these dissolved gases. Schmitz and Kufferath (1955) suggested a bacterial origin for the methane. K. Burke and Müller (1963) proposed a magmatic origin. Deuser et al. (1973) advanced a model where bacteria use simultaneously organic and inorganic carbon to produce methane. (However, the isotopic composition of the methane which was reported by Deuser et al. could not be verified.)

A detailed study of the physical and chemical properties of the water and the dissolved gases by Tietze (1978) and Tietze et al. (1980) revealed a measurable ^{14}C concentration in the dissolved methane which was, however, considerably lower than the ^{14}C concentration of organic matter in the sediments (Fig. 2). The sediment organic carbon had a lower ^{14}C concentration than expected from the pollen-dated age. Several "dilution" processes with inactive or low ^{14}C carbon must accompany the formation of the sediment organic matter and the methane to explain the ^{14}C geochemistry. Tietze et al. (1980) suggested that one step of ^{14}C dilution occurs in the biozone where magmatic CO_2 is assumed to be mixed with atmospheric CO_2, leading to a lower ^{14}C concentration in the biomass and, consequently, in the sediment. A further lowering of the ^{14}C activity in the methane is explained by formation of one-third of the methane in the upper sediment and two-thirds in the deeper sections of the sediments where the ^{14}C activity is low.

This mixing model has been further refined by Schoell (1984) and will be discussed here in more detail. The model assumes that the methane is formed by two microbial processes: (1) reduction of the magmatic CO_2 dissolved in the lake water; and (2) microbial fermentation of sediment-derived carbon. This model provided a consistent explanation for both the ^{14}C concentration and the stable isotopic composition of the methane. Here we explain the implications and the results of this model in more detail and outline how this model could be tested with further sampling and analysis techniques. The basic data are compiled in Fig. 2. Isotope values are given in the common δ-notation as per mil deviation from PDB and SMOW as standards for carbon and hydrogen, respectively.

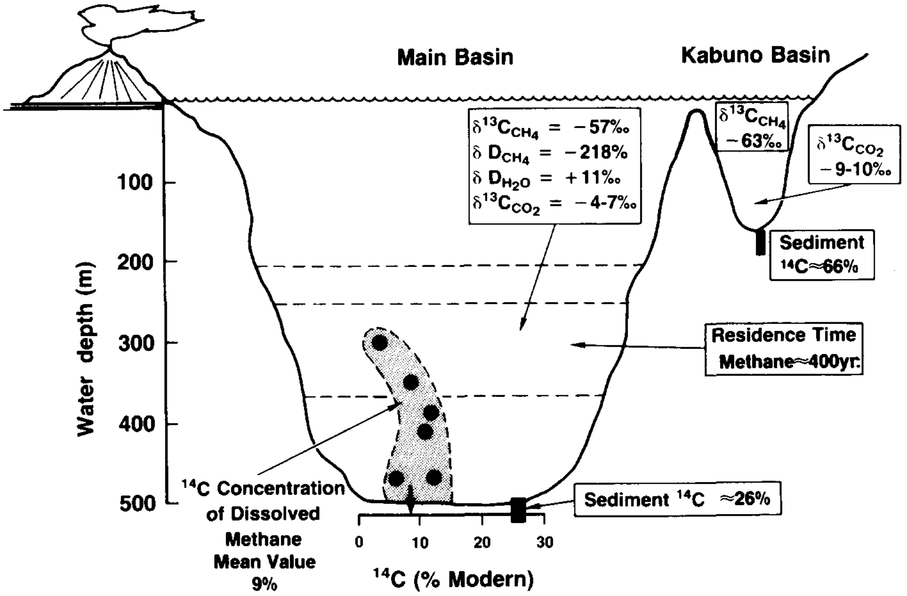

Fig. 2. Graphical representation of geochemical data so far available on Lake Kivu. Data are taken form Tietze (1978), Tietze et al. (1980), Schoell (1984). Note ^{14}C activity in dissolved methane and the discrepancy between the ^{14}C activity of the sediment. The $(^{3}He/^{4}He)[(^{3}He/^{4}He)_{atm}]^{-1}$ ratio of the helium in the lake is ~3 (H. Craig, pers. commun., 1988).

3. Culture experiments with Lake Kivu sediments

Systematic bacteriological studies were performed with an inoculum originating from Lake Kivu sediment. These studies have been reported in detail by Bochem et al. (1982). A thermophilic methanogenic consortium, which consisted of morphologically distinct bacterial granules, could be grown in a fermentor. This consortium grew on acetic acid at 60°C and produced 6–8 l of biogas per liter of culture during one day. The methanogens in the consortium resembled thermophilic *Methanosarcina* and *Methanococcus* strains. These culture experiments were used to investigate the relationship between the deuterium content in the water of the culture and the produced methane. Varying amounts of deuterated water were added to aliquots of the culture medium to provide different deuterium concentrations in the water. The resulting methane was collected for carbon and hydrogen isotopic analysis (Schoell, 1984).

The relationship between the deuterium concentration of the methane and the deuterium concentration of the water as found in this experiment is:

$$\delta D_{CH_4} = 0.15 \delta D_{H_2O} - 318 \qquad (1)$$

and is depicted in Fig. 3 as line *1*.

This is the first report of a deuterium pathway experiment with purely acetate-fermenting methanogens. The slope of the water–methane δD relationship is significantly lower than that obtained from an experiment involving fermentation in a sewage sludge (Schoell, 1980). These results using the Lake Kivu inoculum confirm the reasoning of Jenden and Kaplan (1986) who calculated the H isotope correlation between acetate methane and water to be:

$$\delta D_{CH_4} = 0.143 \delta D_{H_2O} - 393 \qquad (2)$$

This equation was derived by assuming that 70% of the methane produced during sewage sludge fermentation is derived from acetate and 30% from CO_2 reduction. In particular, it is of interest that our experimental results do not support the theoretical assumptions of several authors (Schoell, 1980; Woltemate et al., 1984; Whiticar et al., 1986) who assumed that acetate fermentation follows a water–methane deuterium relationship with a slope of 0.25. Whether our experiment is representative of all types of acetate-metabolizing methanogens is not clear. The difference between the constant in eqs. 1 and 2 indicates that there are differences in the absolute deuterium concentration of fermentation-derived methane, but that there is little dependence on the deuterium concentration of the associated water. Further systematic culture studies will be needed to understand the details of the hydrogen pathway during fermentation.

4. Conceptual model for the formation of methane in Lake Kivu

Isotopic studies of the formation of bacterial gases in shallow sediments resulted in compelling evidence that the two basic processes which are responsible for bacterial methane formation are CO_2 reduction and acetate fermentation (Schoell, 1980; Woltemate et al., 1984; Jenden and Kaplan, 1986; Martens et al., 1986; Whiticar et al., 1986; R.A. Burke et al., 1988). Acetate fermentation seems to play a more important role in freshly deposited sediments whereas CO_2 reduction predominates in older sediments. Jenden and Kaplan (1986) pointed out that acetate fermentation could possibly be dominant in very young sediments with input of organic matter of terrestrial origin.

The important observation is, however, that both CO_2 reduction and acetate fermentation are two bacterial processes which are simultaneously operative in sediments. It is widely acknowledged among microbiologists that both processes are operative during degradation of complex organic matter by methanogenic bacterial communities (Schlegel et al., 1976). Yet for natural systems in sediments, the evidence for a dual microbial origin of methane has only been recognized for recent or very young sediments (Jenden and Kaplan, 1986; Whiticar et al., 1986; R.A. Burke et al., 1988). The relative importance of acetate fermentation or reduction in a sediment may depend on many factors, such as the type of sediment, temperature, sulfate supply, type of organic matter, and others (Jenden and Kaplan, 1986; Martens et al., 1986; R.A. Burke et al., 1988). These basic concepts of methane formation, applied to Lake Kivu, lead to a better understanding of measured data which so far could not be easily explained.

The assumptions are the following: In Lake Kivu there are two bacterial processes simultaneously producing methane. One process is the direct reduction of CO_2 by methanogens which strictly use the dissolved CO_2 in the lake water near and in the sediment. This CO_2 reduction does not necessarily require free magmatic hydrogen, as has been postulated by Deuser et al. (1973). Rather we assume that the CO_2-reducing process is similar to that observed in other sediments in which hydrogen is provided by other microbial processes during degradation of the sedimentary biomass. Simultaneously, methane is formed in the lake sediments by a fermentation process similar to that which we were able to reproduce in the culture experiment described above.

The assumptions hereby are that the hydrogen isotope relationships between water and methane, as well as the carbon isotopic composition of the methane, in the lake are the same as those found in the experiment. The relative amounts of methane formed by CO_2 reduction and acetate fermentation result from a simple mass-balance equation for deuterium as has been used by Jenden and Kaplan (1986):

$$\delta D_K = f\delta D_F + (1-f)\delta D_R \tag{3}$$

where δD_K is the measured deuterium concentration in the combined methane; δD_F is the deuterium concentration in the methane formed by acetate fermentation; δD_R is the deuterium concentration in the methane resulting from CO_2 reduction; and f is the fraction of the methane from fermentation. δD_F is defined in eq. 1, and for δD_R we use the equation which applies to CO_2 reduction (Schoell, 1980):

$$\delta D_{CH_4} = \delta D_{H_2O} - 160 \quad (4)$$

Inserting the deuterium concentration δD_{H_2O} of Lake Kivu water of +11‰ into eq. 4 (Fig. 2), the deuterium concentration of the methane in the lake which forms from CO_2 reduction can be determined. The fraction of methane which originates from acetate fermentation results from eq. 3 that is recombined to:

$$f = (\delta D_K - \delta D_R)/(\delta D_F - \delta D_R) \quad (5)$$

Using eqs. 1 and 4, and introducing these into eq. 5 with $\delta D_K = -218$‰ (see Fig. 2), we calculate the resulting fraction of methane from acetate fermentation to be $f = 0.41$, which means that 41% of the methane in Lake Kivu is derived from acetate fermentation. Whiticar et al. (1986) suggest from their compilation of worldwide data that the constant in eq. 4 possibly should be −180 rather than −160. With this new constant, the fraction of methane derived from acetate fermentation is $f = 0.33$, i.e. 33% of the methane comes from acetate fermentation. The carbon isotopic composition of the methane which forms from CO_2 reduction can be found from eq. 3 by substituting $\delta^{13}C$ for δD using the average carbon isotopic composition from the culture experiment of −45‰ (Table I). A carbon isotopic composition of −65‰ and −63‰ is derived for $f = 0.44$ and 0.33, respectively (Fig. 3).

The isotopic compositions of the two types of methane in Lake Kivu, according to this model, are then −64‰ and −159‰ for carbon and hydrogen of the methane from CO_2 reduction, and −45‰ and −316‰ of the methane from acetate fermentation, respectively. These mixing relationships are graphically summarized in Fig. 3, and in Fig. 4 as "model *1*".

TABLE I

Hydrogen and carbon isotopic composition of methane and water in culture experiment (Schoell, 1984)

δD_{H_2O} (‰)	δD_{CH_4} (‰)	$\delta^{13}C_{CH_4}$ (‰)
−45	−324	−44.5
+33	−315	−42.2
+86	−303	−46.5
+181	−291	−45.7
+271	−276	−45.4

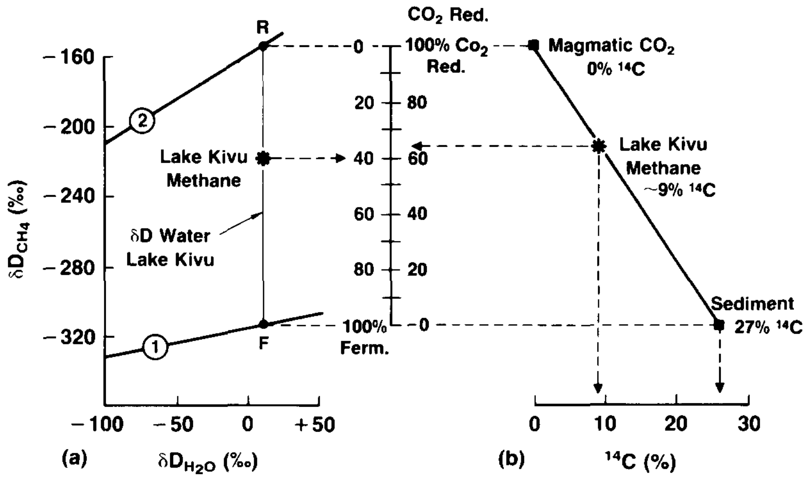

Fig. 3. Mixing models for bacterial methane formation in Lake Kivu: (a) hydrogen isotopes and (b) ^{14}C concentration in methane can be explained by mixing of two bacterially formed types of methane. *R* and *F* denote the end-member compositions of methane from CO_2 reduction of magmatic CO_2 and from fermentation of sediment organic matter, respectively. Straight lines *1* and *2* are those of eqs. 1 and 4, respectively.

5. Implications and predictions of the model

The concept of a dual bacterial origin for the methane in Lake Kivu offers an immediate explanation for the discrepancy between the ^{14}C concentration of the organic matter in sediments of ~27% modern and that of methane, which is only ~9% modern. The dissolved CO_2 in the lake water is mainly of magmatic origin and, therefore, is deficient in ^{14}C. The methane, which forms from CO_2, must also be deficient in ^{14}C. On the other hand, the methane from acetate fermentation should have a ^{14}C concentration equivalent to the sediment organic matter which is ~27% modern. Because methane from acetate fermentation accounts only for 33–41% of the total methane, the ^{14}C concentration of the mixed methane is accordingly lower and can be estimated to be ~9% or ~11%, respectively. Most importantly two independent isotopic tracers, i.e. deuterium and ^{14}C reveal similar proportions of the two types of methane that are formed in the lake (Fig. 3).

The theory of microbial transformation of biomass predicts that 67% of the methane should be derived from acetate fermentation and 33% from CO_2 reduction unless major intermediate metabolites are gained or lost from the system (Schlegel et al., 1976). For Lake Kivu the proportion of methane from the two processes is almost opposite, i.e. 30–40% of the methane comes from acetate fermentation and 60–70% from CO_2 reduction. The explanation for this observation is not yet clear. There may exist non-methanogenic, acetate-consuming processes that deplete the acetate pool. Under certain circumstances, acetate fermentation can lead to H_2 and CO_2:

$$CH_3COOH + 2H_2O \rightarrow 4H_2 + 2CO_2$$

This process could simultaneously deplete the acetate reservoir and provide hydrogen for the CO_2 reduction. Admittedly, these explanations are speculative and show that a better understanding of the microbial processes of this environment is needed.

An interesting implication of the model is that the dissolved CO_2 in the lake water should show a slight but significant ^{14}C concentration. Although the bulk of the CO_2 is of magmatic origin, the fermentation process adds equal molar amounts of CO_2 and CH_4 to the water:

$$CH_3COOH \rightarrow CH_4 + CO_2$$

This CO_2 should have the same ^{14}C concentration as the sediment, i.e. ~27% modern. Because the CO_2/CH_4 ratio in the lake is ~5 : 1, an average ^{14}C concentration of the CO_2 between 1.8% and 2.2% modern is predicted for the above calculated *f*-values of 0.33 and 0.41, respectively. If this low activity can be measured with modern ^{14}C techniques, the results will provide an excellent test for the model discussed here.

A further observation also, is explained with this model: Methane in the Kabuno Bay (Figs. 1 and 2) has a stable carbon isotopic composition of −63‰, which is very close to the calculated composition of the end-member of the CO_2 reduction methane. This result could mean that in Kabuno Bay, methane is predominantly derived from CO_2 reduction and that, for whatever reason, the conditions for fermentation in the sediments are not favorable. It is still not clear, however, why the CO_2 in Kabuno Bay is slightly depleted in ^{13}C compared to the main basin. This depletion could possibly be due simply to influx of river or groundwaters with ^{13}C-depleted bicarbonate. These explanations could be tested with ^{14}C analyses of the methane in the Kabuno Bay.

6. Production rates of bacterial methane

The methane in Lake Kivu has a residence time of ~400 yr. (Tietze, 1978), which allows the calculation of the production rate of methane. Using the data of Figs. 1 and 2, a produc-

TABLE II

Microbial methane production rates

CH_4 production	(mmol CH_4 m^{-2} day^{-1})	Reference
Cape Lookout Bight	13	[*1*]
Lake Mendota	29	[*2*]
Lake Kivu	5.5	[*3*]
Lake Kivu	8	this work
Total	8	
CO_2 reduction	5-6	
Acetate fermentation	2-3	

References: [*1*] = Martens et al. (1986); [*2*] = Ingvorsen and Brock (1982); [*3*] = Jannasch (1975).

tion rate for the methane of Lake Kivu of ~8 mmol CH_4 m^{-2} day^{-1} can be estimated. Accordingly, methane from CO_2 reduction amounts to 5-6 mmol CH_4 m^{-2} day^{-1} and from acetate fermentation 2-3 mmol CH_4 m^{-2} day^{-1}. This production rate is low when compared to that of other lake environments (Table II). But the estimate for Lake Kivu is certainly very conservative as most likely methanogenesis is not operative over the whole area of the lake. The production rate is, however, almost identical to the average yearly bacterial production rate in Cape Lookout Bight (Martens et al., 1986). Again this comparison supports the bacterial formation of methane in Lake Kivu.

7. Bacterial vs. mantle origin of methane

The dissolved CO_2 is predominantly of magmatic origin as indicated by the geologic setting and carbon isotopic composition. The lake is in the East African rift close to an active volcano. The isotopic composition of the CO_2 is very close to the values of CO_2 of volcanic origin at many other localities (Hulston and McCabe, 1962). The dissolved He has also been found to contain a significant amount of the mantle-derived isotope ^{3}He (H. Craig, pers. commun., 1988). This observation indicates that a major portion of the He is of mantle origin.

The question of course arises whether the methane is also of a mantle origin. In our opinion there is no compelling reason to assume that the methane is from the same source as the He. If the methane in the lake is assumed to be of mantle origin, a similar mixing process would have to be invoked to account for the ^{14}C concentration in the dissolved methane. Similar to our bacterial mixing model, the mantle methane, which is devoid of ^{14}C, would dilute bacterial methane with a ^{14}C activity close to that of the sediment. If we assume the same isotope values for mantle methane of −18 to −15‰ for carbon and −125 to −100‰ for hydrogen as were measured in methane from the East Pacific Rise (Welhan and Craig, 1983), an unrealistic isotope value for the fermentation methane of ~ −140‰ and ~ −430‰ for carbon and hydrogen, respectively, would result (Fig. 4). Methane of such isotopic composition has so far never been observed. The fact that both CO_2 and He are of mantle origin cannot be accepted as evidence that the methane also

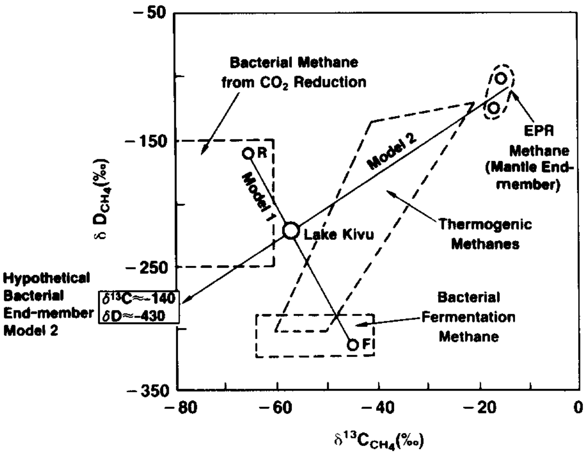

Fig. 4. Alternative mixing models of methane to explain the origin of the Lake Kivu methane. Model *1*: *R* and *F* are the end-member compositions of bacterial methanes derived from CO_2 reduction of dissolved CO_2 and formation of sediment organic matter, respectively. Our model assumes the origin of Lake Kivu methane from these two processes. Model *2*: Alternatively, mixing of methane of a composition similar to "mantle methane" encountered at the East Pacific Rise is mixing with bacterially formed methane. This model would lead to a very unrealistic isotopic composition of the bacterial end-member of −140 and −430‰ for carbon and hydrogen, respectively.

is of mantle origin as has been hypothesized by Gold and Soter (1980).

This reasoning is corroborated by a comparison of other occurrences where methane is associated with mantle-derived He (Fig. 5). Lake Kivu methane is the most depleted in ^{13}C of all these occurrences. Methanes from vents at the sea bottom of the Guaymas Basin (Gulf of California) have a clearly thermogenic origin as indicated by their isotopic similarity with thermogenic gases and by their association with C_{2+} hydrocarbons (Welhan and Lupton, 1987). Methanes from both Yellowstone, Wyoming, and Salton Sea, California, are associated with ^{3}He (Welhan, 1981) but have a striking resemblance with pyrolysis-derived methane, suggesting that in these continental geothermal systems pyrolytic processes account for the formation of traces of methane. Methane emanating with He at the East Pacific Rise seems to be the only one of a truly basaltic, i.e. mantle origin (Welhan, 1988). The sharp contrast between the isotopic composition of methane in Lake Kivu and the East Pacific Rise underscores their different origins.

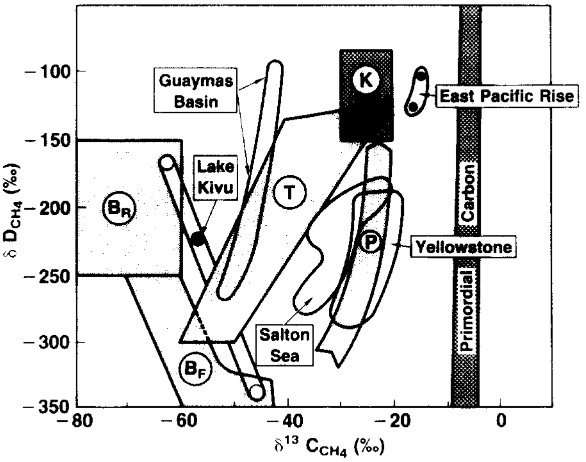

Fig. 5. Carbon and hydrogen isotope composition of Lake Kivu methane in comparison with methane occurrences which are associated with mantle-derived He (Guaymas Basin, Salton Sea, Yellowstone and East Pacific Rise). The *areas* indicated outline isotope variations of other naturally occurring methanes: B_R = bacterial methanes formed through CO_2 reduction; B_F = bacterial methanes formed through fermentation processes; and T = thermogenic methanes (Schoell, 1980; Whiticar et al., 1986). The field P designates pyrolytically-formed methanes (Chung, 1976); K denotes the isotope variations in kerogens and oils from which all "biogenic" methane is ultimately formed.

8. Conclusions

The measured geochemical data of Lake Kivu and its dissolved gases can be satisfactorily explained by the model of a dual bacterial origin of the methane. The fact that magmatic emanations of CO_2 and He are dissolved together with the bacterial gases in the same layered water system simply shows that the differently sourced gases became mixed in the same trap for a transient storage. He and CO_2 are of magmatic origin introduced into the lake through hydrothermal vents and emanations. Bacteria contribute methane to the dissolved gases in the lake at a rate similar to that observed in other shallow sedimentary environments (one-third by acetate fermentation, two-thirds by CO_2 reduction).

We consider the presented data, therefore, as strong evidence for a bacterial origin of the methane in Lake Kivu. In our opinion, the hypothesis of a mantle-derived methane in Lake Kivu (Gold and Soter, (1980) which is not based on measurements should be rejected.

Acknowledgements

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