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ISOTOPE GEOCHEMISTRY OF CARBONATE SEDIMENTS FROM LAKE KIVU (EAST-CENTRAL AFRICA)

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Abstract

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Isotopic investigations of carbonates from Lake Kivu show that most of the carbonate in the main basin is precipitated in isotopic equilibrium with the lake water bicarbonate (near isotopic equilibrium with the atmosphere). However, aragonite precipitated from the surface water of the separate Bukavu basin was periodically enriched in ^{13}C ($\delta^{13}C$ up to +13.6‰) due to a preferential removal of ^{12}C-enriched sedimentary organic matter. This occurred during times of low water-level stands when the Bukavu basin was isolated from the main lake and its waters were "chemically" stratified.

1. Introduction

Lake Kivu is located within the great western rift zone of East Africa. It consists of the main basin and four smaller basins (Ishungu, Kalehe and Bukavu basins and Kabuno Bay) which are separated from the main basin by sills. Table I gives some background information on Lake Kivu. More detailed information about the mineralogy of the sediments as well as the water and sediment chemistry are given by Kilham (1972), Degens and Kulbicki (1973), Degens et al. (1973), Stoffers (1975), Stoffers and Hecky (1978), Tietze (1978), and Tietze et al. (1980).

Lake Kivu is well known for its unique carbon dioxide (CO_2) and methane (CH_4) gas content in the water column. The dissolved CO_2 is believed to be of magmatic origin whereas the CH_4 may largely be generated by bacteria from the organic material in the sediment [models of CH_4 genesis are discussed by Tietze et al. (1980)].

TABLE I

Selected morphometric and hydrological parameters of Lake Kivu

Area, A (km^2)	A_B (catchment)	~7,000
	A_L (lake)	~2,400
Depth, Z (m)	$\bar{Z}$ (mean depth)	240
	Z_{max} (maximum depth)	485
Volume, V (km^3)		~580
Outflow (km^3 yr.$^{-1}$)		3.2*

Modified after Stoffers and Hecky (1978) and Tietze (1978).
*Ten-year average discharge supplied by Amenagement Hydro-Électrique des Chutes de Mururu, Bukavu, Zaire, for its dam on the upper Ruzizi River.

During recent years, stable-isotope analysis of carbonates (and associated organics) has been of great value in clarifying the mode of formation of carbonates. The carbon isotopic composition of primary and diagenetic carbonates reflects the source of the dissolved bicarbonate in the (pore) water whereas the oxygen isotopic composition of the carbonates depends on the ^{18}O content of the water and the carbonate precipitation temperature.

Carbonate minerals in Lake Kivu sediments are of primary and probably also of secondary origin. For example, aragonite and monohydrocalcite are primary precipitates from the (surface) water of the lake (Stoffers, 1975), whereas siderite, calcite (and dolomite?) most likely formed during early diagenesis (see Section 4). The carbon isotopic composition of the various carbonate minerals should, therefore, reflect the

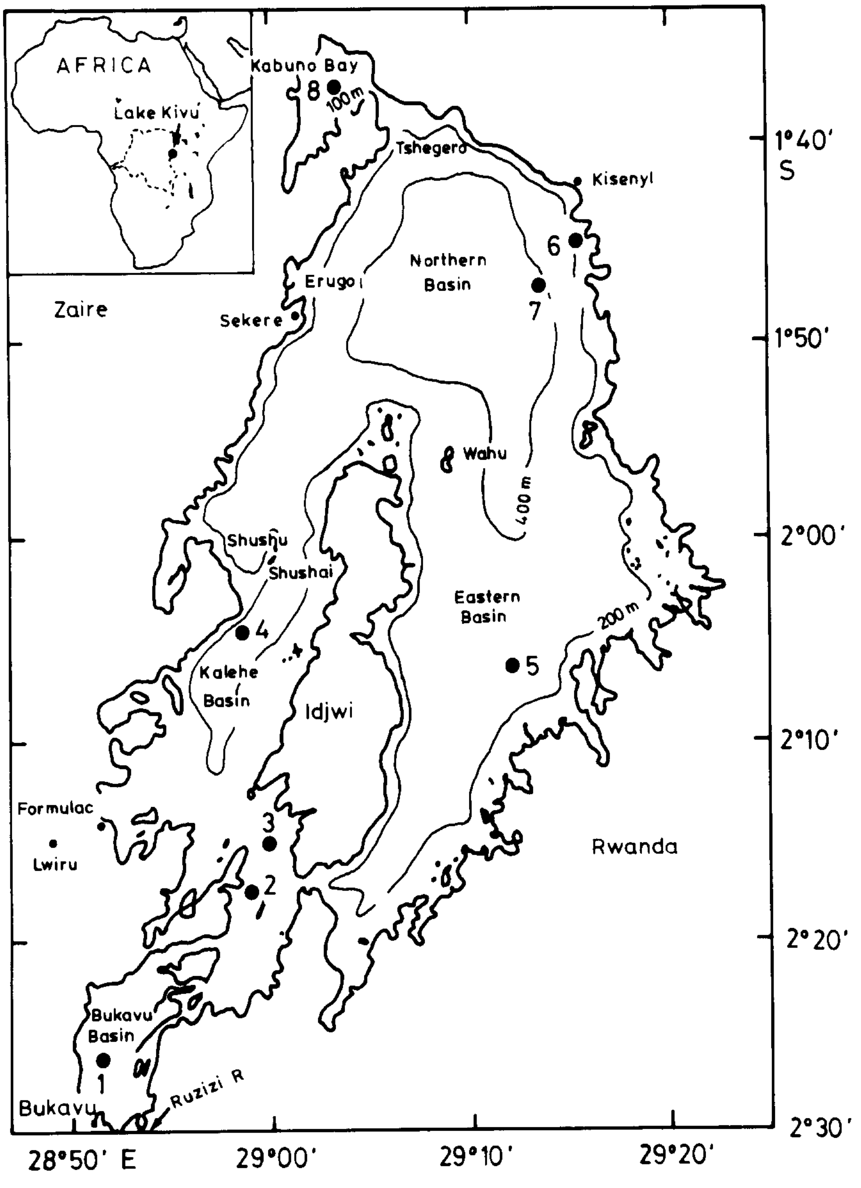

Fig. 1. Area under investigation and the various sampling sites (St Nos. as given in Table II) in Lake Kivu. Rough depth contours are in meters.

carbon isotopic evolution from the lake water bicarbonate to the pore-water bicarbonate, which may differ significantly due to contributions of biogenic CO_2 from early degradation of organic material.

To our knowledge, only a few carbonate samples of Lake Kivu have been investigated isotopically so far. This is mainly due to the scarcity of sample material left from the expeditions conducted by scientists from Woods Hole Oceanographic Institution in 1972 and from the German expedition from the Bundesanstalt für Geowissenschaften und Rohstoffe (B.G.R.) in 1975. We were therefore fortunate to get samples from Woods Hole as well as from the B.G.R. for our studies. However, due to this scarcity of material, the down-core sampling intervals are not narrow enough (except St *1* from the Bukavu basin) to study the isotopic composition of the various minerals in great detail. Nevertheless, major trends in isotope geochemistry of the carbonates can be seen.

Fig. 1 shows the area under consideration as well as the sampling sites where some core material was still available.

2. Methods

*2.1. X-ray diffraction (*XRD*)*

Forty-nine samples were investigated by XRD (Cu-K_α radiation) after grinding to determine the carbonate mineralogy. The relative

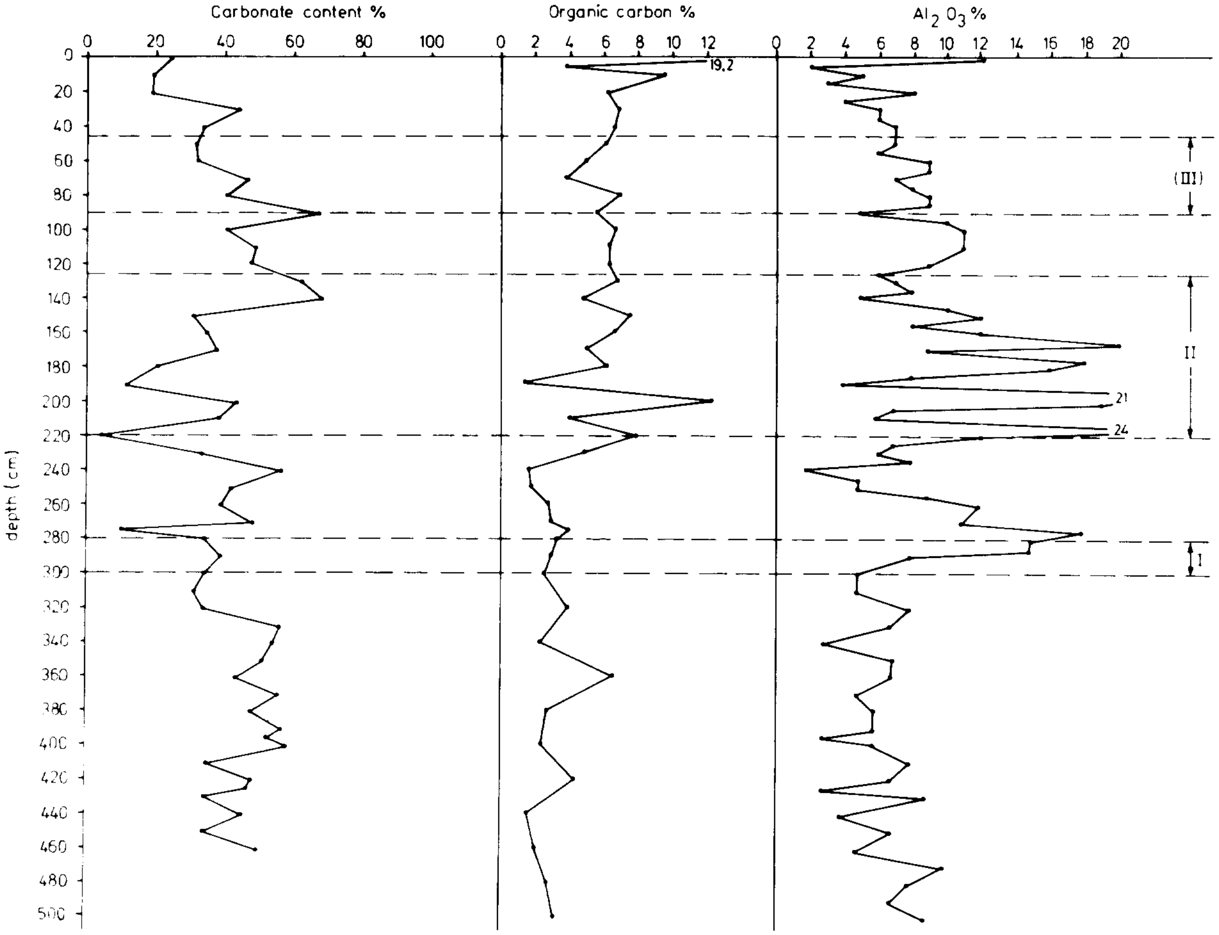

Fig. 2. The carbonate, organic carbon and Al_2O_3 content of the sediments of St *1*, Lake Kivu.

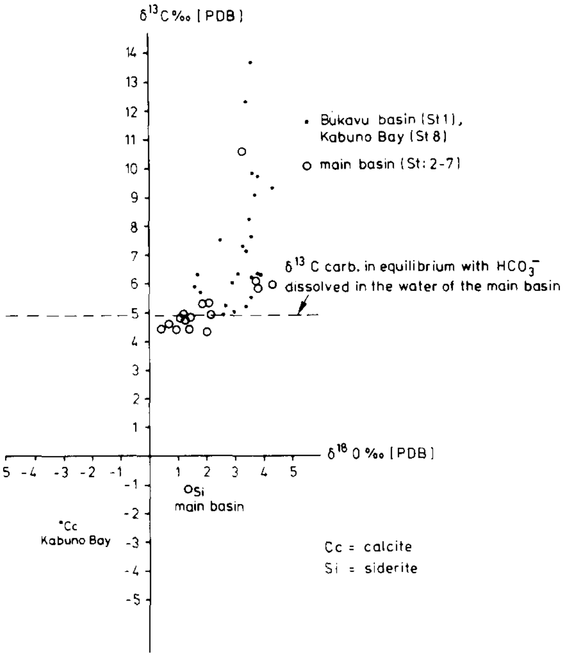

Fig. 3. $\delta^{13}C$–$\delta^{18}O$ crossplot of all samples investigated.

amounts of calcite, aragonite, monohydrocalcite, dolomite and siderite were estimated by the heights of their major peaks (Gavish and Friedman, 1973; von der Borch, 1976). This method is believed to reveal the major trends in carbonate mineralogy of Lake Kivu sediments.

2.2. *Isotopic analysis*

Prior to isotopic analysis, the samples were treated with a 6% sodium hypochlorite solution to remove organic matter. The samples were then washed several times with distilled water and dried at 60 °C. The carbonates were reacted with 100% phosphoric acid at 25 °C (siderite at 80 °C) according to the standard method (McCrea, 1950) and the evolved CO_2 was collected and analysed in a Varian® MAT *250* mass spectrometer. The results are given in permil deviations from the PDB standard. The $\delta^{18}O$-values of dolomite samples were corrected by -0.8‰ (Sharma and Clayton, 1965). The $\delta^{13}C$-values of aragonite samples are lowered by 1.8‰ and their $\delta^{18}O$-values are lowered by 0.6‰ to account for the mineral-specific fractionation (Rubinson and Clayton, 1969).

3. Results

Detailed information on the mineralogy of carbonate sediments of Lake Kivu has been given by Stoffers and Fischbeck (1974), Stoffers (1975) and Stoffers and Hecky (1978). The following is only a brief presentation of results important for this study.

Fig. 2 shows the carbonate content, the organic carbon content and the Al_2O_3 concentration of core St *1* from the Bukavu basin (all data from Degens and Kulbicki, 1973). The carbonate content varies between 5% and 70% with low values for thin layers in the middle section (150–300 cm) of core St *1*. The organic carbon content in sediments of St *1* ranges from < 1% to 19% with high values in the upper half of the core. As Fig. 2 shows, the Al_2O_3 concentrations (used as a parameter to show the detrital influence) is variable (2–24%). The highest Al concentrations were found between 160- and 220-cm and between 260- and 300-cm depth in core St *1*.

Aragonite, calcite, monohydrocalcite, dolomite and siderite are the carbonate minerals identified by XRD. Dolomite is poorly-ordered and Ca-rich (general composition Mg_{37-40}-Ca_{63-60}; Stoffers, 1975).

Fig. 3 shows the $\delta^{13}C$–$\delta^{18}O$ crossplot of all samples investigated. Table II and Fig. 4 show the mineralogical as well as the isotopic results of core St *1*. Aragonite mainly occurs in the middle and lower part (e.g., 120–220 and 280–560 cm, respectively) of the core. There are three distinct horizons rich in monohydrocalcite noticeable in Fig. 4. Dolomite and calcite are mainly found in the upper part of the core (although calcite is associated with monohydrocalcite between 220- and 280-cm depth as well).

There are three major positive $\delta^{13}C$ excursions in core St *1*. One is found at a depth of 287 cm ($\delta^{13}C = +12.3$‰), another at 209 cm ($\delta^{13}C = +13.6$‰) and a third at 82 cm

TABLE II

δ-values and mineralogy of carbonate sediments from Lake Kivu

Samples	Depth (cm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C^*$ (‰)	cc (%)	ar (%)	mhc (%)	dol (%)	sid (%)
St *1*	10-12 cm	+6.3	+3.1		-	-	61	39	-
	18-20	+6.2	+3.6		43	46	11	-	-
	24-26	+6.3	+3.8		76	-	24	-	-
	40-42	+5.5	+3.6	−26.0	54	-	46	-	-
	45	+7.3	+3.3		60	20	-	20	-
	60-62	+7.7	+3.6		50	8	-	42	-
	75-77	+9.3	+4.3		18	-	-	82	-
	80-82	+8.2	+3.5		44	8	-	48	-
	82	+9.7	+3.8		26	-	32	42	-
	84	+9.0	+3.7		30	-	55	15	-
	105-108	+5.2	+2.7	−28.4	11	23	66	-	-
	112	+6.0	+2.9		24	14	62	-	-
	115	+4.9	+2.6		6	68	26	-	-
	124-126	+6.3	+3.9		3	92	5	-	-
	164-166	+9.8	+3.6		-	100	-	-	-
	208-210	+13.6	+3.6	−25.6	-	100	-	-	-
	213	+12.8	+3.3		n.d.	n.d.	n.d.	n.d.	n.d.
	227-228	+7.1	+3.4		19	-	81	-	-
	232-234	+5.0	+3.0		63	-	37	-	-
	263-265	+5.7	+1.8	−25.9	31	-	69	-	-
	267	+7.5	+2.5		21	13	66	-	-
	272-273	+5.9	+1.6		17	14	69	-	-
	273-275	+6.3	+1.7		22	27	51	-	-
	286-288	+12.3	+3.4	−24.5	-	100	-	-	-
	298-300	+4.4	+2.0		-	100	-	-	-
	349-351	+5.2	+1.9		-	100	-	-	-
	410	+4.9	+2.3		-	100	-	-	-
	441-443	+4.6	+2.4		-	100	-	-	-
	492-494	+5.2	+3.4	−25.9	-	100	-	-	-
	531-533	+4.7	+1.7		-	100	-	-	-
St *2*	50	+4.4	+1.4		-	100	-	-	-
	62	+4.4	+0.4		-	100	-	-	-
	100	+4.9	+2.2		-	100	-	-	-
	110	+4.7	+1.3		-	100	-	-	-
	177	+5.3	+2.1		-	100	-	-	-
	420	−1.2	+1.4		-	-	-	-	100
St *3*	0-30	+6.1	+3.7		×	×	-	-	-
	30-50	+5.9	+3.8		×	×	-	-	-
St *4*	0-45	+10.6	+3.3		-	100	-	-	-
St *5*	0-60	+5.8	+4.3		-	100	-	-	-
St *6*	70	+4.4	+1.0		-	100	-	-	-
	130	+4.8	+1.1		-	100	-	-	-
St *7*	70	+5.3	+1.9		-	100	-	-	-
	160	+4.9	+1.2		-	100	-	-	-
	242	+4.6	+0.7		-	100	-	-	-
	260	+4.8	+1.4		-	100	-	-	-
	280	+4.3	+2.0		-	100	-	-	-
St *8*	120	−2.3	−3.1		100	-	-	-	-

Legend: $\delta^{13}C^*$ = value of kerogen; $\delta^{13}C$ = values of carbonate; cc = calcite; ar = aragonite; mhc = monohydrocalcite; dol = dolomite; sid = siderite; n.d. = not determined; × = present (percentages not calculated).

($\delta^{13}C = +9.7‰$). Intervals with positive $\delta^{13}C$-values are numbered I, II and III in Fig. 4. The most positive $\delta^{13}C$-values were found for aragonite samples (I and II). All other $\delta^{13}C$-values are near +5 to +6‰. The only two negative $\delta^{13}C$-values were measured for a calcite from

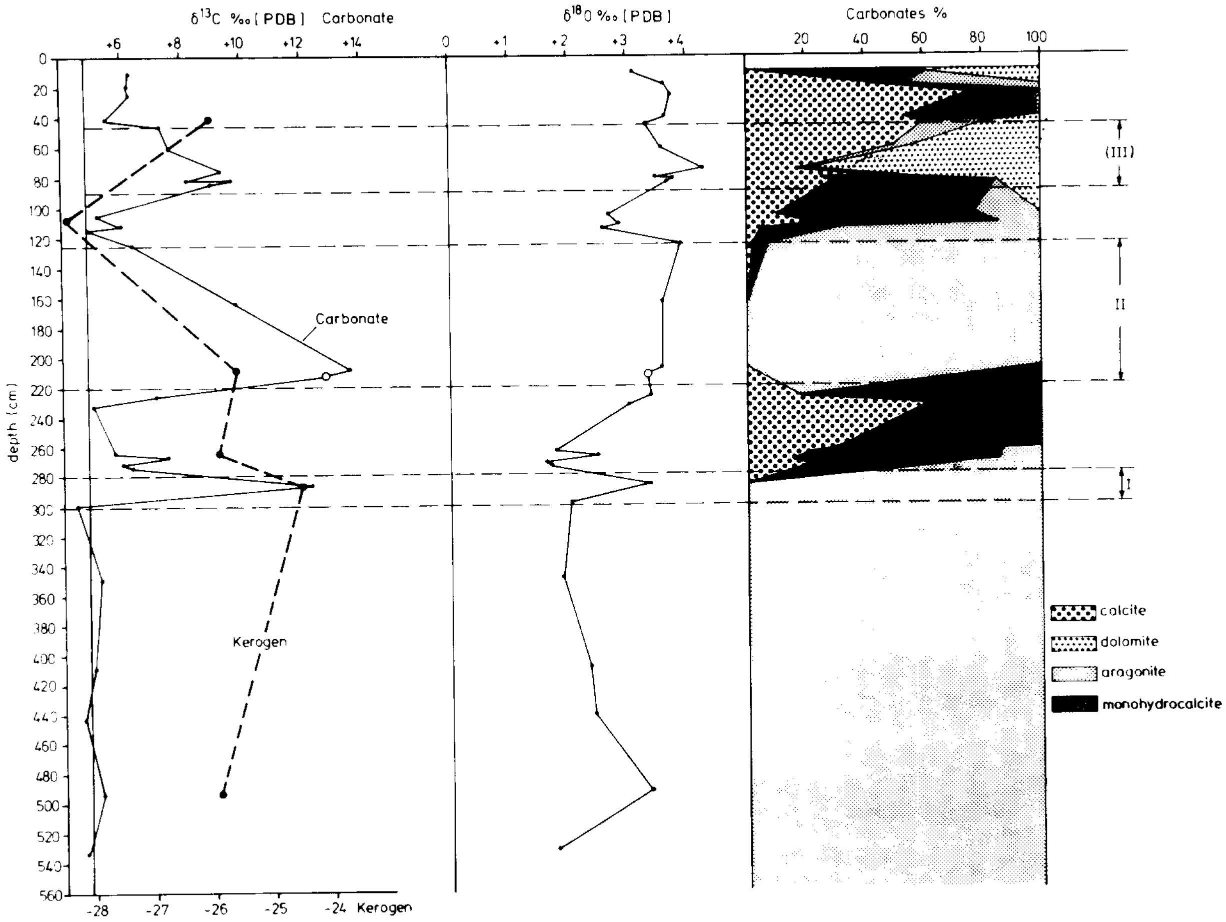

Fig. 4. δ-values and mineralogy of the carbonate sediments of St *1*, Lake Kivu.

Kabuno Bay ($\delta^{13}C = -2.3‰$) and a siderite from St 2 at 420-cm depth ($\delta^{13}C = -1.2‰$).

The isotopic composition of organic matter in sediments of the Bukavu basin (only six samples were analysed) ranges from −28.4 to −24.5‰ (Table II).

4. Discussion

The $\delta^{13}C$-values of dissolved CO_2 in the water of the main basin of Lake Kivu usually fall in a narrow range from −6 to −5‰ (with a best-fit curve pointing to −5.4‰; Tietze et al., 1980). The fractionation between solid calcium carbonate and gaseous carbon dioxide is 10.2‰ at 20°C (Emrich et al., 1970). This results in a $\delta^{13}C$-value of +4.8‰ for calcite in isotopic equilibrium with the CO_2 dissolved in the lake water. The value of +4.8‰ is shown in Fig. 3 by a straight line. (Note that the line gives the equilibrium value for the system CO_2–calcite. As was already mentioned, however, aragonite samples were corrected for their larger fractionation relative to calcite so that the isotopic composition of the aragonites can directly be compared with that of calcite.) Fig. 3 shows that most samples of the main basin plot close to the line at +4.8‰. This clearly shows that the carbonates from the main basin precipitated in isotopic equilibrium with the CO_2 dissolved in the lake water.

There are only two samples with negative $\delta^{13}C$-values. One is a calcite from Kabuno Bay (separate basin in the north of Lake Kivu) where the dissolved CO_2 has a $\delta^{13}C$-value near $-9.4‰$ (Tietze et al., 1980). This results in a $\delta^{13}C$-value of $+0.8‰$ for calcite in isotopic equilibrium with CO_2 dissolved in the lake water of Kabuno Bay. As we measured a $\delta^{13}C$-value of $-2.3‰$ for the calcite, a diagenetic origin of the mineral, with biogenic CO_2 added to the pore-water bicarbonate, is probably indicated. The other sample with a negative $\delta^{13}C$-value ($-1.2‰$) consists of siderite. Assuming that siderite is not detrital in origin, this mineral most likely formed during early diagenesis as siderite does not form in the presence of dissolved sulphide ions (Berner, 1971). The lake water contains at least 23.8 mg l^{-1} sulphate at the surface (with increasing concentrations at greater water depth; in 440-m water depth 220 mg l^{-1} SO_4^{2-}; Degens et al., 1973). This sulphate is reduced to sulphide within the sulphate reduction zone where pyrite forms. Siderite forms after the sulphide is removed from the pore water, probably in the fermentation and carbonate reduction zone below the sulphate reduction zone (Hesse, 1986). However, the $\delta^{13}C$-value of $-1.2‰$ found for siderite from core St *2* (420-cm depth) is not indicative of CH_4 generation. In the methane generation zone, positive $\delta^{13}C$ carbonate values up to $+30‰$ can be found (Arthur et al., 1983; Gautier, 1985; Hennessy and Knauth, 1985). As there is a systematic increase in $\delta^{13}C$ of residual pore-water CO_2 during the onset of CH_4 generation, however, the value of $-1.2‰$ might well represent pore-water bicarbonate derived from anaerobic bacterial degradation of organic matter during early stages of methane generation by fermentation and/or CO_2 reduction.

Fig. 3 also shows that several carbonate samples have more positive $\delta^{13}C$-values than the equilibrium value of $+4.8‰$. In fact, the $\delta^{13}C$-values of carbonate can reach $+1\ 3.6‰$. All samples (except one) with positive $\delta^{13}C$-values are from the separate Bukavu basin. This is also shown in Fig. 4 where the $\delta^{13}C$-values are plotted relative to the depth in core St *1*. More specifically, there are three major excursions of $\delta^{13}C$. They occur at depths of 287, 209 and 82 cm. Fig. 4 shows that the thickness of these horizons with positive $\delta^{13}C$ carbonate values varies. Theoretically, two possible explanations could be given for these positive $\delta^{13}C$ carbonate values. Fermentation and CO_2 reduction processes result in positive $\delta^{13}C$-values of diagenetic carbonates (Irwin, 1980; Hesse, 1986); however, CH_4 generation by these processes only occurs in the absence of dissolved sulphate (Claypool and Kaplan, 1974). As already mentioned, the water of Lake Kivu has sulphate concentrations from 23.8 (surface) to 220 mg l^{-1} (440-m depth). CH_4 generation within the water column is, therefore, unlikely to occur. On the other hand, aragonite forms in the lake surface water where photosynthesis takes place (Stoffers, 1975). This implies that a primary enrichment of ^{13}C must have occurred in the lake water.

^{13}C-rich dolomites (up to $+13.6‰$) were reported for the Lomagundi carbonate province (Zimbabwe) by Schidlowski et al. (1976). The authors interpreted the "heavy" dolomites to be the results of an extensive removal (within sedimentary organics) of organic carbon from a closed basin. In general, primary induced shifts towards positive $\delta^{13}C$ carbonate values indicate increased rates of burial of organic carbon (Scholle and Arthur, 1980). It is assumed that the positive $\delta^{13}C$-values of primary aragonite from the Bukavu basin are caused by changes in the ratio of C_{org}/C_{inorg} in the water by the preferential removal of organic carbon from the water into the sediment. The deposition of large amounts of organic matter occurs during stagnation periods when only minor oxidation of organic matter takes place. It appears that these stagnation periods coincide with times of low water level when the Bukavu basin was separated from the main basin. This is indicated by the positive (evaporitic) $\delta^{18}O$-values ($\delta^{18}O$ up to $+4.3‰$) of those carbonates with positive $\delta^{13}C$-values and also by a concomitant increase of aluminosilicates (Fig. 2). The detrital component is believed to be high during times of low water level. At present, however, no relation of water level changes to the age of the sediments can be established. This is due to sampling and dating problems (soft sediment from the surface was probably lost during sampling; Stoffers and Hecky, 1978).

A further indication of the early enrichment of ^{13}C in the lake water would be the parallel $\delta^{13}C$ trends for the carbonates and the (autochthonous) organic matter both produced in the surface water of the lake. Six kerogen samples only were analysed from St *1* in the Bukavu basin. The $\delta^{13}C$ trend is shown in Fig. 4. This trend is not conclusive as there are only two samples (at 108 and 288 cm) with significantly different $\delta^{13}C$-values (-28.4 and -24.5‰, respectively), the others falling in the narrow range of -26.0 to -25.6‰. However, both extreme values correspond to the isotopic compositions of associated carbonates (e.g., a relatively positive $\delta^{13}C$-value of carbonate coincides with the positive $\delta^{13}C$-value of the kerogen and vice versa), indicating a possible genetic relationship.

In contrast to the aragonite samples (stages I and II, see Fig. 3), the positive $\delta^{13}C$-values of stage III (82-cm depth) in core St *1* was noted for calcite–dolomite mixtures (although the lowermost samples at 82 and 84 cm contain also monohydrocalcite). Calcite is probably an alteration product of metastable monohydrocalcite (Stoffers, 1975). Dolomite is generally believed to be a diagenetic product rather than a primary precipitate (see, however, Hardie, 1986). Hence, the positive $\delta^{13}C$-values of calcite–dolomite mixtures probably cannot be attributed to primary fluctuations of the ^{13}C content of the lake water. It is likely that diagenetic CH_4 generation caused the ^{13}C enrichment in those carbonates formed during early diagenesis.

5. Monohydrocalcite formation

The formation of monohydrocalcite in Lake Kivu was discussed by Krumbein (1975) and Stoffers and Fischbeck (1975). In contrast to the model proposed by Stoffers and Fischbeck (1974) (e.g., periodical opening of water stratification and successive diatom blooms which caused the formation of monohydrocalcite), Krumbein (1975) suggested a biogenic origin of monohydrocalcite associated with algal mats.

Although we only analysed bulk sediment samples (monohydrocalcite–calcite mixtures), it can be inferred that the $\delta^{13}C$-values of pure monohydrocalcite are also positive near the equilibrium value of $+4.8$‰ (Fig. 4) similar to the monohydrocalcite–calcite mixtures (note that calcite forms from monohydrocalcite under solid-state conditions without alteration of the initial CO_3^{2-} unit). It is therefore unlikely that biogenic CO_2 contributed to the monohydrocalcite formation as proposed by Krumbein (1975); benthic algal mats live on both biogenic CO_2 from the aerobic and anaerobic oxidation of organic matter during early diagenesis and lake water CO_2. Biogenic monohydrocalcite should have a carbon isotopic value different from the equilibrium value of $+4.8$‰. It is more likely that monohydrocalcite formed during times of high water level when a connection to the main lake was established. The opening of the main lake to the south caused an extensive mixing of the water in the Bukavu basin, which probably led to the precipitation of monohydrocalcite as envisioned by Stoffers and Fischbeck (1974). The $\delta^{18}O$-values of monohydrocalcite (+calcite)-containing samples are always lower than the $\delta^{18}O$-values of the aragonites adjacent to the monohydrocalcite. This possibly also supports the model of dilution of the highly evaporitic water in the (separate) Bukavu basin by surface water from the main lake during high water-level periods. Hecky and Degens (1973) assumed changes in the water level of the main lake by ~400 m during the last 15,000 years.

6. Conclusions

Carbonates of Lake Kivu are primary precipitates (aragonite, monohydrocalcite) as well as diagenetic products (siderite, calcite, and possibly dolomite).

Aragonite from the main basin formed in isotopic equilibrium with dissolved lake water bicarbonate (near equilibrium with atmospheric CO_2). ^{13}C-enriched aragonite of the separate Bukavu basin was, however, formed periodically from ^{13}C-enriched bicarbonate during low water level. This ^{13}C enrichment resulted from the preferential removal of ^{12}C-rich organic matter into the sediment (causing a decrease of C_{org}/C_{inorg} ratio in the water) during stagnation periods.

Monohydrocalcite formation is more likely to be the result of periodical openings of the main lake to the south (Bukavu basin) with concomitant diatom blooms rather than biogenic in origin.

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