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Microcrystalline Sphalerite in Resin Globules Suspended in Lake Kivu, East Africa

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The origin and chemical nature of micron-sized spheres found as suspended particles in Lake Kivu are examined. It can be shown that the hollow spheres, with a wall thickness of 500 Å, consist of a complex polymeric resinous material which has little functionality, except for hydroxyl groups. The spheres arise in the process of degassing of water samples at depth. Tiny gas bubbles, about 1 micron in size, act as scavengers of dissolved resinous material. The newly created resinous membrane promotes the selective coordination of zinc dissolved in the water column. In the prevailing H_2S regime, formation of sphalerite crystals is induced. The size range of the crystals, 5 to 50 Å, corresponds to 1 to 10 unit cells and suggests that the resinous membrane also acts as a template in sphalerite growth processes. The sources of the zinc and dissolved gases (CO_2, CH_4, H_2S) are hydrothermal springs seeping from the lake bottom into the basin. Water discharge is substantial; about 100 years are required to fill the lake to its present level (ca. 550 km^3 water). The average Kivu water contains 2 ppm zinc. Thus, 1 million tons of zinc are contained in Lake Kivu in the form of sphalerite.

Harzkügelchen von etwa 1μ Durchmesser treten in suspendierter Form im Kivusee auf. Die Kügelchen sind hohl und besitzen eine äußere Membrane von rund 500 Å Dicke. Sie sind das Ergebnis von Entgasungsvorgängen die sich in einer Wassertiefe von mehreren hundert Metern abgespielt haben. Die Oberfläche kleiner Gasblasen diente als „Kristallisationszentrum" für die im Wasser gelösten Harze, die ihrerseits eine selektive Koordinierung von gelöstem Zink bewirkten. Die Anwesenheit von H_2S führte zur Bildung von Zinkblende mit Kristallgrößen zwischen 5 und 50 Å. Gase (CO_2, CH_4, H_2S) und Zink entstammen salinaren hydrothermalen Lösungen, die im Gefolge vulkanischer Tätigkeit dem Seeboden auch heute noch entweichen. Der Durchschnittsgehalt von Zink im Kivusee beträgt 2 ppm, was mehr als einer Million Tonnen an Zink für den Gesamtsee entspricht.

Introduction

In the spring of 1971, several scientists from the Woods Hole Oceanographic Institution were engaged in a multi-disciplinary study of Lake Kivu, one of the deep lakes of the East African Rift System. Our program was concerned with the structural and hydrographical settings of this lake in relation to other East African rift lakes (Degens *et al.* 1971a; von Herzen and Vacquier 1967) and the Red Sea and Gulf of Aden Rifts (Degens and Ross 1969). A small segment of this program, concerning the presence of sphalerite-containing

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resin globules suspended throughout the water column of Lake Kivu, could not be treated appropriately within the framework of our principal publications (DEGENS *et al.* 1971b; 1972). In view of the interesting mechanism responsible for the occurrence of these globules, a more detailed discussion seemed warranted.

Background Information

Lake Kivu, almost 100 miles to the north of Lake Tanganyika, is situated at the highest point of the Rift Valley at an elevation of 1,500 m above sea level; the lake is surrounded by active volcanoes and geothermal springs. The greatest water depth, almost 500 meters, occurs in the central part of the Northern Basin (Fig. 1).

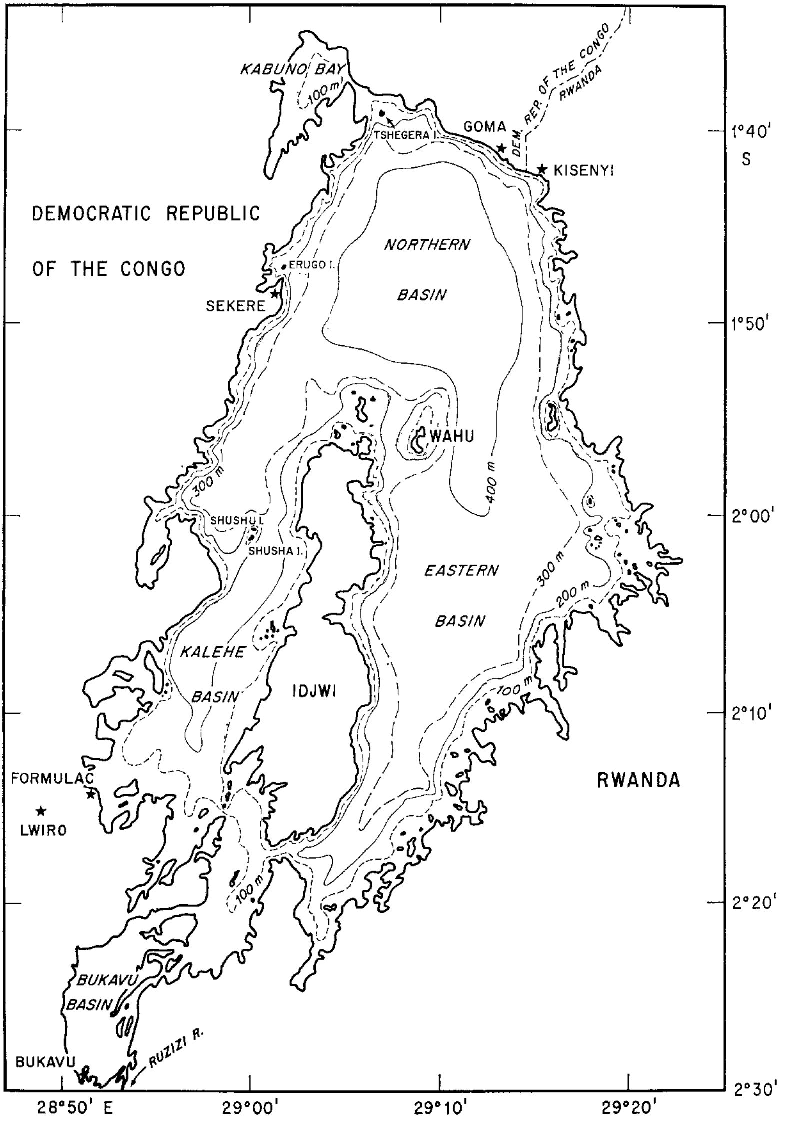


Fig. 1. Bathymetry of Lake Kivu, showing the Bukavu, Eastern and Northern Basins. The greatest water depth, almost 500 m, occurs in the central part of the Northern Basin

The only outlet of the lake is the Ruzizi River which, after a drop of 700 meters, flows into Lake Tanganyika.

Lake Kivu is well-stratified with a combination of halo- and thermoclines. Of significance in the present study is the boundary, at a depth of about 60 m, which subdivides the lake into layers. The top layer contains dissolved molecular oxygen, and the reducing bottom layer contains hydrogen sulfide in solution. The maximum content of dissolved S^{-2} is about 10 mg/l (KISS 1966). Some data on the water chemistry and temperature, from DEGENS *et al.* (1972), are shown in Table 1. It is noteworthy that the pH of the surface water is 9.2 and gradually decreases with depth to a value of 7 at 100 m. Determination of pH below this depth is difficult due to extensive degassing when the water samples are raised to the surface. It is also of note that in the H_2S zone Lake Kivu contains appreciable amounts of dissolved gases, principally carbon dioxide and methane; for instance, samples taken from a 400 meter depth will release ca. 1.5 liter of CO_2 and 0.5 liter of methane at atmospheric pressure. In the spring, the temperature of the surface water is around 24.5 °C. Below the O_2/H_2S interface, the temperature increases with depth, sometimes in a stepwise fashion, and reaches a maximum of almost 27 °C at the deepest point of the lake.

Table 1. *Water analyses Lake Kivu (Northern Basin)*

Depth	Ca	Mg	K	Na	Cl	SO_4	ΣCO_2 (m mole/ kg)	NH_4	P	Si	NO_3 + NO_2	Temp (°C)	pH
	(mg/l)							(µgA/l)					
Surface	4.8	87	97.4	121.6	55	23.8	12.5	18	.8	231	1.9	24.3	9.2
100 m	64.0	147	145.4	192.0	int.**	25.0	29.3	487	18.8	424	.38	22.6	7.1
200 m	83.1	182	178.8	244.6	int.	166.4	42.0	1314	32.7	428	.27	23.5	6.8*
350 m	110.9	394	315.2	465.2	int.	214.0	133.0	5460	53.2	1056	.48	25.7	6.6*
440 m	112.6	417	338.0	487.4	int.	220.0	121.0	7105	54.8	1226	.32	26.2	n.d.***

* Questionable ** analytical interference *** not determined

Problematics

The globules were first recognized when we passed Lake Kivu waters through membrane filters with a pore size of 0.45µ. We noticed the formation of a greyish or pale brownish film of particulate matter on the filters; these films were especially well developed from samples taken at 100 m and below 250 m depth. When 100 ml of water were passed through a filter area of 1.5 cm², the filter "cake" had a thickness of up to 40µ, as later ascertained by electron microscopy. We were puzzled that comparatively little particulate matter was present in the top 70 meters and between 150 and 250 meters of the water column. Initially, we attributed the films to the release of gases during filtration or the presence of oxygen, causing a change in pH and Eh which in turn would promote precipitation of minerals such as carbonates, hydroxides, or sulfides.

Methods of Analysis

After the sample material was brought to Woods Hole, we examined the films of particulate matter on the filter in detail, employing the following methods of analysis.

Electron Microscopy

The surface of a Millipore® filter was coated uniformly with a thin carbon film using a rotating stage (rotates 4 times/sec) after lightly shadowing with Pt-Pd from a 30° intake angle. The filter was then dissolved in a series of acetone baths, and the particulate material adhering to the carbon film was removed by bathing in strong oxidizing solutions such as chromic acid mixture. After rinsing in distilled water, a piece of replicated film was mounted

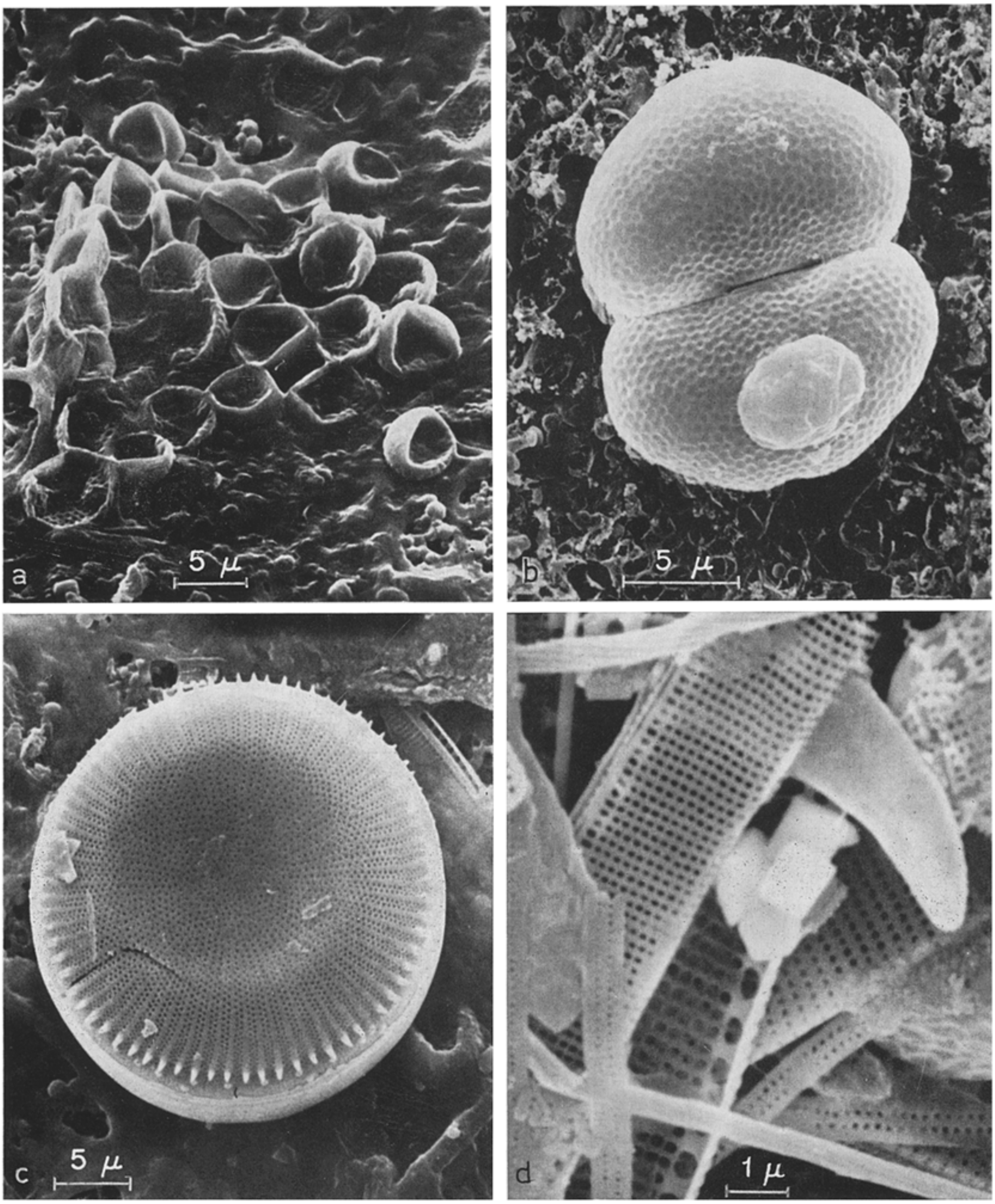


Fig. 2. Scanning electron micrographs of suspended particles in surface waters of Lake Kivu. Particles are collected on 0.45μ millipore filters. Pollen grains are shown in (a) and (b). Note the presence of some round particles ca. 1 micron in diameter (a). Typical diatoms are *Stephanodiscus astrea* (c) and various species of *Nitzschia* (d)

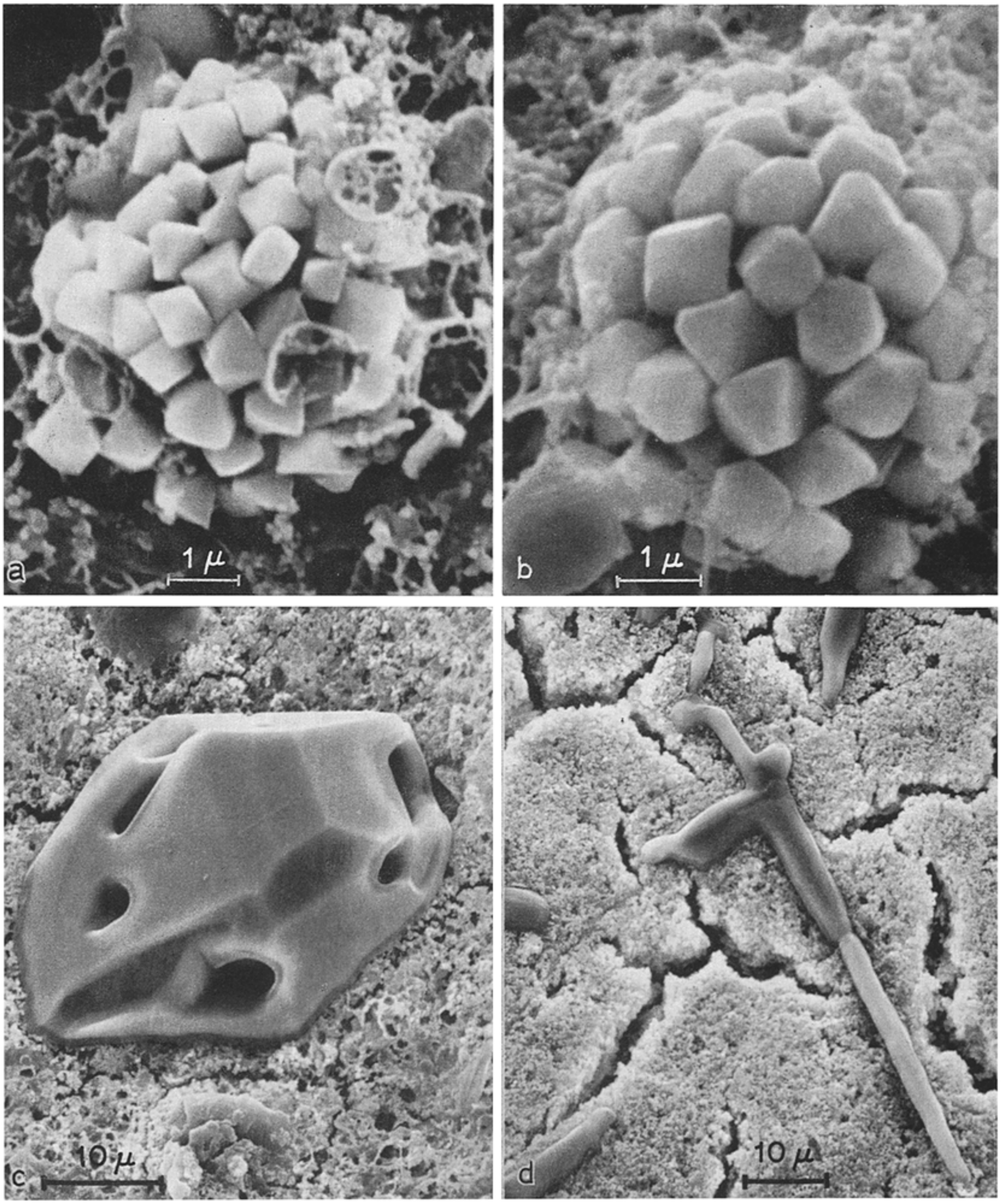


Fig. 3. Scanning electron micrographs of suspended pyrite framboids (a and b) which have been collected on millipore filters in the central part of the Northern Basin at a depth of 100 m. Pyrite framboids are always plentiful where sphalerite–containing globules are most abundant. Farrand (1970) shows the syntheses of iron sulfide spheres when passing hydrogen sulfide through cold aqueous solutions of ferrous sulfate. Most interesting is his observation that aerated water induces microcyst formation whereas de-aerated water inhibits the formation of discrete iron sulfide particles. For a recent review on the origin of framboids see Rickard (1970) and Roberts *et al.* (1969). Electron micrographs of filter cake showing a partial dissolved elemental sulfur crystal (c) and a layer almost entirely composed of sphalerite–containing globules (d). The topping on the filter cake is elemental sulfur

on a 150 mesh grid for transmission electron microscopy. Hitachi HU 11B and HU 12 electron microscopes were used for this investigation.

Scanning Electron Microscopy

The scanning electron microscope was used where it was necessary to study the detailed morphology of the particles on the membrane filter. A gimbal stage and an electronic film thickness monitor were used to deposit a thin (120 Å) Pt-Pd film on the specimens. We used an Hitachi SSM-2 scanning electron microscope and Hitachi TVF-2 electronic gimbal stage.

Energy-dispersive X-ray Analysis

Energy-dispersive X-ray analyses were conducted with a Kevex® system attached to our scanning microscope. Samples were coated with an approximately 120 Å thick gold film using a gimbal stage and were mounted on a specimen stage of the scanning microscope which was made exclusively of spectroscopic grade graphite. We used a detector with a 10 mm^2 area and a 3 mil thick Be-window. The analyses were performed at an acceleration voltage of 20 KV and counts were accumulated for 120 seconds.

X-ray Diffraction

X-ray diffractometer patterns were made of suspended matter from the water column and of samples from cores of the bottom sediment using a Norelco diffractometer with a graphite curved crystal monochromator. The small size of the suspended matter samples required the use of collodion film mounts (Gude and Hathaway 1961).

Other Techniques

For a further chemical and structural characterization of our samples, a series of standard analyses were performed by means of atomic absorption spectroscopy and infrared analysis. All material was examined under the optical microscope.

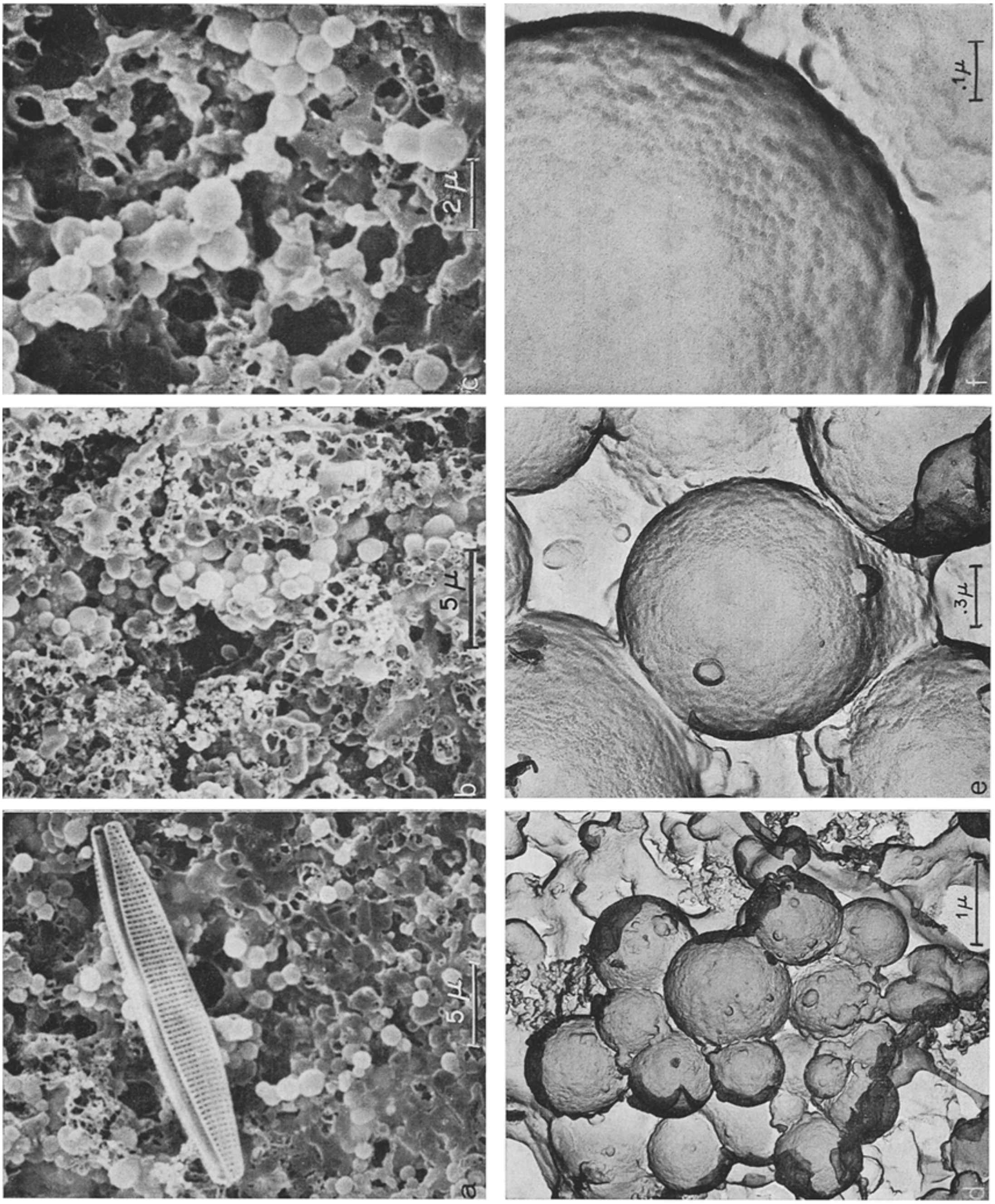
Observations

In the oxygenated zone, the suspended particles are principally diatoms. Most prominent is one *Nitzschia* species; next in abundance is *Coscinodiscus* sp., followed by *Stephanodiscus astrea*. In addition, scales of flagellates (golden brown algae) and pollen grains were found on the filters, as well as occasional round particles with diameters up to 1 micron (Fig. 2).

The composition of particulate matter changes abruptly in entering the H_2S zone. Organic remains become less abundant and thick deposits (up to 40 microns) of the spheres noticed in the oxygenated zone are laid down on the filter. The filter cake frequently is topped by a "frosting" with an amorphous appearance but occasionally exhibiting crystalline faces (Fig. 3). Under the optical microscope these cake-like layers are brown and isotropic; shrinkage cracks are abundant. Birefringent fibers (cellulose?), pollen grains, diatoms and remains of algae occur sporadically. It is of interest that the particle size of the spheres is often much smaller than the pore opening of the membrane filter. The close packing of the larger spheres and the disc- or boat-shape form of some of the diatoms acts as a kind of suprafilter, and particles as small as 0.1 micron may thus be retained. The bulk of the spheres (roughly 90%) range in size between 0.8 and 1 micron. It can also be seen (Fig. 4) that many of the spheres are empty. Since we find all stages from intact spheres to open rims, we conclude that the spheres are hollow and have a wall thickness in the order of 500 Å.

We were surprised to frequently find pyrite framboids of about 5 to 10 microns in diameter as suspended material within the H_2S zone. Microcrystallites contained in these framboids range between 0.5 and 1 micron in size (Fig. 3).

Fig. 4. Scanning electron micrographs (a—c) of a millipore filter of a sample from a hydrographic station near the island of Shushu (Fig. 1) at a depth of 70 m. Note the presence of spheres in all stages from intact globules to open rims. Carbon replicas of globules (d—f). The "blisters" visible on the globule surface (d and e) may have been produced by the leakage of gas entrapped inside the larger sphere; subsequent solidification through resinous material fossilized this event. The position of the sphalerite crystals (black spots) on the globule surface as well as the accretion pattern can be seen in (f)


a
5 μ
b
5 μ
c
2 μ
d
1 μ
e
.3 μ
f
.1 μ

Analytical Data

The material on the membrane filters was subjected to a number of analytical tests. Energy-dispersive X-ray analysis was performed on 10 different specimens and two representative runs are shown in Fig. 5. The spheres yield peaks only for zinc, sulfur, sodium and traces of silicon; the presence of gold is due to the plating of the specimens. Note that the spectrum lacks iron and cadmium, elements known to be frequently associated with zinc sulfide. The pyrite framboids exhibit the expected iron and sulfur lines plus traces of zinc and silicon. The latter two elements are "contaminants"; it should be remembered that the electron beam covers an area of about 500 Å^2. The crystal shown in Figure 4c has sulfur as the only major peak.

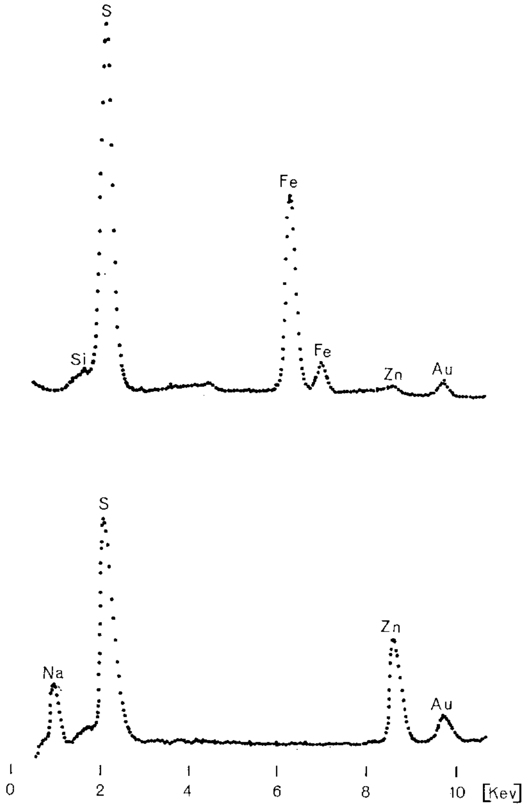


Fig. 5. Energy-dispersive X-ray analysis on individual suspended particles. Upper figure shows scan of a pyrite framboid (Fig. 3b); lower figure is the scanning pattern of a 500 Å^2 area of globule material (Fig. 3d)

In order to determine the nature of the spheres, direct studies of unstained dispersed filter cake material were made under the electron microscope (Fig. 6d–f). The spheres produce a high contrast image of the kind generally observed in organic material stained with a heavy metal. After treatment of the spheres with 2 N HCl at 50° for one hour the spheres become almost transparent (Fig. 6a), but upon shadowing they again reveal their spherical shape (Fig. 6b). We therefore conclude that the acid treatment only removes the contrast-producing material and does not affect the gross morphology of the spheres. Treatment with either 2 N NaOH or a chloroform/methanol mixture dissolves the spheres completely, leaving only a residue of electron dense particles 5 to 50 Å in size (Fig. 6c). No dissolution is observed by extracting the spheres with either hexane or benzene. The chloroform/methanol extract was subjected to gas chromatography. There is no evidence for the presence of hydrocarbons in the C_{13} to C_{30} range. When the column temperature is raised above 220 °C, pyrolysis of the sample takes place, as is evidenced by the sharp increase in the base line far above the normal bleeding curve observed in the region where hydrocarbons greater than C_{30} commonly occur. The infrared spectrum shows the presence of bonded and non-bonded phenolic hydroxyl (3300—3600 cm^{-1}), carbon-hydrogen stretching vibrations (2850—3000 cm^{-1}) and complex aromatic absorptions in the 1900—1500 cm^{-1} range. The lack of carboxyl absorption and the broad nature of the absorption bands indicates the presence of a complex polymeric resinous material with very little functionality other than hydroxyl.

X-ray diffraction analysis of the untreated filter cake reveals the presence of sphalerite, and one sample also showed reflections for elemental sulfur. The same sphalerite pattern is obtained by analyzing the residual particles of the NaOH-treated material (Fig. 7).

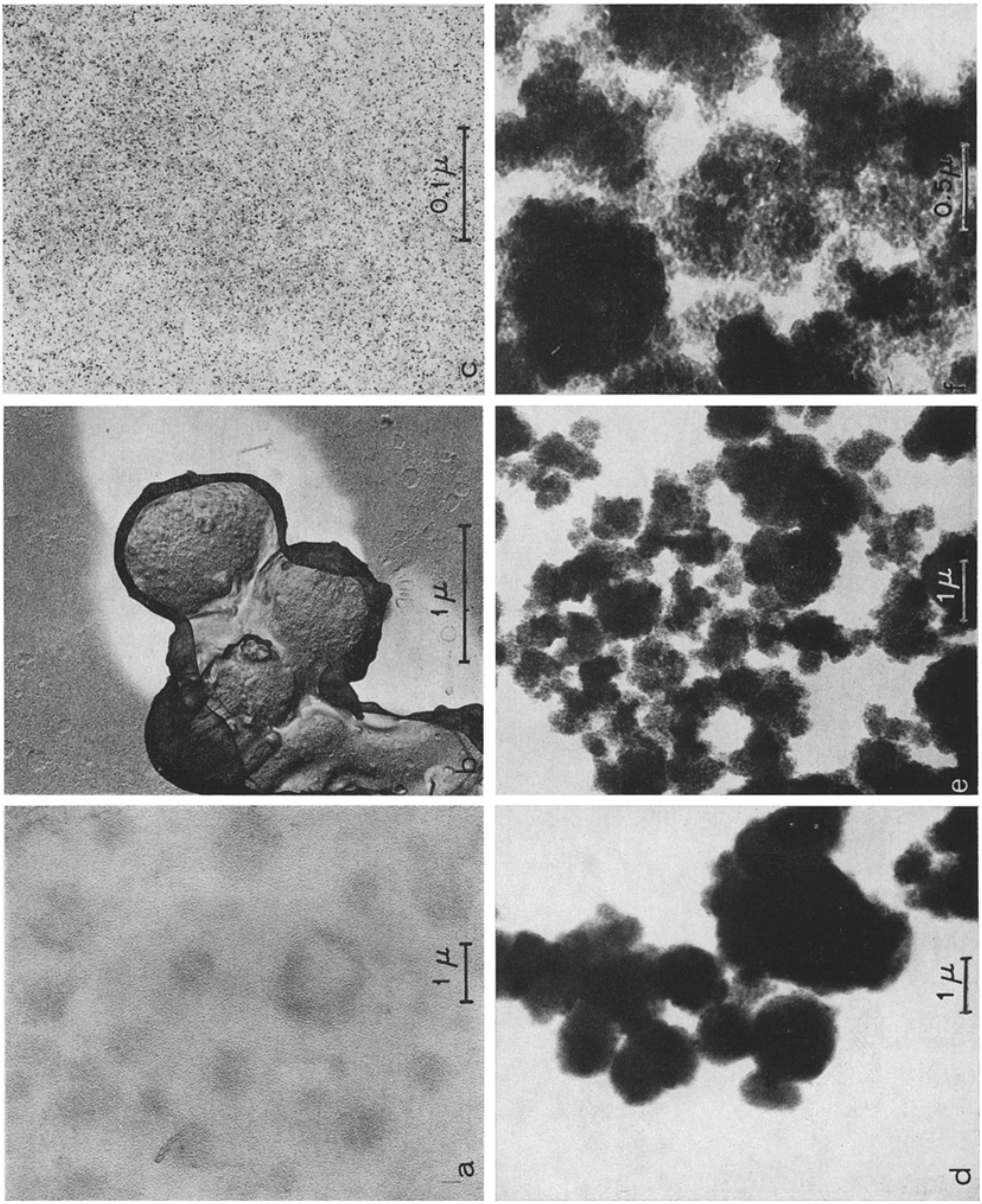


Fig. 6. Electron micrographs of globule material showing various analytical preparation stages described in the text

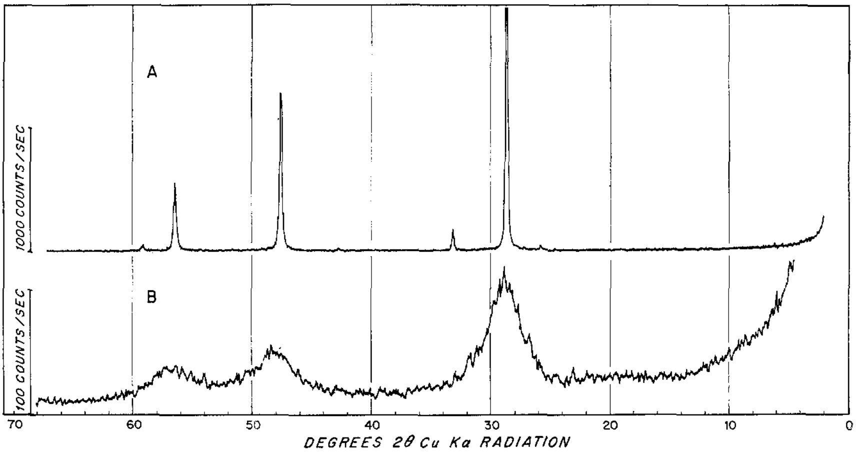


Fig. 7. X-ray diffractometer pattern of sphalerite. A well-crystallized standard sphalerite ground to less than 200 mesh (A). Sphalerite residue (Fig. 6c) of Lake Kivu globule material (B). Patterns were made using copper Kα radiation and a curved crystal monochromator at 2 degree 2 θ per minute scanning speed. For pattern (A), a scale factor of 2,000 and time constant of 0.5 sec was used; for pattern (B) scale factor equals 200 and time constant equals 2 sec

Table 2 gives the interplanar spacings and calculated unit cell dimensions (a_0) for the lines observed. The conclusion that a_0 does not differ from that of standard sphalerite is supported at the 95% confidence interval.

Table 2. *X-Ray Diffraction Data of Suspended Material*

2θ(CuKα) (in degrees)	d (in Å unit)	hkl	a_0* (calculated)
28.71	3.1094	111	5.3856
48.00	1.8953	220	5.3608
56.75	1.6221	311	5.3800
77.20	1.2357	331	5.3861

* $a_0 = 5.378$ Å ± .033

The crystallite size was determined by line broadening in the X-ray diffraction pattern using the Scherrer equation (Klug and Alexander 1954, p. 530):

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where: $K = 0.9$; $\lambda = 1.5418$; β = line breadth at half intensity in radians; and θ = diffracted angle of the line. The mean crystallite size (D) for three peaks was 24.6 Å. This calculated crystallite size agrees well with the observed size of the crystal particles (Fig. 6c) which ranges between 5 and 50 Å, corresponding to 1 to 10 unit cells of sphalerite.

Table 3. *Distribution of Zn, Cu, Mn, and Fe in Lake Kivu Waters (in ppm; water acidified with HCl)*

Depth (m)	No. of Samples	Zn (ppm)	Cu	Mn	Fe
0	4	0.04	0.03	—	—
50	8	0.09	0.05	—	0.08
100	5	4.79	0.13	0.40	0.39
150	2	0.09	0.03	0.33	—
200	3	0.13	0.11	0.32	0.27
250	3	7.10	0.08	0.35	0.24
300	5	1.73	0.12	0.38	0.19
350	5	3.95	0.09	0.37	0.20
400	3	3.51	0.17	0.35	0.19

The zinc, copper, manganese and iron content of Lake Kivu waters is shown in Table 3. High zinc values occur only where the globule material is plentiful, namely below approximately 250 m and at a 100 m water depth. The average Lake Kivu water thus has about 2 ppm zinc; that is, the lake contains more than 1 million tons of zinc in the form of sphalerite. It was therefore of interest to examine the sediments for possible zinc concentrations. Although the values determined are far above the normal zinc content for sediments of this kind, the concentrations of zinc are low in view of the enormous enrichment in zinc in the waters above (Table 4).

Table 4. *Iron, manganese, zinc, and copper concentrations in sediments of the Northern Basin, station 10 (in percent)*

Depth (cm)	Fe HCl sol.	Fe sulfide	Mn	Zn	Cu
5	2.17	2.24	0.033	0.041	0.004
25	1.28	4.32	0.069	0.008	0.005
60	2.40	2.62	0.035	0.009	0.003
90	1.98	1.78	0.013	0.009	n. d.
100	2.19	2.38	0.012	0.009	n. d.
128	0.76	4.02	0.006	0.008	0.002
135	2.02	2.68	0.052	0.010	0.003
220	1.95	4.49	0.023	0.014	0.005
270	2.18	6.87	0.025	0.004	0.002
320	1.68	3.54	0.012	0.010	n. d.

Discussion

The high zinc content in Lake Kivu is a result of hydrothermal events which fill up the lake basin from below with water. Since these hydrothermal waters have different salinities and temperatures than the waters already present in the lake, a temperature and salinity stratification (thermo- and haloclines) is established. On the basis of temperature diffusion coefficients, it has been calculated (Degens *et al.* 1972) that the role of water discharge is so great that the whole lake is filled up in about 100 years. The stratification is caused by the formation of convecting layers due to the applied heating from the lake floor.

The zinc originates in the rock formation through which the hydrothermal solutions pass before being discharged into the lake. In other words, leaching phenomena preferentially remove zinc and a few other heavy metals such as iron and manganese from the wall rock. On the basis of stable oxygen isotope studies (Degens *et al.* 1972) the hydrothermal solutions have been found to be local rain waters which disappear underground where they become "activated" with CO_2 and H_2S. After having leached salts and heavy metals from the rocks through which they pass, they emerge in the form of hydrothermal springs. The geochemical process is thus of the same kind that is at work in the hot brine area of the Red Sea (Degens and Ross 1969). It is noteworthy that Lake Kivu sediment cores give clear evidence not only that such processes are proceeding today, but that within the last 12,000 years at least three major hydrothermal events are recorded which coincide with pluvial times.

The origin of the resin globules can best be explained by assuming that a degassing of water samples at depth produced tiny gas bubbles about 1 micron in size which acted as scavengers of organic material at the phase boundary. The ability of foams and bubbles (colloidal surfactants) to collect distinct organic molecules has been extensively demonstrated by Shinoda and co-workers (Shinoda *et al.* 1963). Dissolved organic matter can also be extracted by passing a stream of bubbles through sea water (Sutcliffe *et al.* 1962). The organic matter content in Lake Kivu is high (14—41 mg/l). As is the case for zinc, a large part of the organic content has been contributed by the hydrothermal "jets." Lignin degradation products are assumed to be the ultimate source of the resin.

Certain phenolic compounds have an affinity for the water/gas boundary surface and introduce solidification in the form of a resinous membrane. Zinc readily coordinates to the hydroxyl groups displayed at the newly created solid surface; most probably for structural reasons, other heavy metals cannot become part of the metal-organic complex. Selective chelating resins are known which collect gold, platinum metals, and mercury to the exclusion of other metals (Law 1971). Such resins are a promising tool for the removal of certain metal pollutants, and may find other commercial applications in concentrating valuable metals.

In the presence of hydrogen sulfide, the zinc-organic complex is "metasomatically" replaced by sphalerite. Since the crystallite size falls in the range of 5 to 50 Å, corresponding to 1 to 10 unit cells, we believe that epitaxial growth processes are involved. This would be comparable to mineralization processes in biological systems.

The amount of zinc present in the sediments is small in view of the high zinc concentration in the waters above. We thus assume that the sphalerite-containing globules are buoyant and, for the most part, will end up in the surface waters rather than being deposited in the sediments. The introduction of such high zinc concentrations to surface waters will undoubtedly have a severe impact on the biological population. The toxicity of zinc—even in a particulate form—on fishes is a well-studied subject (LLOYD 1960; WILLIAMS and MOUNT 1965). A review of zinc in biological systems has been prepared by VALLEE (1955) and MARTIN *et al.* (1971). Part of the zinc present in surface waters may be removed by specific (e. g. synthesis of zinc-containing enzymes) and non-specific uptake and eventually settle as tripton to the lake floor. The remainder will be swept via the Ruzizi River into Lake Tanganyika. Studies of the kind performed in the present investigation, involving millipore filtration of the waters of Lake Tanganyika will most likely recover sphalerite-containing globules and attest to the former hydrothermal activity in Lake Kivu.

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