these observations can be explained by introducing a "core" with a radius between 600 and 800 km, in which S waves are highly attenuated [Q of about 100 or less (*8*)]. The P-wave velocity within this zone may be slightly lower than that in the mantle. The maximum allowable velocity decrease for P waves is about 0.3 km/sec. These limiting values are found to be relatively insensitive to assumed velocities in the mantle.

Seismic wave attenuation is strongly dependent on temperature, showing a rapid increase with increasing temperatures, and a sharp increase with the onset of melting (*9*). Thus, a high temperature approaching the solidus temperature in the lunar interior may account for the lack of S-wave transmission indicated by the seismic data. A silicate interior would have a solidus temperature between 1450° and 1650°C at a depth of 1000 to 1100 km. This model is in substantial agreement with several thermal models recently proposed by Toksöz *et al.* (*10*). Partial melting of silicate material is considered to be a possible explanation of the zone of low Q values and low seismic velocities in the upper mantle of the earth (*9, 11*). Thus, partial melting of a few percent of the material may explain the present data. A completely molten core of the size indicated is not likely, however, because it would require a decrease of the P-wave velocity by more than the value of 0.3 km/sec obtained in our preliminary analysis. Other possibilities, such as increased volatiles in the deep interior of the moon, cannot be ruled out at present.

The possibility of a very dense, molten, metallic core similar to that of the earth is ruled out by considerations of both moments of inertia and seismic wave velocities. The radius of about 700 km is too large for such a core.

Several observations suggest that there is a gradual transition from the solid material of the lower mantle to the material of different physical properties below: (i) the spectrum of S waves from moonquakes appears to shift toward lower frequencies with increasing depth for sources of approximately equal strength; (ii) the direct S waves recorded at station 15 from the large impact are abnormally small compared with the P waves; and (iii) no signals corresponding to reflections from a well-defined boundary at a depth of 1000 km have yet been observed.

The suggestion of a partially molten zone at great depth has an important bearing on the question of the focal mechanisms of moonquakes. The recognized categories of moonquake signals now number 41, corresponding to 41 different active focuses. Moonquake signals from numerous other active zones are too weak to be analyzed in detail. Moonquakes occur with a monthly periodicity, strongly suggesting that they are induced by lunar tides (*4*). The moonquake focuses for which depths have been determined (18 cases) are concentrated in the depth range from 800 to 1000 km. The localization of moonquake activity in a zone 200 km thick, falling immediately above the zone of high attenuation, may be explained as resulting from one or more factors: (i) reduced rigidity in the zone of high temperature or partial melting would tend to concentrate the dissipation of tidal energy at great depth; (ii) weak convective motions beneath a thick, rigid mantle might generate deep moonquakes without the surface manifestations associated with terrestrial plate tectonics; and (iii) fluids injected into the moonquake zone from below, under the influence of tides, would reduce the effective friction along zones of weakness, or weaken the silicate bond, leading to dislocation.

Making an analogy with the earth, we may consider the lunar lithosphere—the relatively rigid outer shell of the moon—to be about 1000 km thick. The central core of the moon would be equivalent to the asthenosphere (the low-velocity zone) of the earth.

Y. Nakamura, D. Lammlein
G. Latham, M. Ewing, J. Dorman
Earth & Planetary Sciences Division,
University of Texas Medical Branch,
Galveston 77550
F. Press, N. Toksöz
Department of Earth and
Planetary Sciences,
Massachusetts Institute of
Technology, Cambridge 02139

References and Notes

1. G. Latham *et al.*, *Moon* **5**, 272 (1973).
2. The Apollo 12 and Apollo 14 stations together occupy a corner of the triangle.
3. M. N. Toksöz *et al.*, *Moon* **4**, 490 (1972).
4. G. Latham *et al.*, *Science* **174**, 687 (1971).
5. Station 14 data were not used because the long-period vertical component (LPZ) seismometer of this station was inoperative, adding uncertainty to the initial P-wave measurement.
6. G. V. Latham *et al.*, *Science* **167**, 455 (1970); *ibid.* **170**, 620 (1970).
7. This interpretation is based only on the arrival time of the wave train. No well-defined surface-reflected phases have previously been identified, probably because they are completely obscured by the presence of the direct-phase wave train. Thus, surface-reflected compressional waves are not identifiable on the same record.
8. The quality factor Q is used to specify the attenuation of energy in a vibrating system; $2\pi/Q$ is the fractional loss of energy per cycle of vibration of the system.
9. D. D. Jackson and D. L. Anderson, *Rev. Geophys.* **8**, 1 (1970).
10. M. N. Toksöz, S. C. Solomon, J. W. Minear, D. H. Johnston, *Moon* **4**, 190 (1972).
11. S. Solomon, *J. Geophys. Res.* **77**, 1483 (1972).
12. Supported by NASA contract NAS 9-13143. Earth & Planetary Sciences Division, Marine Biomedical Institute, Contribution No. 17.

29 March 1973

■

Methane in Lake Kivu: New Data Bearing on Its Origin

Abstract. *Lake Kivu, an African rift lake, contains about 50 cubic kilometers of methane (at standard temperature and pressure) in its deep water. Data resulting from two recent expeditions to the lake and a reevaluation of earlier data suggest that most of the methane was formed by bacteria from abiogenetic carbon dioxide and hydrogen, rather than being of volcanic origin or having formed from decomposing organic matter.*

Lake Kivu is the westernmost and most elevated of the string of rift lakes which curves through east-central Africa. It has a surface area of about 2400 km^2 and a maximum depth just under 500 m. The lake's peculiar hydrochemistry was first recognized by Damas (*1*), who discovered large quantities of dissolved gas in the deep water. The gas was later identified as consisting principally of carbon dioxide [up to 1.4 liters at standard temperature and pressure (STP) per liter of water] and methane [up to 0.37 liter (STP) per liter of water] (*2*). The lake is anoxic below 50 m and both temperature and salinity increase stepwise with depth, which suggests the existence of convecting layers (*3*). The total temperature increase below 50 m is about 3.2°C, and the content of Na, Mg, K, and Ca increases from 311 to 1355 mg/liter. The consequent density stratification of the water column severely restricts vertical mixing and the deep water acts as a trap for solutes. The large accumula-

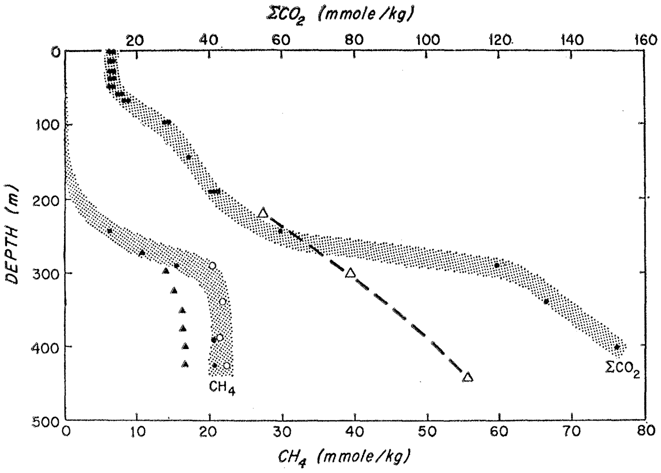

Fig. 1. Concentrations of dissolved methane and inorganic carbon in Lake Kivu water. (Open circles) Shipboard determinations, this work; (filled circles) laboratory determinations, this work; (filled triangles) methane concentrations determined by Schmitz and Kufferath (*2*); (open triangles) solubility of methane (*5*).

tion of methane in the lake is unique, and various explanations for its origin have been advanced in the past. As a result of two expeditions to Lake Kivu in 1971 and 1972 we now present evidence which refutes some earlier proposals and points toward an origin for the gas which has hitherto not been seriously considered (*4*).

Figure 1 shows measured concentrations of methane and total dissolved inorganic carbon (ΣCO_2) at various depths in the lake. Our analyses of methane include preliminary shipboard analyses made with a portable gas chromatograph and laboratory analyses performed on samples stored for several weeks. All measurements were made on samples brought to the surface at in situ pressure and kept under pressure until the time of analysis. Also shown in Fig. 1 are earlier results obtained by Schmitz and Kufferath (*2*), and the solubility of methane in water at pressures corresponding to the depths shown (*5*). The shaded trend shown for the methane concentrations at depths shallower than 240 m is based on semiquantitative observations that indicated the presence of only minor amounts of methane above 200 m, but distinct traces of it at least up to the bottom of the oxygenated surface layer. If the difference between our methane data and those of Schmitz and Kufferath is real, it indicates a substantial addition of methane in less than 20 years (about 20 percent of the total). It is interesting to note that data taken with reversing thermometers in 1935 and 1936 by Damas (*1*) and in 1971 and 1972 by us show a temperature increase during the intervening 35 years of 0.2° to 0.3°C throughout most of the water column below 50 m. The highest temperature measured by us was 25.85°C at 460 m.

The solubility curve in Fig. 1 indicates that the water is nowhere saturated with methane, but that deep water being raised to the surface becomes oversaturated with methane at about 200 m. Effervescence is, in fact, observed in all samples brought up from depths exceeding 100 m unless they are kept at their in situ pressure.

We estimate the total volume of methane at about 50 km^3 (STP) (*6*). The total water volume of the lake is 580 km^3. In searching for an explanation of such an unusual gas accumulation we have, in addition to reevaluating earlier evidence, carried out the following analyses: $\delta^{13}C$ measurements (*7*) on methane, dissolved inorganic carbon, sedimentary organic matter, and recent plankton; radiocarbon measurements on two mixtures of methane and carbon dioxide released from deepwater samples and on organic matter of sediment samples; gas chromatographic checks for methane in hot springs in the immediate vicinity of the lake; and gas chromatographic analyses of deep water for higher hydrocarbons.

Neither gas nor water discharged from two hot springs located ~ 0.2 and 3.2 km, respectively, from the lake shore was found to contain any methane. Two gas samples released from deep water (242 and 290 m) had ratios of methane to ethane of 530 and 650 by weight and minor amounts (0.01 to 0.1 percent) or traces of C_3 to C_6 hydrocarbons. The carbon isotope measurements are summarized in Table 1.

Since Lake Kivu is situated in an area of active volcanism and methane is a common volcanic exhalation (*8*), a volcanic origin of the methane in the lake has been repeatedly considered (*2, 9*). However, neither we nor earlier workers (*2, 10*) were able to detect methane in emanations around Lake Kivu; nor can the higher hydrocarbons associated with the methane in the lake be attributed to volcanism, as none of these have ever been found in truly volcanic emanations. For these reasons we consider a volcanic origin of the methane very unlikely. There is little doubt, on the other hand, that much of the carbon dioxide has its origin in subaqueous discharges within the lake (*2*).

In considering a biological or early diagenetic origin of the methane, it is useful first to compare the amounts of methane with the amount of available organic carbon. We presently find an average of about 40,000 liters of methane (STP) over each square meter of sediment in the deeper parts of the lake. By comparison, the average amount of organic carbon in the top 30 cm of sediment, which represents deposition over the last 1000 years, is about 14 percent of the dry weight (*4*). If an equivalent amount of carbon were converted to methane, it would yield only 12,000 liter/m^2. Similarly, on the basis of primary productivity, the bacterial methane production from decomposing plankton has been estimated to be 46 liters m^{-2} year^{-1} or less (*4*). Thus, even if no loss of methane occurred (in fact there are diffusional, advective, and oxidative losses), it would take about 1000 years to accumulate the present amount of methane from this source alone. Estimates of the lake's water and salt budgets (*4*) and of the turbulent transport between the convecting layers make it appear very unlikely that the residence time of any substance dissolved in the deep water can be of the order of 1000 years. The calculated residence time for sodium, probably the most conservative element dissolved in the lake, is 350 years. Thus, on the basis of these considerations alone, it appears that decomposing plankton and other organic matter cannot be the sole or even the main source of the methane, as had been concluded by Schmitz and Kufferath (*2*). This conclusion is underscored by the results of radiocarbon measurements on two mixtures of carbon dioxide and methane from the deep water (Table 1). Both measurements indicate that less than 10 percent of the carbon in the mixture is "modern." Even if all of this were in the methane, the average methane would be far in excess of 1000 years old; in fact the data are more consistent with a higher ^{14}C activity in the

Table 1. Carbon isotope data for Lake Kivu samples.

Material	Samples (N)	$\delta^{13}C$ (per mil)	^{14}C age (years)	Modern carbon (%)
Methane below 250 m	4	− 45 ± 1.5		
ΣCO_2 below 250 m	3	− 2 ± 1		
Plankton	3	− 21 ± 0.5		
Organic carbon, surface sediment	2	− 25 ± 0.5		
Mixture of methane (40 percent) and carbon dioxide (60 percent) from 415 m	1	− 19.3 ± 0.1	22,000 ± 4,000	7 ± 4
Mixture of methane (35 percent) and carbon dioxide (65 percent) from 395 m	1	− 16.5 ± 0.1	20,500 ± 2,000	8 ± 3

carbon dioxide, probably originating from anaerobic oxidation of recent organic matter. It is possible, of course, that the surface water of the lake is not in equilibrium with the atmosphere with respect to ^{14}C. However, radiocarbon dates of organic matter in the sediment suggest that any deviation from equilibrium must fall far short of being able to account for the low ^{14}C activity of the methane if the gas had formed primarily from recent plankton. Examples of sediment ages are 6200 ± 215 years at a depth of 175 cm and 10,670 ± 280 years at 350 cm (*4*).

The northern basin of the lake contains up to 500 m of sediments, which may date back to the late Pliocene (*4*). The traces of C_5 and C_6 hydrocarbons (pentane and hexane) detected in the water should probably be attributed to thermal decomposition of older sediments, as microbial processes in sediments are known to form only traces of C_2 to C_4 hydrocarbons (*11*). However, the very high ratio of methane to the other hydrocarbons (> 300), the very young geological age of the sediments, and the relatively high ^{13}C content of the methane strongly argue against a thermal origin for the bulk of the methane (*12*). Methane in natural gases of Pliocene or younger age very rarely has a $\delta^{13}C$ greater than −55 per mil, the majority of values being around − 65 per mil; and the higher the methane content of the gas, the lower the $\delta^{13}C$ of the methane. Isotope exchange with the carbon dioxide might have raised the ^{13}C content of the methane. The observed difference between the carbon isotope ratios of the two gases could be explained by equilibration at a temperature of about 130°C (*13*). Heat flow measurements (*4*) suggest that such temperatures are not likely within the sediments, nor is it to be expected that the bulk of the CO_2, which is of volcanic origin and appears to escape along localized vents, was in intimate contact, deep down in the sediments, with methane formed there.

A methane source which has not been seriously considered thus far is bacterial production from abiogenetic substrates. The deep parts of the lake contain a rich fauna of methane-producing bacteria (*4*) which utilize carbon dioxide and hydrogen (*14*). In the normal, natural situation both of these gases are supplied by a variety of microorganisms during the breakdown of organic matter. We suspect that in Lake Kivu the bacteria also utilize carbon dioxide and hydrogen derived from inorganic processes to form methane. Carbon dioxide is available in great quantities, most of it supplied by the volcanic emanations. Hydrogen may also enter the deep water in this way, and two facts make it appear likely that inorganic hydrogen is available. Gas escaping from the lava lake of Nyiragongo volcano, situated on the northern shore of Lake Kivu, contains 1 to 2 percent of free hydrogen (*8*), and the formation of heavy-metal sulfides in the lake liberates hydrogen. Analyses of sediment cores show that the recent sediments contain an average of 10 to 15 percent sulfides on a dry-weight basis.

The utilization of abiogenetic substrates in the production of methane can account for all the puzzling facets of the large methane accumulation in the lake. Some of these were mentioned above. It also explains the relatively high ^{13}C content of the methane, about 20 per mil higher than normal. If the source carbon has a $\delta^{13}C$ near zero instead of near −20 per mil, as does organic matter, the usual source in natural situations (Table 1), the resulting methane should also have a $\delta^{13}C$ about 20 per mil higher than that normally encountered. The inferred origin also resolves the problem posed by the relatively low phosphorus content, compared to carbon and nitrogen, of the methane-loaded water, which had already been noted by Schmitz and Kufferath (*2*). If decomposing plankton were the only source of the methane, as they proposed, then an amount of phosphorus should be liberated which is far in excess of that found in the water. They suggested that it is precipitated and accumulates in the sediment. However, none of our sediment analyses revealed phosphate in remotely adequate amounts, nor could any reduced forms of phosphorus be detected.

Based on the ^{13}C and ^{14}C data, it appears that only a minor fraction—certainly less than 20 percent—of the methane contains carbon originating in the decomposition of plankton. If the differences between the methane concentrations measured by Schmitz and Kufferath (*2*) and those measured by us are real, they suggest a growth of the reservoir of about 1 percent per year. The rise in temperature observed for the last 35 years could be accounted for by the energy released during the formation of that much methane from carbon dioxide and hydrogen. The process liberates 60 kcal/mole, only a fraction of which is utilized by bacteria. The methane content of the deep water may have risen by 4 mmole/liter in 17 years, corresponding to the release of 240 cal/liter. If half of this had been available for heating the water, the temperature would have risen by 0.12°C in 17 years, an average yearly increase of the same magnitude as the observed increase of 0.2° to 0.3°C between 1935–1936 (*1*) and 1971–1972 (*4*).

W. G. DEUSER
E. T. DEGENS
G. R. HARVEY
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543
M. RUBIN
U.S. Geological Survey, Washington, D.C. 20242

References and Notes

1. H. Damas, *Verh. Int. Ver. Theor. Angew. Limnol.* **8** (No. 3), 51 (1937); *Explor. Parc. Nat. Albert Mission H. Damas 1935–1936* (1937).
2. D. M. Schmitz and J. Kufferath, *Bull. Seances Acad. Roy. Sci. Colon.* **1**, 326 (1955).
3. J. S. Turner and H. Stommel, *Proc. Nat. Acad. Sci. U.S.A.* **52**, 49 (1964).
4. A detailed account of the results of the first expedition is given by E. T. Degens, R. P. Von Herzen, H. K. Wong, W. G. Deuser, H. W. Jannasch, *Geol. Rundsch.* **62**, 245 (1973).
5. O. L. Culberson and J. J. McKetta, Jr., *Petrol. Trans. Amer. Inst. Min. Metall. Eng.* **192**, 223 (1951).
6. The volume of methane dissolved in Lake Kivu roughly equals the natural gas consumption of the entire United States in 1 month during 1970.
7. The per mil enrichment in ^{13}C relative to the standard Pee Dee belemnite (PDB) carbonate is

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{\text{sample}}}{(^{13}C/^{12}C)_{\text{standard}}} - 1\right] \times 1000$$

8. D. E. White and G. A. Waring, *U.S. Geol. Surv. Prof. Pap. 440-K* (1963).

9. K. Burke, *Nature* **198**, 568 (1963); G. Mueller, *ibid.*, p. 569; H. Tazieff, *ibid.* **200**, 1308 (1963); K. Burke, *ibid.*, p. 1308.
10. M. Chaigneau, H. Tazieff, R. Fabre, *C.R. Acad. Sci. Paris* **250**, 2482 (1960).
11. J. B. Davis, *Petroleum Microbiology* (Elsevier, Amsterdam, 1967), p. 125.
12. U. Colombo, F. Gazzarrini, G. Sironi, R. Gonfiantini, E. Tongiorgi, *Nature* **205**, 1303 (1965); W. M. Sackett, *Amer. Ass. Petrol. Geol. Bull.* **52**, 853 (1968).
13. H. Craig, *Geochim. Cosmochim. Acta* **3**, 53 (1953); Y. Bottinga, *ibid.* **33**, 49 (1969).
14. M. P. Bryant, E. A. Wolin, M. J. Wolin, R. S. Wolfe, *Arch. Mikrobiol.* **59**, 20 (1967).
15. We thank Dr. P. Kunkel for valuable advice and logistics support during the expeditions, and E. H. Ross and W. G. Steinhauer for laboratory assistance. Supported by NSF grants GA-19262 and GA-30641. Contribution No. 2985 from the Woods Hole Oceanographic Institution.

26 January 1973; revised 13 April 1973 ■

Oil Spills: Measurements of Their Distributions and Volumes by Multifrequency Microwave Radiometry

Abstract. *Aircraft-borne multifrequency passive microwave observations of eight marine oil spills revealed that, in all cases, over 90 percent of the oil was confined in a compact region comprising less than 10 percent of the area of the visible slick. These measurements show that microwave radiometry offers a means for measuring the distribution of oil in sea-surface slicks; for locating the thick regions; and for measuring their volumes on an all-weather, day or night, and real-time basis.*

Mounting concern is being voiced by the public and by officials affiliated with governmental agencies over the ever-increasing number of marine oil spills and the resulting pollution. Before appropriate corrective action can be taken, information on the nature, thickness, areal extent, direction, and rate of drift of the particular oil spill must be promptly obtained. The spreading of sea-surface oil spills is not uniform, nor is it without limit (*1*). Regions with thicknesses of a millimeter or more are formed which contain most of the oil, and these areas are surrounded by very much thinner and larger slicks. Reliable information on the thickness of the oil film is needed in order that the volume of the slick may be estimated. A knowledge of the volume of oil is essential for litigation and damage claims resulting from major oil spills as well as for an assessment of the impact of the spill on marine life and environment. Perhaps most important, a knowledge of the distribution of the oil and the location of those regions containing the heaviest concentration of oil is necessary for effective confinement, control, and cleanup.

Microwave radiometry offers a unique potential for the determination of oil slick thicknesses greater than about 0.05 mm. The apparent microwave brightness temperature is greater in the region of an oil slick than in the adjacent unpolluted sea by an amount depending upon the slick thickness. In effect, the oil film acts as a matching layer between free space and the sea, enhancing the brightness temperature of the sea (*2*). As the thickness of the oil film increases, the apparent microwave brightness temperature at first increases and then passes through alternating maxima and minima due to the standing-wave pattern set up by the sea surface (*3*). The maxima and minima occur at successive integral multiples of a quarter of the observational wavelength in the oil. By using two or more frequencies, thickness ambiguities introduced by the oscillations may be removed and the film thickness determined for a wide range of thicknesses (*4*).

A series of eight controlled oil spills was conducted during the period from August 1971 through August 1972 in cooperation with the NASA–Wallops Island Station, the Virginia Institute of Marine Science, and the U.S. Coast Guard to investigate the possibility of determining oil slick thickness with passive microwave radiometry. The spills, of from 760 to 2380 liters (200 to 630 gallons) of either No. 2 fuel oil or No. 4 or No. 6 crude oil, were conducted in accordance with the guidelines established by the Environmental Protection Agency for the discharge of oil for research purposes (*5*). All of the spills were conducted in relatively calm sea conditions with swell of less than 2 m and surface winds of less than 10 m/sec. The oil was transported to the ocean test site, about 10 miles (16 km) east of Chesapeake Light Tower off the east coast of Virginia, in 190-liter drums. The drums were unloaded, collected, and emptied from small rubber boats so as to obtain as nearly as possible an undisturbed point release.

Figure 1 shows a series of drawings traced from color photography of the 11 July 1972 oil spill. This spill consisted of 2380 liters of No. 2 fuel oil dyed with an oil-soluble red dye (*6*). The dye allowed the thick regions of oil to be easily identified visibly. The oil formed a well-defined thick region surrounded by a very much larger and thinner region. In situ thickness measurements (*7*) showed the oil to be

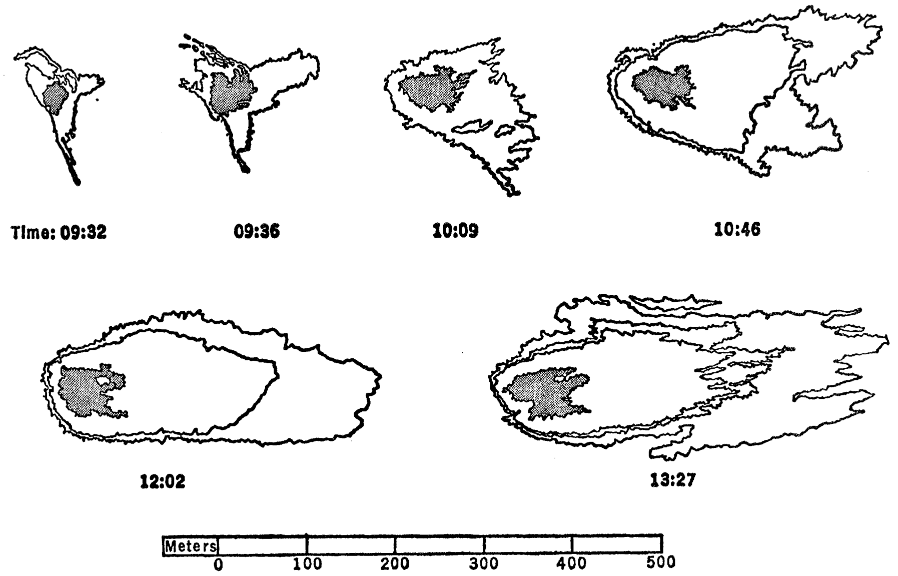

Fig. 1. The drawings are tracings of color photography of the oil slick resulting from a controlled oil spill of 2380 liters of No. 2 fuel oil. The oil had been dyed red in order to allow the thick regions of oil to be identified visibly. The outer line in each drawing represents the extreme edge of the visible slick, the next inner line is the region of color fringing when visible in the photograph, and the crosshatched area is the region of thickest oil.