Table 1 Average Abundances of Mn, Fe, Ni, Co and Cu in Ferro-manganese Oxide Concretions from the Atlantic, Pacific and Indian Oceans (in weight %)

	Average	Atlantic* Maximum	Minimum	Average	Pacific† Maximum	Minimum	Average	Indian‡ Maximum	Minimum
Mn	16.18	37.69	1.32	19.75	34.60	9.87	18.03	29.16	11.67
Fe	21.82	41.79	4.76	14.29	32.73	6.47	16.25	26.46	6.71
Ni	0.297	1.41	0.019	0.722	2.37	0.161	0.510	2.01	0.167
Co	0.309	1.01	0.017	0.381	2.58	0.052	0.279	1.04	0.068
Cu	0.109	0.884	0.022	0.366	1.97	0.034	0.223	1.38	0.029

* This work.   † Data from Cronan and Tooms[10], recalculated on a detrital free basis.

From the maximum and minimum values of the elements determined in Table 1, it is apparent that the Atlantic concretions are equally, or more, variable in composition than are those from the Pacific and Indian Oceans. Regional variations in their composition are, however, less distinct than in the other two oceans. Manganese and iron vary inversely and are most abundant in different areas of the South Atlantic, Fe in the south-west and Mn in the south-east. Each varies irregularly in the North Atlantic, although there are zones of Mn enrichment associated with low Fe values in mid-latitudes on either side of the mid-Atlantic Ridge. In the equatorial area, low Mn values are associated with intermediate to high Fe concentrations. Nickel, copper and cobalt tend to follow manganese.

The compositional differences between Atlantic nodules and those from the Pacific probably result from a number of factors. Their less distinct regional variations in composition can perhaps, in part, be related to the more uniform pattern of sedimentation in the Atlantic than in the Pacific, coupled with the more restricted incidence of submarine vulcanism in the former. The lower Mn/Fe ratio and minor element contents of the Atlantic concretions may be a result of the relatively greater importance of continentally derived material in the Atlantic. Manheim[9] has shown that in view of the greater amounts of Fe relative to Mn available in continental runoff and in a releasable form in terrigenous particulate material, iron tends to dominate over manganese in nodules with increasing continental influence.

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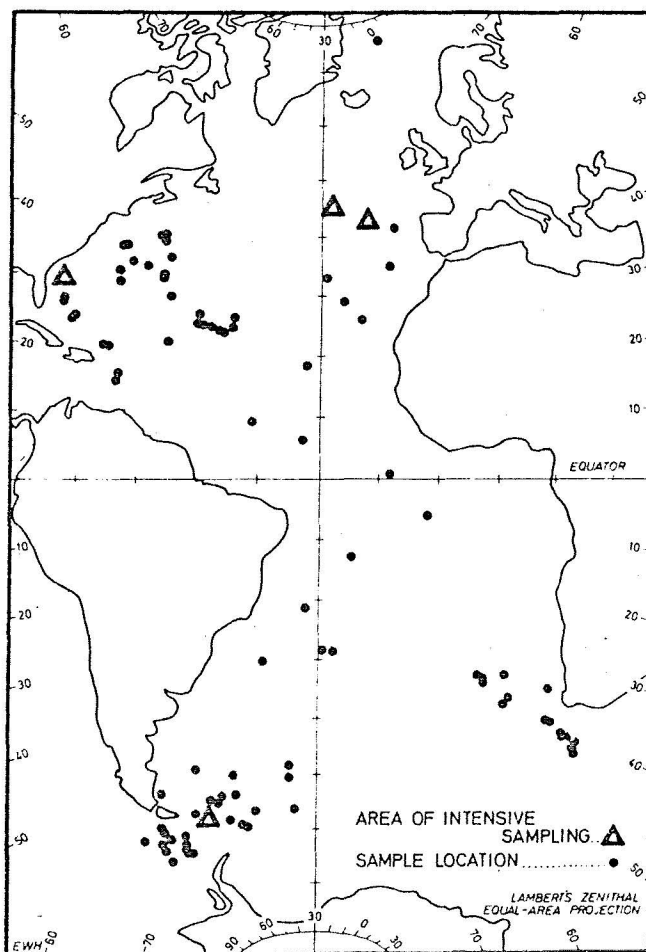

Fig. 1 Locations of manganese nodule sampling stations in the Atlantic Ocean.

Preliminary Heat Flow Data from Ghana

IN view of the absence of heat flow data from Africa, particularly north-west Africa, we report preliminary evidence for normal Precambrian shield or platform heat flow in Ghana.

Temperature measurements were made early in 1969 in four holes located at (Fig. 1) Nasia (1), Tibogona (2), and Yendi (3) in northern Ghana and at Prang (4) in central Ghana. Depths of measurements range from 300 to 500 m. The holes were drilled in the Volta basin for hydrogeological purposes as part of the USSR aid programme to Ghana. The holes were completely cored with various sizes of drill bits, but no hole was less than 20 cm in diameter. We checked the possibility of the existence of convection currents within the

borehole, which would cause an abnormally low temperature gradient; the internal and external evidence suggests that if they are present they are of little significance. This is in agreement with the findings of Diment[1] and Gretener[2], who, after detailed measurements in wells drilled for oil exploration purposes, concluded that in large diameter boreholes where convection cells exist they are only a few borehole diameters long. This has the effect of reducing the accuracy of the temperature measurement at a point by anything up to an order of magnitude of the precision of the thermometer. The equipment used was of the general type described by Beck[3] with a precision of 1 cK (0.01° C); we therefore feel that our temperature measurements at a point are accurate to better than 10 cK (0.1° C). Temperature profiles with depth are shown in Fig. 2.

Tibogona and Yendi are located on the west and east flanks of the Volta basin with Nasia at the northern boundary and Tamale roughly in the centre of the basin. The borehole at Prang lies just beyond the southern edge of the Volta basin proper. All holes pass through formations of the early Palaeozoic Voltaian group.

It has been impossible to sample cores adequately for thermal conductivity measurements. Because the hydrological programme was terminated rather suddenly, most of the core was left in the open, or in temporary quarters, for two or three years before we made temperature measurements in the boreholes. Difficulty was experienced in locating the cores, but, fortunately, the memory of some of the Ghanaian technicians who worked on the drilling project was good enough to find the cores of the three northern holes; there is still some doubt about the location of the core from the Prang borehole. Detailed drill logs were not kept, and only a draft map and
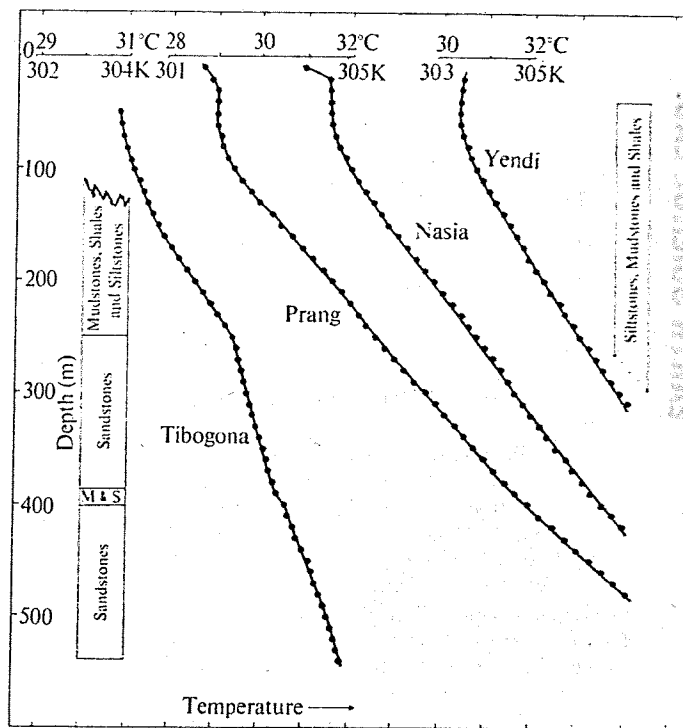

Fig. 2 Profiles of temperature with depth for boreholes.

section of the Volta basin, giving borehole locations, was available. Because the rocks consisted chiefly of poorly welded sediments, the long period of exposure had led to severe weathering so that most of it had already disintegrated, or disintegrated as soon as attempts were made to sample it. Detailed thermal conductivity determinations therefore await measurement by use of a chip method suggested by Beck[4] and recently developed by Sass et al.[5]. It is, however, possible to set an upper limit on the heat flow values for Ghana by examining the temperature gradients in the boreholes.

The holes at Nasia and Yendi pass through a series of interbedded and generally impervious shales, mudstones and siltstones. At Tibogona, the hole passes through the mudstones and siltstones and into sandstones which have porosities ranging up to 20%. The upper 100 m or so of each borehole are clearly thermally disturbed; this could be a consequence of water movement near the surface or of recent climatic changes of a local or global nature[6]. Below 100 m, however, there is associated with the rock types characteristic gradients of 18 ± 2 mK m^{-1} ($18 \pm 2°$ C km^{-1}) for the siltstones and mudstones, and 8 ± 1.5 mK m^{-1} ($8 \pm 1.5°$ C km^{-1}) for the sandstones.

If the sandstone was in fact pure and fresh quartzite with a conductivity of 7 W m^{-1} K^{-1} (17 mcalorie cm^{-1} s^{-1} ° C^{-1}), the heat flow value would be 60 mW m^{-2} (1.4 μcalorie cm^{-2} s^{-1}). This represents an absolute upper limit for heat flow in Ghana. The correct value is likely to be considerably lower than this, because, as pointed out earlier, the sandstones are generally poorly welded as well as porous. Measurements have in fact been made on three of the sandstones which did not disintegrate during handling and preparation, giving a mean conductivity of 5 W m^{-1} K^{-1} (12 mcalorie cm^{-1} s^{-1} ° C^{-1}). This gives a heat flow value of 45 mW m^{-2} (1.1 μcalorie cm^{-2} s^{-1}) for Ghana; even this value may be too high and should be treated with caution as the three samples are clearly nonrepresentative because they are the only ones to have survived modest mechanical handling and must therefore be suspected of having a higher thermal conductivity than those samples which disintegrated; some support for a figure close to 45 mW m^{-2} (1.1 μcalorie cm^{-2} s^{-1}) is, however, given by using a typical conductivity of 2.5 W m^{-1} K^{-1} (6 mcalorie cm^{-1} s^{-1} ° C^{-1}) for poorly welded shales, similar to the Ghanaian ones[6], with the 18 mK m^{-1} (18° C km^{-1}) gradient.
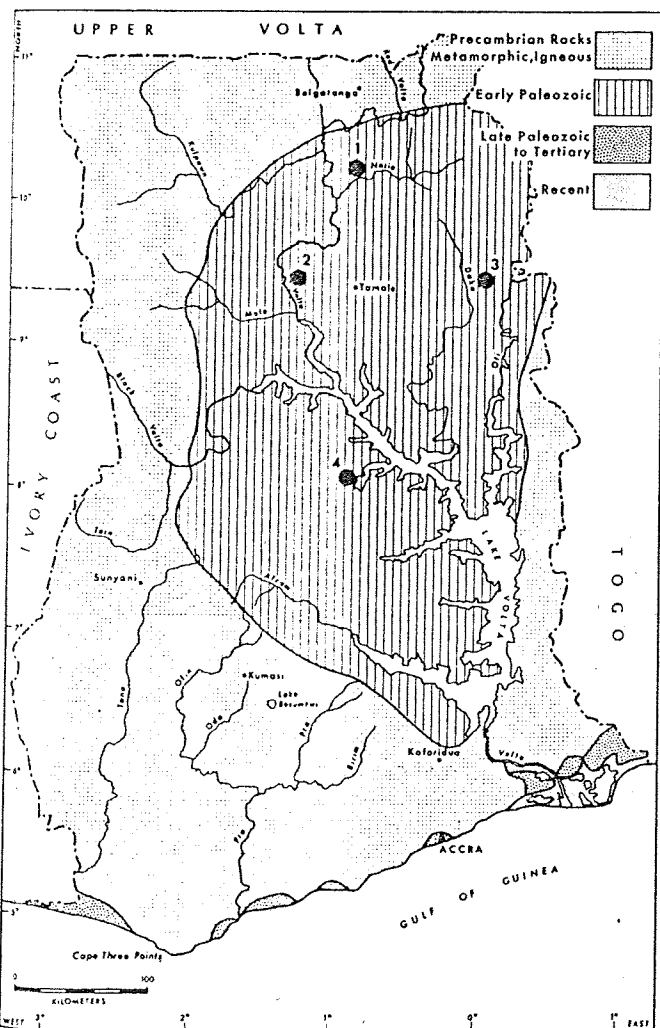

Fig. 1 Regional geology of Ghana and location of boreholes.

For the Prang borehole, not even generalized sections were available. This combined with absence of core makes it of little value for heat flow purposes. Nevertheless, the two possible interpretations of the temperature depth curve require some explanation. There is an almost continuous increase of gradient with depth which for rocks of uniform conductivity would suggest the possibility of a climatic change a few thousand years ago. If, as has been suggested[7], such a change is of a global nature, the effects should also be present in the other holes. There is some indication of these effects in the Nasia and Yendi holes, which remain in the same type of formations over the depth of useful measurement, but the data are inconclusive; at Tibogona the effects would be masked by the large change in gradient with change in rock type.

The relatively smooth increase in gradient with depth in the Prang borehole could be accompanied by a continuous decrease in conductivity, similar to the situation near Flin Flon, Manitoba[8]. Because of the absence of samples for conductivity measurement, the preferred interpretation, as with the three northern holes, is to fit straight line segments where possible. This yields gradients of 21 mK m^{-1} (21° C km^{-1}) from 140 to 350 m and 26.5 mK m^{-1} (26.5° C km^{-1}) for the lowest 100 m. These are significantly higher than the gradients in the northern holes and are difficult to explain without detailed knowledge of the section through which the hole passes. From the regional geology[9], however, it seems likely that the hole passes from the red shales and mudstones, in which it was started, into pebbly grit, arkose and conglomerate of the Obosum Beds. It is not unlikely that these latter would have conductivities of 1.7 to 2.1 W m^{-1} K^{-1} (4 or 5 mcalorie cm^{-1} s^{-1} ° C^{-1}) giving heat flow values at Prang reasonably consistent with those in the north.

We therefore conclude that the upper limit for heat flow in Ghana is 60 mW m^{-2} (1.4 µcalorie cm^{-2} s^{-1}) with the correct value being within 20% of 42 mW m^{-2} (1 µcalorie cm^{-2} s^{-1}). This value is at variance with the high heat flows indicated for the northern part of Africa in the spherical harmonic analysis of Lee and Uyeda[10]. The value, however, is consistent with the oceanic values found off the western coast of north and north-west Africa and with values found for a sedimentary basin close to the Canadian Precambrian shield[11].

Many more heat flow values are clearly required from the African continent before much reliance can be placed on spherical harmonic analysis of the data.

This work would not have been possible without the cooperation of the director of the Geological Survey of Ghana, Mr S. J. Cudjoe, who allowed us generous use of the Survey facilities, and personnel, among whom we particularly thank Dr M. Khan and Mr M. Kirton for assistance in organizing the transport and locating reports, and Mr Y. Wumbla for helping to locate the boreholes.

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Triboluminescence in Solid Methanol

RECENTLY we reported[1] that decomposition of methanol is found to accompany successive transitions through the liquid–solid phase change region of temperature. There are two phase changes: the liquid–solid transition 175.37 K and the solid–solid λ transition at 157.8 K (the higher temperature solid form is designated β, and the lower as the α-form[2]). The liquid–solid transition was then favoured as the source of the decomposition because of the apparently greater structural and energy changes involved. But further work has revealed that the liquid–solid transition is not involved. Smaller volumes than used previously (40 ml. compared with 100 ml. of methanol in a 250 ml. flask) do not exhibit decomposition on freezing with liquid air. When 100 ml. volumes are used the previously reported evolution of CO, H_2 and CH_4 is found to commence only some 5 min after all the methanol has frozen and then to continue for some time as the methanol cools (Fig. 1).
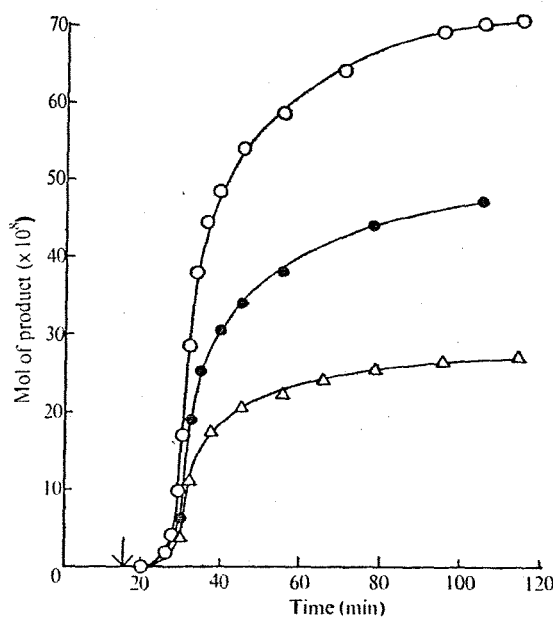

Fig. 1 Yields of gaseous products as a function of time. Zero time is taken when the liquid air is first brought in contact with the flask containing the liquid methanol. The arrow indicates the completion of freezing. O, H_2; ●, $CH_4 \times 10$; △, CO.

The evolution of gaseous substances is accompanied by gradual changes in the surface of the solid methanol, from an originally smooth surface to a broken, uneven surface with undulations 1 mm or more in depth.

When a small sample of methanol (~10 ml. in a 100 ml. flask) was frozen to the high temperature β form using an iso-octane liquid-N_2 slush bath[3] (166 K) no decomposition was observed. On further cooling with a liquid air bath, gas evolution began at once. Freezing of similar volumes of liquid methanol with liquid air apparently produces the low temperature α-form directly and no gas evolution is observed, indicating that the decomposition is associated with the $\beta \to \alpha$ transition. This transition involves only changes in secondary coordination, from an orthorhombic to a monoclinic crystal form which, in methanol, results in crystal breakdown[4]. Crystal breakdowns are often accompanied by the emission of light, known as triboluminescence. When the methanol $\beta \to \alpha$ transition is viewed in the dark, flashes of white light can be observed accompanying the decomposition. Light emission begins at the circumference of the methanol surface on cooling and moves radially inward as the methanol passes through the phase change. Fig. 2 is a photograph of the light emission taken on Kodak 2475 recording film—the dotted circle marks the circumference of the methanol surface.