matters arising

Volatilisation of methylmercuric chloride by hydrogen sulphide

of TREATMENT methylmercuric chloride with hydrogen sulphide in aqueous solution has been shown by Rowland et al. to result in volatilisation of mercury¹. The volatile product was not identified but was considered to be a 'volatile sulphur compound of methylmercury'. Volatilisation of mercury and concurrent lowering of the pH of the aqueous solution¹ can be explained by formation of bis(methylmercuric) sulphide (A).

$$2MeHgCl+H_2S \rightleftharpoons (MeHg)_2S(A)+2HCl$$
(1)

This reaction has previously been carried out in ethanol^{2,3}. The foul odour of A(ref. 2) indicates that it is volatile, even though it is a solid at room temperature. Loss of mercury caused by ammonium sulphide¹ can also be attributed to formation of A.

$$2MeHgCl + S^{2-} \rightleftharpoons (MeHg)_2S + 2Cl^{-} \qquad (2)$$

The reduced effectiveness of this reagent compared with hydrogen sulphide¹ can be explained by the simultaneous occurrence of reaction (3).

 $MeHgCl + S^{2-} \rightleftharpoons MeHgS^{-} + Cl^{-} \quad (3)$

Reactions analogous to (2) and (3) have been observed between MeHgBr and Na_2S (refs 4, 5).

Absorption of the volatile mercurial by alkali¹ can be attributed to formation of the known⁶ *tris*(methylmercuri)oxonium hydroxide (B) (contrast with doubtful existence of MeHgOH⁶).

$$3(\text{MeHg})_2\text{S} + 3\text{OH}^- + \text{H}_2\text{O}$$

$$\rightarrow 2(\text{MeHg})_3\text{O}^+\text{OH}^-(B) + 3\text{SH}^- \quad (4)$$

The ionic character of B would explain the failure of the base-soluble species to undergo chromatography¹. Although chloride ions, from absorption of volatilised HCl, would also be present, the equilibrium (5) would lie well to the left. However, extraction with toluene would remove the non-ionic methylmercuric chloride and drive the equilibrium to the right, explaining recovery¹ of MeHgCl by this method.

$$(MeHg)_{3}O^{+}OH^{-} + 3Cl^{-} + H_{2}O$$

$$\implies 3MeHgCl + 3OH^{-} (5)$$

The volatilisation of methylmercury could also be explained by formation (6)

$MeHgCl + H_2S \rightleftharpoons MeHgSH + HCl \quad (6)$

of MeHgSH (reported preparations^{7,8}), and reactions (2) and (4) could be modified to accommodate this. However, reaction (6) has not previously been demonstrated, whereas there is precedent for $(1)-(3)^{2-5}$, hence A is preferred as the source of volatility. Since A is unstable, decomposing by $(7)^2$, dimethylmercury and mercuric sulphide would probably be the ultimate products from MeHgCl and H₂S in an environmental situation.

 $(MeHg)_2 S \rightarrow Me_2Hg + HgS$ (7)

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World's oldest animal traces

BIOLOGISTS and biogeologists would like to know when multicellular animal life began. Well authenticated records show that it was present by ~ 680 Myr ago, but older records have not withstood scrutiny. Clemmy's report¹ of metazoan burrows from 1,000 Myr old rocks in Zambia therefore excited great interest. I have examined the specimens and seen Clemmy's coloured slides of the outcrops, and this examination and subsequent research led to a different conclusion from his. The Zambian burrows are undoubtedly metazoan and indigenous to the sedimentary deposits in which found, but they are of post-depositional origin and related to a geologically recent surface. Evidence for this conclusion rests in the bleached, saprolitic nature of the host rock and the contrasting red and pink banded burrow-fillings, containing rounded, ferromanganese-coated quartz grains that are much larger than particles of the adjacent matrix. Such characteristics suggest introduction of burrow-filling material from a relatively recent lateritic weathering surface.

Further study and inquiry among students of the social insects led to the additional conclusion that Clemmey's burrows are the work of termites, digging through and parallel to the softer layers of the steeply dipping saprolitic rock to obtain water for humidification of their nests. From publications and correspondence with termite specialists M. Lüscher, Ch. Noirot, M. L. Roonwal and W. A. Sands, I found that termites do burrow to depths of 70 or more metres to reach the water table, that they burrow preferentially in the least resistant parts of the rock and that they backfill unused burrows with surface matter producing laminated burrow-walls and a banded 'spreite' pattern like that illustrated by Clemmey. His observation that the burrows are parallel or nearly so to the bedding, and that they favour particular stratigraphic levels, would be consistent with descent along the softer of the steeply dipping strata of the Zambian Copperbelt.

The above comments apply mainly to burrows of the type of Clemmey's Fig. 1. The oval profile, pinching and swelling along their lengths, and terminal branching of such burrows is also termite-like. The bioturbation of his Fig. 2 may represent a zone of termite foraging or collapse. Specimens like his Fig. 4 (with a hollow interior) resemble the covered passageways through which termites cross lighted areas.

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CLEMMEY REPLIES—I agree that the burrows I described are only obvious after weathering, but this is a feature shared by much of the internal fabric of rocks and in this case has an explanation. The red and pink banding results from weathering of the microchemical/mineralogical differences between bioturbated and nonbioturbated sediment. Within the burrows it reflects the differences between sediment passed around the body or through the gut of the animal and such differences are to be expected in bioturbated sediment¹.

The burrow, as a microreducing environment, attracted the precipitation of iron sulphides, which ideally would be more concentrated in the zones of the bioturbated sediment richest in organic matter. On weathering the ferrous iron is oxidised to the ferric state and hence the