

Both the percolation model and the measurements by Schwander and Stauffer⁷ determine the time of bubble trapping relative to the time of snow deposition and do not directly determine the age of the air that is trapped. However, measurements of ³⁹Ar indicate that air in the 'open' volume is well mixed throughout the firn¹⁸, so that the trapping time distribution should be close to the age distribution.

For use in solving equation (1), the percolation model will require an empirical calibration using data such as that plotted by Schwander and Stauffer⁷ even if only to determine the amplitude of the singularity. Direct theoretical calculation of $P(z)$ seems impractical mathematically since even highly structured lattice percolation problems do not have closed form solutions. Even an approximate calculation of $P(z)$ would require more detail of the firn structure than is readily available.

Given the singular nature of $R(z)$, it is of interest to note that the ice-core deconvolution problem is less poorly posed than many typical geochemical inversion problems. Equation (1) becomes

$$q(z) \sim \int_{z-z_c}^z (z_c - z + z')^{\beta-1} c(z') dz', \text{ for } z > z_c \quad (4a)$$

or putting $t = z_c - z$, $t' = -z'$

$$q(z_c - t) \propto \int_{t-z_c}^t (t - t')^{\beta-1} c(-t') dt' \quad (4b)$$

Apart from the variable lower limit (which has little influence on the integral) this is proportional to the expression given by Ross¹⁹ for defining a β -fold integration of $c(-t)$ for non-integer β . The inverse operation of obtaining c from q corresponds to the operation denoted by

$$c(t) \propto \frac{d^\beta}{dt^\beta} q(t) \quad (5)$$

Anderssen and de Hoog²⁰ have characterized the numerical difficulty of unstable inverse problems as being given by the

equivalent order of differentiation when this is applicable. Most source deduction problems in geochemistry are essentially equivalent in difficulty to a single numerical differentiation since observed concentrations represent the integrated effects of sources. If the percolation model is valid, the deconvolution of bubble concentrations in ice cores is formally equivalent to about a 0.454th-order differentiation and so is less poorly posed than typical source deduction problems in geochemistry. Thus the resolution which can be achieved for the reconstruction of c should be somewhat better than the time period over which the firn closes.

Since submission of this manuscript we have learnt that the bubble trapping problem has also been considered in terms of the percolation model by B. Stauffer, J. Schwander and H. Oeschger (unpublished data). They performed simulations using a regular lattice approximation and concentrated on determining the critical point rather than discussing the critical exponent.

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Prokaryotic and eukaryotic microfossils from a Proterozoic/Phanerozoic transition in China

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Cherts of the Doushantuo Formation in the Yangtze Gorges, South China, contain a superbly preserved heterogeneous assemblage of bacteria, cyanobacteria, planktonic algae, submillimetre-sized burrows and problematica. The microbiota has a bearing on defining the Precambrian-Cambrian boundary. *Baltisphaeridium* and associated spinose microfossils in the chert suggest an early Cambrian age whereas other acritarchs, vendotaenids and pretrilobite small shelly fossils from the conformably overlying the Dengying Formation, indicate a late Proterozoic age for the Doushantuo. This mixed benthic-planktonic assemblage preserved in silicified, laminated, microbial mat-like fabrics, provides a unique sample of diverse microbiotic elements existing at the dawn of the Phanerozoic and records the earliest evidence of meiofauna.

The fossil record of the latest Proterozoic is best known from Ediacaran and allied soft-bodied animals^{1,2}, acritarchs³ and stromatolites⁴. This record, though meagre, is fascinating, for it

was during this interval that animals originated and began to diversify⁵. Much of our understanding of pre-700-Myr-old palaeobiology has been based on interpreting fossils preserved in chert⁶; unfortunately such occurrences are not well known from post-700-Myr old deposits.

The Doushantuo Formation in the Yangtze Gorges, China, conventionally viewed as late Proterozoic^{7,8}, contains cherts with well-preserved, abundant and diverse microfossils such as coccoid and filamentous cyanobacteria, bacteria, large spiny organic-walled microfossils, problematic tubular microfossils, other problematica and submillimetre-sized backfilled burrows. In addition to a benthic mat biota, the cherts preserve elements of the phytoplankton that lived in the overlying water column.

The Doushantuo Formation is a dark brown to grey-black dolomite with chert, interbedded with shale. It unconformably overlies tillite of the Nantuo Formation and is conformably overlain by dolomite and limestone of the Dengying Formation⁹ (Figs 1, 2).

The Yangtze Gorges region contains the type section for the Chinese Sinian System¹⁰ (composed, in ascending order, of the

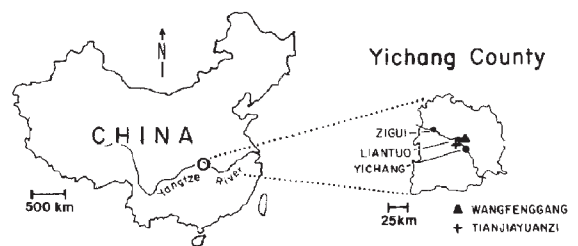


Fig. 1 Index maps showing location of measured sections.

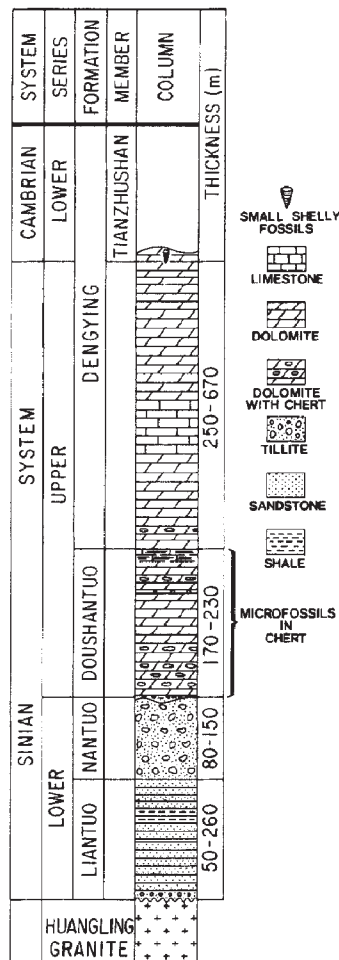


Fig. 2 Generalized stratigraphical column of Sinian System in the Yangtze Gorges, Yichang County, Hubei, China.

Liantuo, Nantuo, Doushantuo and Dengying formations). It would be a potential candidate for any global stratotype section that may be established for a new geological system to embrace the pre-shelly fossil record during which metazoans appeared¹¹. Here the Sinian is a thick succession with such lithological and palaeontological curiosities as tillite, phosporite, acritarchs, vendotaenid algae, stromatolites, oncolites, microfossiliferous chert, putative Ediacaran-type metazoans, sponge-like spicules, trace fossils and is conformably overlain by the small shelly fossil-bearing Tianzhushan member (upper Dengying Formation), regarded as signalling the base of the Cambrian^{9,12}.

Within this stratigraphical framework, the Doushantuo is usually taken to be Late Sinian (Vendian or Ediacarian), probably <700 Myr-old. Although their reliability may be questioned, Rb-Sr whole rock isochron ages from the top of the formation yield 700 ± 5 and 691 ± 29 Myr (ref. 13). Other potential radiometric age constraints include an ion-probe U-Pb age of 740 ± 16 Myr on zircons in tuff from the Lower Sinian Liantuo Formation¹³, and ages of 806 ± 6 Myr (Rb-Sr isochron) and 823 ± 7 Myr (K-Ar on biotite) from the crystalline basement underlying the Liantuo¹³. Shale from the upper part of the Tianzhushan member (Dengying Formation) has an inferred isotopic age of 610 ± 10 Myr based on whole rock Rb-Sr isochron analyses¹⁴. Palaeontologically, acritarchs from acid residues of Doushantuo elastic rocks have been interpreted to indicate a late Proterozoic age (<700 Myr)^{7,15}. The overlying Dengying Formation's palaeontology (vendotaenids from the lower part⁷; pre-Cambrian acritarchs from shale^{7,9}, and small shelly fossils of Meichucunian or Tommotian character at the top⁷) also indicates a pre-Cambrian age for the Doushantuo. Following guidelines set forth by the International Union of Geological Sciences/International Geological Correlation Program Project

29 Working Group on the Precambrian-Cambrian Boundary¹⁶, the small shelly fossils appearing in the Tianzhushan member (Dengying Formation; Fig. 2) would define the base of the Cambrian. Hence, until now, the overall palaeontology, stratigraphy, isotope age data and correlations with other areas suggested a late Proterozoic age for the Doushantuo.

Previously reported fossils from the Doushantuo Formation include stromatolites¹⁷, acritarchs¹⁵ and chitinozoans¹⁷. Cyanobacteria¹⁸⁻²⁰ and spiny microfossils^{21,22} have been described from chert and sponge-like spicules from dolomite¹⁷. No megascopic algal, metazoan trace or body fossils have yet been found in the Doushantuo.

The microfossils that we describe here were detected in petrographic thin sections of chert nodules in dolomite from two measured sections of the Doushantuo Formation; one ~150 m east of Wangfenggang Village, the other ~700 m south-southeast of Tianjiayuanzi Village, Yichang County, Hubei, China (Fig. 1). Of the coccoidal microfossils detected, solitary specimens are rare; the more abundant pluricellular varieties are represented by such Proterozoic taxa as *Myxococcoides*, *Palaeoanacystis* and *Tetraphycus*. Among the new taxa present are a *Merismopedia*-like pluricellular form with tightly packed cubic cells and an aggregate of small <1- μ m diameter cells that might represent fossilized bacteria. In general, most of the coccoidal morphs resemble cyanobacteria; however, although diverse, the coccoids are only moderately abundant when compared with filaments and large spinose morphs.

The benthic component of the microbiota is dominated by filamentous fossils that resemble cyanobacteria. Bundles, 50-400 μ m across, of filaments, 5-45 μ m in diameter, are common (Fig. 3a) and many superficially resemble the extant multi-trichomous oscillatoriacean *Microcoleus*. Numerous single filaments, ranging from <1 to as much as 100 μ m in diameter, and representing several taxa, occur as solitary strands and in mat-like arrangements. Rare examples of an *Obruchevella*-like fossil have been found. Most filaments resemble the empty sheaths of cyanobacteria although others may be bacteria and algae. Preservation at times is so good that a trichome can be found preserved within its sheath (Fig. 3d). No heterocystous or branched filaments have been detected.

Cyanobacteria-like fossil diversity is high; >20 species are present. These microfossils occur in rudimentary, stratiform stromatolite-like microstructures not too unlike those seen in Proterozoic microfossiliferous stromatolites²³. In some instances, this rudimentary lamination is disrupted in a manner suggesting churning of the sediment by organisms that did not leave clear, well-defined burrows.

Planktonic microfossils include a variety of morphotypes. Among the most conspicuous and abundant plankters found in thin section are diverse spinose vesicles, ranging from 30 to 1,200 μ m across. Important among these are the spiny acritarchs resembling *Baltisphaeridium* (Fig. 3b) hitherto known only from early Cambrian and younger rocks^{24,25}.

The Doushantuo also contains abundant and diverse, morphologically-complex microscopic fossils of uncertain systematic position. First, there are robust, multilayered and partitioned tubes (Fig. 3c). These fossils, 40-100 μ m in diameter, occur in variable abundance in numerous thin sections from several sites. At first glance, these tubes resemble large, lamellated, oscillatoriacean cyanobacterial sheaths. However, oscillatoriaceans and other filamentous cyanobacteria, bacteria, algae, and fungi are not known to possess this type of architecture. Superficially they resemble miniaturized coelomates; however, the small size and apparent partitioning of the innermost tube (which would be equivalent to the gut) make this affinity unlikely. This morph might represent an evolutionary novelty in the prokaryotic or eukaryotic line for which there are no modern analogues.

Also, large, 400-900- μ m wide and 750-1,500- μ m long, morphologically complex, brown coloured vesicles (Fig. 3f) have been found in many thin sections from several sites. The fossils are characterized by a tripartate organization consisting of: (1)

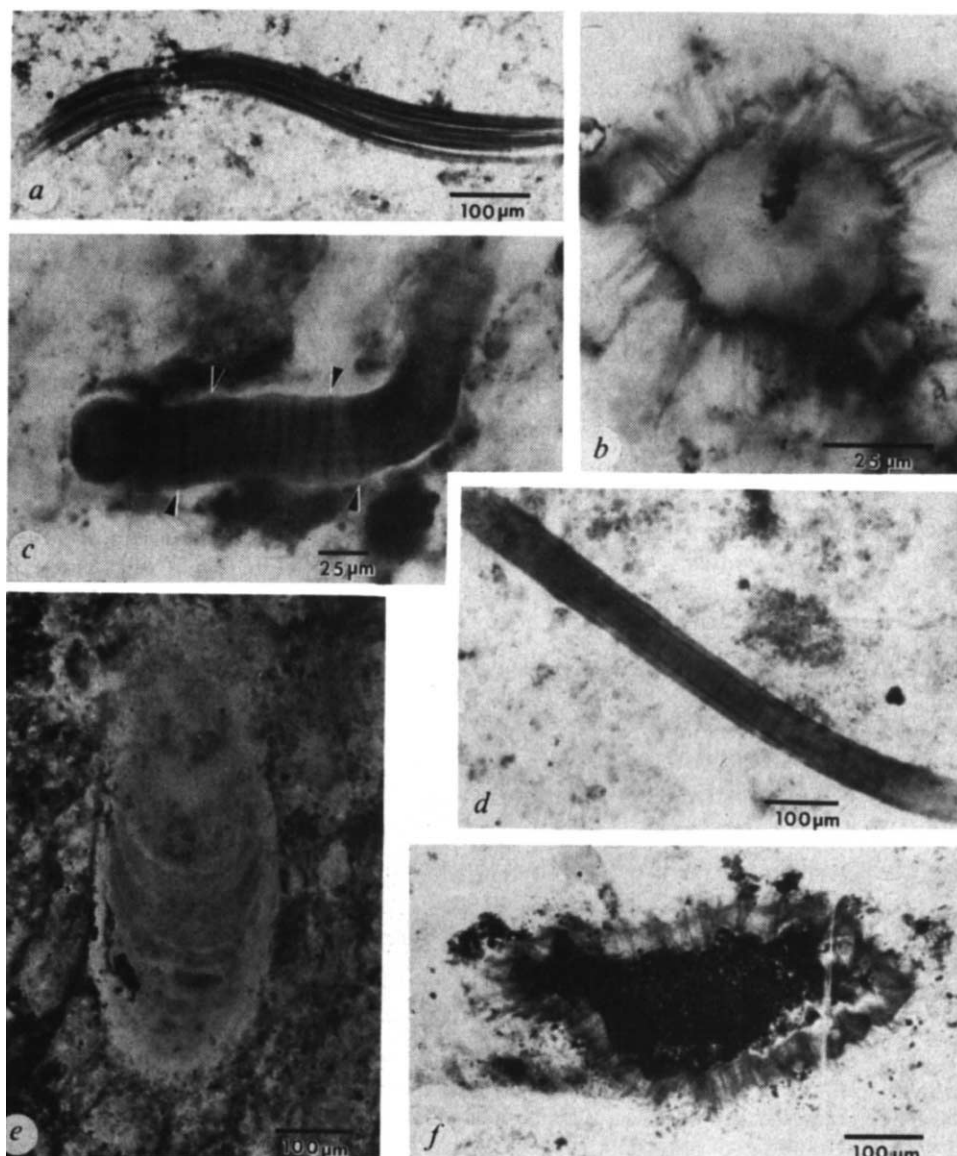


Fig. 3 Microfossils from the Doushantuo Formation. All photomicrographs are from petrographic thin sections housed in the Preston Cloud Research Laboratory. *a*, Bundle of filaments showing possible multitrichomous habit. Sheath is not evident. *b*, *Baltisphaeridium* spiny microfossil; note the closed, tapered ends of the spines. *c*, Partitioned, concentrically-layered tube. Partitions, indicated by arrows, cut the layered cylinder. It is uncertain even to what kingdom this fossil belongs. *d*, Cyanobacterium with trichome preserved within lamellated sheath. The outer sheath is not partitioned and the inner trichome is not layered. *e*, Backfilled burrow. This burrow and others like it (preserved in chert), pre-date previously known bona fide burrows from the Sinian of China. *f*, Complexly organized protistan showing outer layered organic mantle with tube clusters, boundary layer, and interior with particulate contents.

the vesicle interior that typically contains amorphous black particulate organic and pyritic matter and occasionally folded membrane-like material; (2) a well-defined boundary layer or wall that separates an external organic covering from the vesicle interior; and (3) an outer organic covering or mantle that is occasionally layered, as seen in Fig. 3*f*. This organic covering contains clusters of from 3 to 8 small, hollow tubes, each 1–3 μm in diameter. The tubes have closed, tapered ends. Where attached to the boundary, the tubes open to the vesicle's interior. The tubes, wall structure, interior and overall organization of these microfossils are unlike that of previously described spinose acritarchs, although some similarities exist with the Proterozoic morph *Trachyhystrichosphaera*²⁶. Superficially they also resemble certain protozoan sporocysts like those of gregarines. The size and complexity of these fossils indicate some kind of eukaryote, probably a protistan. Again the possibility exists that these fossils have no modern analogues.

Structures resembling backfilled burrows, 150–250 μm across (Fig. 3*e*), are known from two collecting sites. Longitudinal and cross-sections of these burrows are found oriented both parallel to, and oblique to, lamination in chert nodules. Although rare (four examples known) and in the case of Fig. 3*e* composed of chalcedony, they probably represent some worm-like meiofaunal animal that peristaltically moved through sediment. These structures cannot be interpreted as laminated constructional features like microstromatolites for the layering is concave down and disrupts chert matrix laminae. The presence of such

submillimetre-sized, backfilled burrows in the Doushantuo suggests meiofaunal activity and, if the age of the Doushantuo proves to be late Proterozoic, make them among the oldest burrows known.

Clearly, the discovery of *Baltisphaeridium* and related spinose vesicles in Doushantuo cherts raises questions, not only about the age of the Doushantuo, but also concerning criteria and reliability of criteria used to define the Precambrian–Cambrian boundary.

This precise age controversy aside, the exceptional preservation of the abundant and diverse prokaryotic and eukaryotic fossils in the Doushantuo cherts provide a unique microscopic window on a time during the early stages of animal evolution and the waning of stromatolite-building microbial mat communities²⁷. These new data must be considered when defining one of the major boundaries of the geological time scale. The robust nature of many of the cyanobacteria (large size, thick sheaths) as well as some of the problematic morphs may have been an attempt by mat-forming organisms to cope with newly evolved 'meiofaunal' and macrofaunal benthic eukaryotic heterotrophs that ultimately overwhelmed the stromatolite-building biocenoses: an extraordinarily successful biocenose that had flourished for hundreds of millions of years.

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Energy transfer at the surface of clays and protection of pesticides from photodegradation

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Certain potential pesticides are of limited use because of their sensitivity to sunlight. Previous attempts to overcome this limitation have been unsatisfactory because of impairment of insecticidal efficiency or unwanted toxic properties. The photosensitivity results from the balance between the processes, such as energy transfer and chemical reaction, by which photoexcited molecules can release excess energy and return to the ground state. The efficiency of the various energy transfer mechanisms¹⁻⁵ depends, in some cases, on the specific spectroscopic characteristics of donor and acceptor molecules, the distance between them and their relative orientations. We present here an approach aimed at protecting compounds of agricultural interest (for example, pesticides) by exploiting the unique surface properties of certain clays in order to build systems in which fast energy transfer occurs before photodegradation starts.

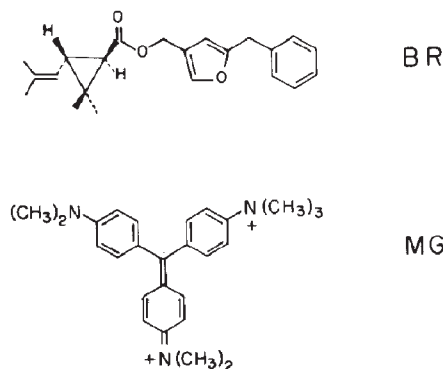
Clays, such as montmorillonite, exhibit outstanding adsorption properties due to their high specific surface areas and high cation-exchange capacities⁶. As organic molecules adsorbed on the clay surface are oriented⁷, their intermolecular distances and orientations might fulfil the requirements for an efficient energy transfer process. Measurements of energy transfer on clay surfaces have been described for certain fluorescent cations⁸⁻¹⁰. However, occurrence of such processes between adsorbed non-fluorescent photolabile organic molecules has not been reported.

A suitable target for study of photostabilization is the synthetic non-halogenated pyrethroid bioresmethrin (BR) (5-benzyl-3-furylmethyl) (1R)-*trans*-chrysanthemate, a powerful contact insecticide effective against a wide range of insect pests and one of the safest pesticides (its acute oral LD₅₀ (50% lethal dose) for rats is 8 g per kg). Despite these advantages, bioresmethrin is not used in agriculture owing to its rapid photodecomposition.

It was found that chemical modification of the pyrethroid structure leads, in some cases, to more stable pesticides¹¹⁻¹⁶. Attempts have been made to stabilize the photolabile pyrethroids using various additives (antioxidants and UV-screensers)¹⁷⁻²². Recently, the photostabilization of cyphenothrin by dinitroanilines at certain relative concentration ratios has been attributed to possible exciplex or charge transfer quenching²².

We have achieved stabilization of BR by adsorbing it on montmorillonite (Clay) together with the divalent cation methyl green (MG). Figure 1 shows the results of a typical bioassay using adults of the flour beetle *Tribolium castaneum*. Control samples of free BR exposed to sunlight completely lost their biological activity in <2 h, whereas samples prepared according to our method were still active after several days of exposure to sunlight. BR adsorbed in a complex with 0.2 mmol of MG per g clay was photochemically more stable than BR in a complex with a higher level of dye (0.4 mmol g⁻¹). This indicates that the stabilization effect is due to specific interactions between the two compounds at the surface of the clay rather than to merely a UV-screening effect.

Some details of these interactions at the molecular level can be obtained using Fourier transform IR (FTIR) spectroscopy (Fig. 2). A comparison of spectrum *a* (free BR) with spectrum *b* (BR adsorbed on clay) reveals that the stretching frequency of the C=O bond shifts from 1,722 to 1,709 cm⁻¹ on adsorption.



The position of this band in spectrum *c* (BR adsorbed in the presence of MG) clearly shows that the BR molecules in the Clay-MG-BR complex are adsorbed in a similar manner as in the case of Clay-BR. Minor changes in the strong absorption bands of MG at 1,568 and 1,371 cm⁻¹ are also induced by the co-adsorption of BR. These changes, although difficult to observe in the measured spectra (Fig. 2*d, e*), are evident in the difference spectrum (Fig. 2*c*). In addition, co-adsorption of MG and BR induces broadening of the 1,497 cm⁻¹ peak of BR. The fact that vibrational frequencies of one organic molecule are shifted due to the co-adsorption of another one (as detected by the differential FTIR technique) indicates that short-distance intermolecular interactions exist between the molecules of these substances on the clay surface. A change in concentration of the adsorbed molecules results in a modification of the intermolecular distances and/or relative orientations in a manner which evidently affects the efficiency of the photostabilization effect (Fig. 1).

The method we propose for protecting pesticides from photodegradation thus consists of adsorbing the photolabile agrochemical to the surface of a clay to which another organic chromophore has been attached. This second organic chromophore may be selected according to its spectroscopic, geometric and charge characteristics, depending on the type of clay to be used and the pesticide to be protected. If the clay is a smectite, such as montmorillonite, with a negatively charged surface, a cationic protective compound may be used. As a result of its adsorption to the clay, the charge at the adsorption site is neutralized and the surface might become hydrophobic (depending on the size of the organic cation). If a non-ionic pesticide molecule is added to this system, it will be adsorbed at these hydrophobic sites or, alternatively, it might be attached

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