the various-sized clusters on time, water vapor concentration, and light intensity can be readily solved in two limiting cases, an initial time solution and a steady-state solution. (These are precisely the solutions we need for comparison with the delay time data and the steady-state nucleation data, respectively.) In both cases we make the reasonable approximation that the concentrations of the clusters rapidly decrease with increasing size. For the initial time solution we also neglect diffusional losses and obtain for the concentration of c-sized clusters

$$[(H_2O^*)_c] = K_c[H_2O]^{cm} I^{cm} t^{c(p+1)-1} \quad (4)$$

where K_c is a constant, m is the number of photons needed to excite a water molecule, I is the light intensity, t is time, and p is the number of substeps involved in the initial excitation process. For the steady-state solution we do not neglect the diffusional losses. Instead, we assume that they are the dominant loss mechanism and thus obtain

$$[(H_2O^*)_c] = K_c'[H_2O]^{cm} I^{cm} \quad (5)$$

where K_c' is a different constant. If there is a unique number c which can cause nucleation at a given supersaturation condition and if the rate of nucleation is proportional to $[(H_2O^*)_c]$, it follows that

$$\alpha = cm \quad (6)$$

$$\beta = -cm/[c(p+1) - 1] \quad (7)$$

The values of α and β in Table 1 were obtained by a least-squares fit of the data in Figs. 2 and 3 and also their uncertainties (1 standard deviation). To obtain the same value of c from the α and β data using Eqs. 6 and 7 (to within the uncertainty in c due to the uncertainties in α and β), we were forced to require that $m = 1$ and $p = 1$. (These are precisely the values one would choose on physical grounds; that is, one photon is required to excite water and this excitation occurs in a one-step process.) No other model (for example, the one that fits the *o*-tolualdehyde data) would produce the same value of c for both the steady-state rate data and the delay time data for any value of the parameters.

Although the above mechanism fits our steady-state nucleation rate and delay time data very well, some questions about the fundamental causes of the photoinduced nucleation phenomenon remain to be answered:

1) Presumably the light has to be absorbed to be effective. However, there is no known absorption by H_2O in the wavelength range from 200 to 320 nm.

2) In this wavelength range, photoexcited molecules typically undergo electronic transitions. The lifetimes of electronic excited states are generally short (submicroseconds to milliseconds). This is difficult to reconcile with our observations that it takes seconds to minutes for nucleation to begin after the light is turned on and to cease after the light is turned off.

3) All current theories of nucleation view the process as occurring by a balance of molecules arriving at and evaporating from the clusters. If the energy of the photoexcited molecules were to be degraded to heat, then its effect (if the excited molecules were actually in clusters, which is what the phenomenological mechanism suggests is the case) would be to increase the evaporation rate. Such an effect would prevent nucleation and not promote it.

These questions force us to the following conclusions. (i) There must be absorption of light over the wavelength range we studied. However, these absorptions are probably very weak and are not readily detectable by other means. (ii) Either the lifetimes of the photoexcited molecules are greatly extended by their interaction with the other excited and the unexcited molecules in the cluster or some kind of photochemistry (for example, radical formation or polymerization) is going on. (iii) It is unclear how a cluster of excited molecules can cause other molecules to condense on it.

The photoinduced nucleation phenomenon we have observed using *o*-tolualdehyde in nonane, pure water vapor, and other substances has several important implications. Its distinctive wavelength dependence can be utilized to detect and identify substances even when they are present in very low concentrations. The observance of an effect at wavelengths where no absorptions have been reported may mean that one now has a new and more sensitive tool for detecting such absorptions. Since the conditions we used in our cloud chamber are comparable to those found in the atmosphere (*9*), the photoinduced nucleation of water vapor may be an important mechanism for cloud formation. The light-sensitive organic substances we studied (*2*) are common photoactive pollutants found in urban atmospheres (*10*). Our study thus suggests that the photochemical aerosol formation mechanism may be due to photoinduced nucleation and not to self-nucleation mechanism as has been suggested (*11*).

F. C. WEN
TIMOTHY MCLAUGHLIN
JOSEPH L. KATZ
Department of Chemical Engineering, Clarkson College of Technology, Potsdam, New York 13676

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2. We have also observed photoinduced nucleation in supersaturated nonane vapor containing benzaldehyde, crotonaldehyde, benzoic acid, *o*-nitrotoluene, acetophenone, and benzylamine.
3. These substances can therefore be used as hosts for the study of the nucleating effects of low concentrations of other photoactive substances.
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The Oldest Bryozoans: New Evidence from the Early Ordovician

Abstract. *An abundant, previously problematic fossil from the Lower Ordovician (Canadian) Black Rock limestone of the Ozark Uplift area is an undescribed dianulitid bryozoan. It is believed to be the oldest unquestionable bryozoan known. The growth morphology varies widely and is believed to be environmentally influenced.*

Bryozoans older than earliest Middle Ordovician in age (Whiterockian Stage) (*1*) have never been recognized with certainty from the fossil record. Previous finds of older forms are of questionable affinities (*2*) or of uncertain stratigraphic position (*3*). The recognition of a previously problematic fossil from the Lower Ordovician (late Canadian) Black Rock limestone (*4*) of northeastern Arkansas and southeastern Missouri as an undescribed dianulitid species is believed to mark the oldest known occurrence of an unquestionable bryozoan.

Fossils from the Black Rock limestone of northeastern Arkansas were suspect-

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ed to be bryozoans many years ago (*5*, p. 3). However, in studies in which the form was reencountered (*6*, *7*), it was designated a problematicum of questionable sclerosponge affinities. The poor internal preservation of available specimens has prevented definitive diagnosis until now. Colony walls are invariably replaced with a rind of granular silica, but when the fossils are found loose in weathered clay residuum, internal details have usually been destroyed by replacement with amorphous silica. Discovery of well-preserved specimens in matrix, however, reveals the zooecial polymorphism (in this case, larger autozooecia and smaller mesozooecia) characteristic of nearly all calcareous bryozoans.

The Black Rock limestone is a shallow marine carbonate facies complex of latest Lower Ordovician (Cassinian) age (*8*). Review of fossil evidence for this age assignment (*6*, p. 57) shows that brachiopods are restricted Canadian genera (*Diparelasma, Polytoechia*), while other taxa are either not diagnostic, or span the Lower-Middle Ordovician boundary. The sponge-algal-bryozoan-brachiopod biota of the Black Rock unit contrasts with the molluskan-dominated Smithville unit, which is regarded as its lateral, associated time-equivalent (*6*, *7*).

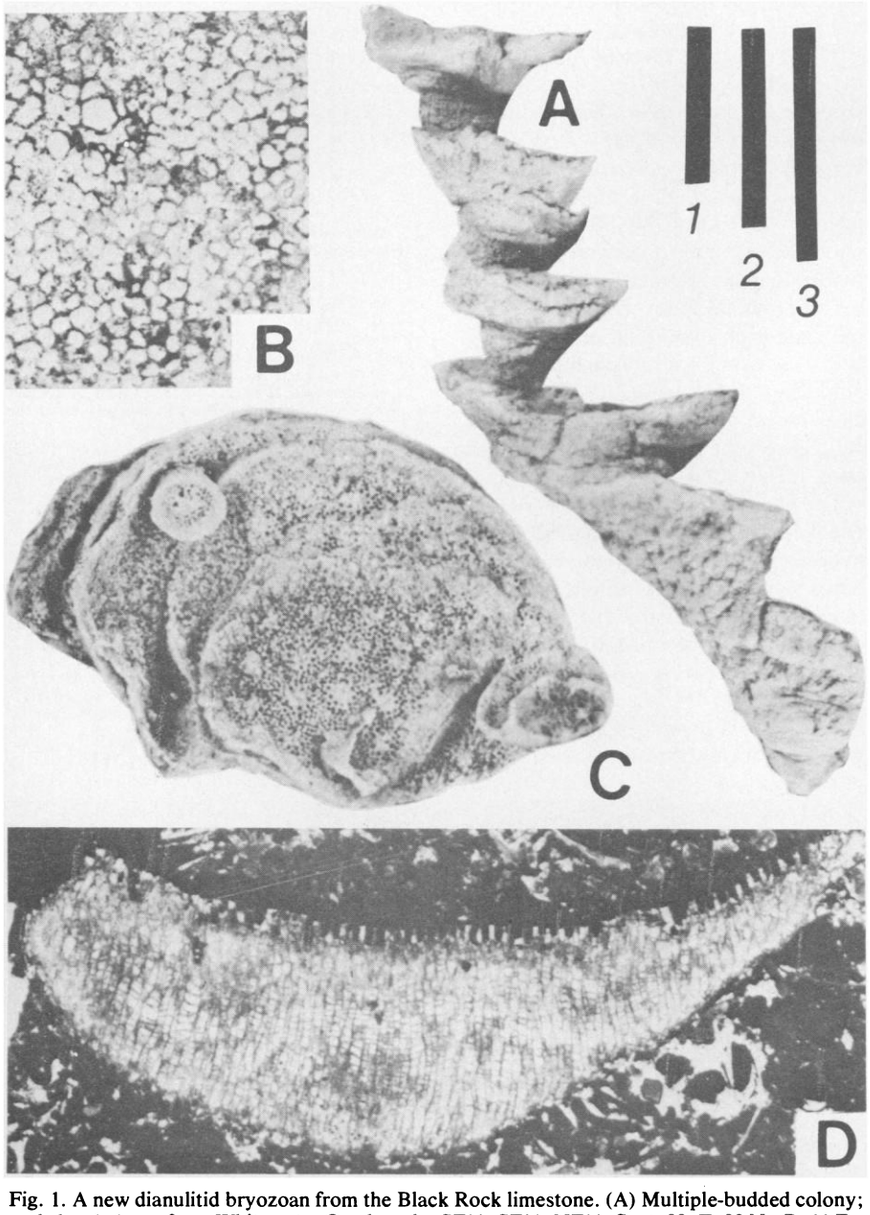

Fig. 1. A new dianulitid bryozoan from the Black Rock limestone. (A) Multiple-budded colony; scale bar 1, 1 cm; from Whitewater Quadrangle, SE¼, SE½, NE¼, Sect. 22, T. 29 N., R. 11 E., near Arbor, Missouri. (B) Transverse thin section; scale bar 2, 0.5 cm; from same place. (C) Living surface with monticules; scale bar 1, 1 cm; from same locality. (D) Saucer-shaped colony, longitudinal thin section; scale bar 3, 1 cm; from Smithville Quadrangle, NW¼, NE¼, NW ¼, Sec. 34, T. 16 N., R. 3W., near Smithville, Arkansas.

The Smithville and Black Rock units are thought to represent contemporaneous, intertonguing landward and seaward carbonate facies complexes, respectively, which developed on the shallowing shelf margin of the North American craton. Black Rock outcrops are restricted to a roughly east-west trending band across Sharp and Lawrence counties in northeastern Arkansas and a single, isolated locality recently discovered in Cape Girardeau County, Missouri, about 150 km to the north-northeast of the others. The relation between the two outcrop areas is unknown, but association of the Black Rock and Smithville is observable in both places.

In Arkansas, bryozoans are most abundant (up to 20 colonies per cubic meter) in silty biomicrudite that is locally altered to dolomite. In Missouri, population densities are much greater (up to 1000 colonies per cubic meter), and the dolomite matrix differs in containing up to 15 percent quartz sand, clay, and other allochthonous clastics. Bryozoans range vertically over an interval of at least 63 m in the subsurface and have been observed over a 10-m interval in one Arkansas exposure. Bryozoans are not known with certainty from the Smithville unit, although small, poorly developed colonies have been reported admixed with Smithville fossils in residuum from Arkansas (*5*).

The systematic position of the dianulitid bryozoans has been controversial for many years (*5*, p. 229; *9*). Despite their proposed removal from the order Trepostomata and inclusion in the order Cystoporata (*10*), recent revision of the *Treatise on Invertebrate Paleontology* retains them as trepostomes.

The new dianulitid has a turbinate (conical) zoarium which expanded upward with lateral increase of zooecial tubes at the periphery of the colony (*11*). Zoarial form varies widely, from steeply turbinate to flattened and saucer-shaped. External variation is reflected internally by the predominance of wide- and close-spaced diaphragms, respectively, in the morphological extremes. Some colonies also show an unusual type of rejuvenescent budding (Fig. 1, A and C) (*12*), in which clusters of undifferentiated zooecia issued from the living surface, forming a new colony, while growth in other zooecia of the parent ceased. Both phenomena are believed to be related to growth rate plasticity, which allowed the colony to fluctuate in the rate of upward growth or undergo rejuvenescence (or both) in response to environmental stimuli. The colony was sediment-supported

in some instances, as indicated by the presence of multiple budded colonies which could not have stood erect independently (Fig. 1A). It is probable that growth in many instances was influenced by the encroachment of sediment on the colony surface, resulting in the concentration of steeply grown and multiply budded colonies in areas of relatively rapid sedimentation. This relationship is evidenced in Missouri, where steeply grown and rejuvenescent forms prevail, and the rock is characterized by an abundance of poorly sorted clastic material, indicating relatively rapid deposition. Other variation in growth rate may have resulted from seasonal changes, storm turbulence, or other environmental parameters.

JOHN D. MCLEOD
Department of Geology, Northern Illinois University, DeKalb, 60115

References and Notes

1. Denotes North American classification. The Lower-Middle boundary corresponds to the Canadian-Champlainian Series boundary, and is currently defined within the *Didymograptus bifidus* graptolite zone, and between the "*Prioniodus*" *evae* and *Eoplacognathus variabilis* conodont zones. This boundary corresponds to the *D. nitidus-Isograptus gibberulus* boundary within the Arenig Series of the British succession. Reports of "Lower" Ordovician bryozoans from Estonia (B_{II} interval) are from beds equivalent to the *I. gibberulus* zone or younger [L. E. Fahreaus, *Bull. Can. Pet. Geol.* **26**, 5 (1977)].
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11. Like other species of *Dianulites*. the walls are thin, and show no apparent thickening in the exozone. The tubes grew parallel, and are polygonal in transverse section (Fig. 1B), with distinct polymorphism between smaller (0.15 mm) mesozooecia and larger (0.25 mm) autozooecia. In longitudinal section (Fig. 1D) the mesozooecia are elevated several diaphragm levels above adjacent, depressed autozooecia. Maculae appear as dense spots on the colony surface (Fig. 1C), and consist of clusters of mesozooecia.
12. Otherwise known to occur in only one other bryozoan, *Dianulites fastigiatus* from B_{II}-B_{III} interval of Estonia.
13. I thank D. B. Blake, R. S. Boardman, R. J. Cuffey, O. L. Karklins, M. T. Jollie, F. K. McKinney, J. P. Ross, G. J. Retallack, and M. P. Weiss for reviewing this report and M. F. Fix, S. H. Frost, J. Utgaard, O. A. Wise, and E. L. Yochelson for help and discussion.

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Collagenase Immunolocalization in Cultures of Rheumatoid Synovial Cells

Abstract. *Cultures of rheumatoid synovial cells that have been enzymatically dissociated and are adherent to a culture vessel are morphologically heterogeneous. When these cells are cultured on a collagenous substrate for 2 to 6 days at 37°C in serum-free medium, they produce collagenase. A monospecific antibody to human collagenase has localized the enzyme extracellularly around cytoplasmic extensions of dendritic cells and intracellularly within a few macrophage-like and fibroblast-like cells.*

Rheumatoid synovial collagenase is a metallo-enzyme with basic charge properties and a molecular weight of 33,000 (*1*). The enzyme is inhibited by Ca^{2+}-chelating agents, thiol reagents (*2*), and by the serum components α_2-macroglobulin and β_1-anticollagenase (*3*). A monospecific immunoglobulin G (IgG) antibody to active human collagenase, prepared in sheep (*4*), has been used to identify the immunoreactive enzyme at the cartilage-pannus junction in diseased articular tissue (*5*). These studies confirmed the association of collagenase with joint destruction in rheumatoid arthritis in vivo (*2*, *6*).

Rheumatoid synovial cells that have been dissociated enzymatically from synovial tissue and are adherent to culture vessel surfaces are heterogenous (*7*). Included among these are cells that morphologically resemble fibroblasts, large rounded cells, and unusual "dendritic" or "stellate" cells with rounded-up cytoplasm and long radial extensions. These cells have a slow doubling time, rarely reach confluence, and make little lysozyme; however, they synthesize and release collagenase in quantities up to 100-fold that reported for rabbit synovial fibroblasts or stimulated macrophages (*8*).

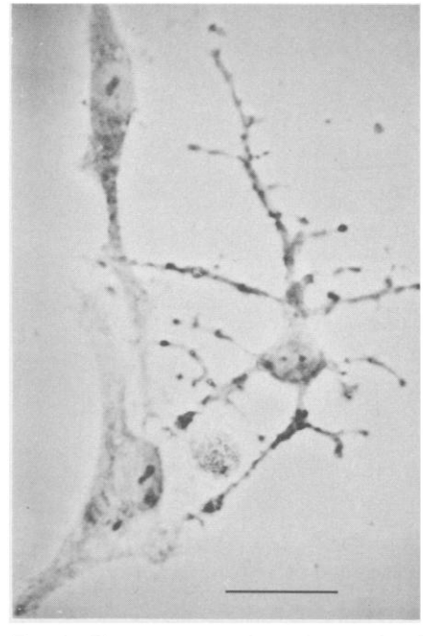

Fig. 1. Phase-contrast photomicrograph of isolated adherent rheumatoid synovial cells stained with toluidine blue. The dendritic cell, characterized by branched cytoplasmic extensions, contains many spherical phase-dense cytoplasmic granules which, from Janus green staining, indicate mitochondria (*9*). Bar represents 20 μm.

A typical dendritic cell and two fibroblast-like cells, which comprise more than 80 percent of the total cell population of such preparations, are shown in Fig. 1. Histological studies with Janus green and toluidine blue have shown that most of these dendritic cells contain many dense bodies packed into the cell processes, and have a stained appearance similar to that of large mitochondria (*9*). The failure of these dendritic cells to phagocytize latex particles suggests that they are functionally different from the fibroblast- and macrophage-like cells (*10*).

Dissociated rheumatoid synovial cells were dispersed in Dulbecco's modified Eagle's medium (DMEM) with 10 percent fetal calf serum, and grown on cover slips coated with thin films of thermally reconstituted collagen that were dried at 37°C (*7*). After 24 hours, the cells were washed free of serum-containing culture medium, and the cultures were continued in DMEM with 0.2 percent lactalbumin hydrolysate. After an additional 48- or 72- hour incubation, the collagen-coated cover slips were fixed for 30 seconds in 80 percent ethanol and air-dried. Indirect immunofluorescence, with monospecific sheep antibody to synovial collagenase and fluorescein isothiocyanate (FITC) labeled rabbit antibody to sheep immunoglobulin G (*5*), was used to localize collagenase in these cultures (Fig. 2).

Immunoreactive collagenase was associated chiefly with dendritic cells. The FITC fluorescence located the enzyme around (and probably within) the cytoplasmic extensions, as if it had been bound or trapped by the collagen substratum. However, only a proportion of the dendritic cells were associated with extracellular enzyme. Some fibroblast-

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