

Condensation probably occurred near ground level and ultimately led to the development of an oil slick. Ultraviolet absorption calculations were related to the temperature and transport model of McGovern (8); the calculations indicate that the important formation of hydrocarbons would occur anywhere from just above the mesopause to tens of kilometers below it. If we assume that a steady state is reached in about 10 years and that the irradiation products are transported into the lower atmosphere within a few years, the methane atmosphere could have been polymerized by solar ultraviolet radiation in 10^6 to 10^7 years.

If 1 atmosphere of methane is polymerized, a universal oil slick some 1 to 10 m thick would be produced. It is not known whether or how fast this material would be removed from the surface of the early oceans by adhering to mineral or rock particles, but the continued presence of an oil slick would have had some rather intriguing consequences. The dilute "prebiotic soup" would have been covered with a very rich hydrocarbon layer that could have acted as a host for prebiotic compounds. These would have been exposed to longer wavelength solar ultraviolet light and lightning discharges as well as to solvent extraction processes at the water-oil interface. Thus the effects of an oil slick on the chemistry of the prebiologic and earliest biologic periods could well have been important and deserve careful evaluation.

The photodissociation rate of molecular nitrogen is negligible at wavelengths longer than 1000 Å. Only a very small fraction of the energy of the solar ultraviolet spectrum is therefore available for N_2 dissociation, and the photochemistry of an early CH_4 - H_2 - N_2 atmosphere was probably quite similar to that of a CH_4 - H_2 atmosphere. The photochemistry of a more oxidizing atmosphere would probably have been quite different.

If the temperature structure of the early atmosphere was similar to that of the present day, water vapor would have been a rare constituent of the upper atmosphere, but CO and CO_2 may have been present, and were surely there during the transition from an early reducing to a later, more oxidizing atmosphere. The effects of these gases on the appearance and composition of an oil slick remains to be determined.

Polymerization reactions similar to those discussed above are surely in pro-

gress on the major planets. However, comparable oil slicks are probably not formed, because the large excess of hydrogen and the high temperatures ($\sim 900^\circ K$) at the base of the atmospheres of these planets favor the thermal decomposition reactions of larger hydrocarbons with hydrogen to form methane (9).

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Fecal Pellets: Role in Sedimentation of Pelagic Diatoms

Abstract. *Membrane-enclosed fecal pellets of planktonic herbivores were sampled at several depths in the Baltic Sea (459 meters deep) and off Portugal (4000 meters deep) by means of a Simonsen multinet. Pellets contained mainly empty shells of planktonic diatoms and silicoflagellates. Two kinds of fecal pellets were found, those with the remains of one species (for example, Thalassiosira baltica) and those with the remains of several species (for example, Chaetoceros, Achnanthes, and Thalassiosira). Siliceous skeletons were protected from dissolution during settling by a membrane around the pellet.*

Pelagic diatoms are a major factor in the biology, chemistry, and sedimentation of the oceans (1). They are the most important primary producers at the base of the food chain (2) and

may be responsible for the general undersaturation of seawater with silica (3), because the rate at which they deposit silica exceeds the influx of dissolved silica. The excess supply of silica demanded by diatom frustules necessitates re-solution of sedimented diatom frustules to maintain the geochemical balance of silica in the water column (4). Evidence for dissolution in the upper centimeters of sediment has been presented (5-7). In addition to their important role in the modern ocean, diatoms are a diversified group of shelled plankton potentially useful in the reconstruction of ancient ocean conditions (8).

In discussions of the biochemical and geological aspects of diatom sedimentation, the role of fecal pellets, although occasionally mentioned (9-11), until recently has not received the attention it deserves (12-14). Membranes surrounding the fecal pellets of planktonic

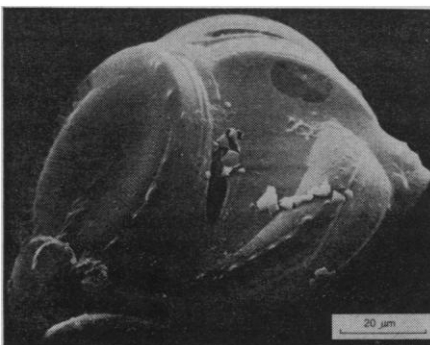


Fig. 1. Fecal pellet of *Calanus finmarchicus* Gunnerus with the centric diatom *T. baltica* enclosed within. The damage to the fecal pellet membrane occurred during coating with metal in a vacuum (scanning electron micrograph).

herbivores are common (15). This report gives additional evidence that certain copepods, mainly calanoid ones, form a membrane encasing voided diatom shells. The resulting pellets sink many times faster than a single shell, thus rapidly transporting silica from surface water to deeper waters. The rate of sinking for a single *Thalassiosira baltica* (Grun.) Ostenfeld frustule (50 μm in diameter) is approximately 10 m/day (14); the rate of sinking for a fecal pellet (100 μm in diameter), however, is about 100 m/day (16). In addition, the membrane (Fig. 1) protects the enclosed diatoms from dissolution during their descent to the ocean floor.

For study of diatom sedimentation, samples were taken at several depths during a cruise in the Baltic Sea (*Planet* cruise 5, 1969) and an expedition off

Portugal (Rossbreiten Expedition, *Meteor* cruise 19, 1970). In the Baltic the Simonsen phytoplankton multinet (17) (mesh size 41 μm) was used to sample at 0 to 70, 70 to 140, 140 to 210, 210 to 280, 280 to 350, and 380 to 420 meters deep in vertical hauls. About 20 m³ were filtered by the closing net towed along about a 70-m transect for each subsample. Samples were also collected with Nansen bottles from various depths (2, 40, 80, 120, 160, 200, 240, 280, and 320 m). One-half liter of the water sample was filtered through a membrane filter. The filters were then dried, and one tenth of each filter was embedded in mounting medium (Aroclor 4465) for slide preparations for examination by light microscopy. All diatoms, feces, and dinoflagellates were counted. Off Portugal, 12 samples were collected from various depths down to 4000 m in one vertical haul with the phytoplankton multinet (18), and about 80 m³ were filtered by the multinet along a 300-m vertical transect. Microscopical strewn slides were made from plankton samples, and all particles (feces, diatoms, dinoflagellates, copepods, and so forth) were counted. The results given here are mainly from the Landsort Basin in the Baltic (depth 459 m).

The centric diatom *T. baltica* was extremely abundant in the Baltic surface waters (25,000 cells per liter) at the time of the expedition (May 1969). Living cells of this species have a characteristic structure of fine, small circular pores with radially arranged teeth projecting from the rim into the center of the aperture (Fig. 2, top). In empty shells caught at depth there is a tendency for a reduction in the number of teeth and for pore enlargement. These morphological changes were interpreted as effects of dissolution. The relative state of preservation of these diatom frustules was measured by calculating (i) the pore density as the percentage of pore space in the total valve area, and (ii) the tooth index, that is, the number of teeth per pore times their length. Both indices were measured in fractions of micrometers. Measurements were made from photo enlargements ($\times 25,000$) of 30 shells of *T. baltica* picked from six multinet subsamples [GIK (Geologisches Institut Kiel) No. 10,064-1; depths as in Fig. 2] and photographed with a scanning electron microscope ($\times 10,000$).

The results demonstrate (Fig. 3) that both indices measure dissolution. Shells

generally are significantly more deteriorated in deeper water than they are in shallow water. The aberrant value for the population at 280 to 350 m (*D* in Fig. 3) reflects a mixture of completely preserved (Fig. 2, top) and strongly attacked frustules (Fig. 2, bottom) found there. I suggest that the preserved shells were transported to this depth within fecal pellets. Feces were abundant in the upper 100 m (2500 diatom-containing pellets per liter). Pellets were of two kinds, those containing but one species (*T. baltica*, or chains of *Achnanthes taeniata* Grunow.) and those containing a variety of species (*T. baltica*, *A. taeniata*, pieces of broken *Chaetoceros* species, Ebricaceae). Fresh pellets are completely covered by the membrane (Fig. 1), and the state of preservation of the shells contained is very similar to that of living diatoms. Thus skeletons of *T. baltica* are not damaged during passage through the gut of the copepod. *Calanus finmarchicus* Gunnerus was at that time the only predominant herbivore in the samples. The fecal pellets shown in the figures were found in guts of many *C. finmarchicus*, so it is probable that most

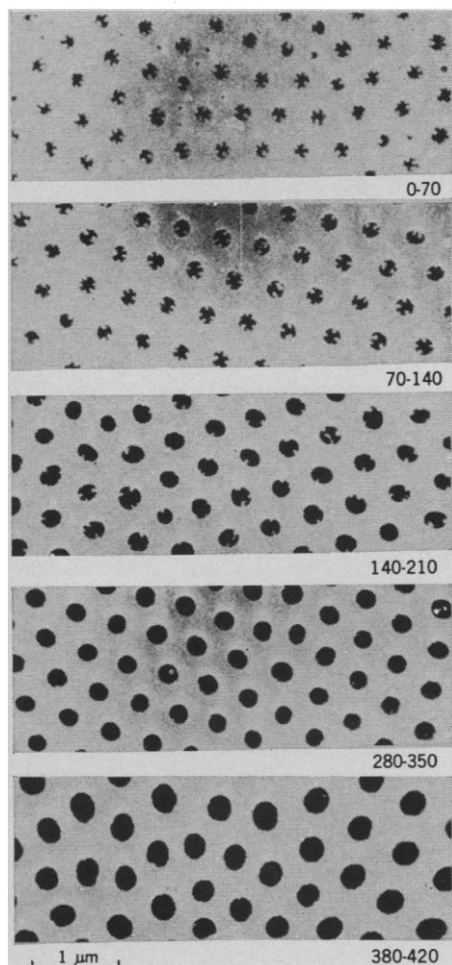


Fig. 2. Fine structure of valves of *T. baltica* frustules collected at various depths (in meters). In the top panel (collected from a transect at 0 to 70 m) the structure of a living cell is given. Other shells (collected from transects at depths of 70 to 140, 140 to 210, 280 to 350, and 380 to 420 m) represent different stages of dissolution during settling (scanning electron micrograph).

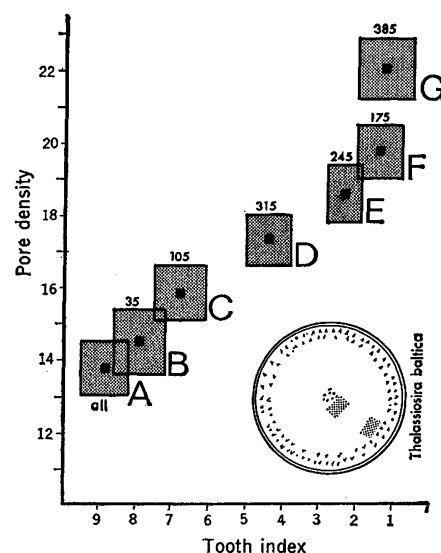


Fig. 3. Dissolution diagram of *T. baltica*. Index letters represent subsamples; the numbers over the squares give medium depths in meters. Index A represents parameters of living shells and those gained from intact pellets independent of depth of sampling. Indices B, C, E, F, and G represent parameters of settling frustules. The aberrant values for index D reflect mixture of completely preserved and strongly corroded shells. The picture of *T. baltica* on the right shows dotted areas where measurements were carried out on each specimen. See text for an explanation of method of calculation and units.

round, ball-shaped feces containing diatoms were produced by this herbivore. As long as the fecal membrane lasts, little exchange of water can take place between the interior and the exterior of the pellet, and the diatom shells are safe from dissolution. Most fecal pellets apparently disintegrated at about 300 m, but a sizable fraction may reach the sea floor intact (Fig. 4). Moore (19) reports that zooplankton fecal pellets were only detected in nearshore sediments of the English coast to a depth of 166 m. In the Baltic diatomaceous feces were found on the surface of the sea floor, down to 459 m deep.

The transport of diatoms within fecal membranes potentially enriches the sediment with species that are preferentially eaten by certain herbivores, and whose shells escape harm during digestion. Selective feeding is reported for several herbivores (20), and differences in resistance to disintegration (10, 21) may characterize the different diatom species ingested. Thus, whereas *T. baltica* shells remained completely unharmed, members of the genus *Chaetoceros*, for example, were crushed to such a degree before being packed into fecal pellets that identification was very difficult. In contrast to previous findings (11, 12), *Calanus finmarchicus* does feed upon *Chaetoceros* species sometimes, as is obvious from its gut contents.

Phytoplankton particles smaller than 30 μm have not been observed to be actively filtered by calanoid copepods. (Some pelagic diatom species, *Fragilariopsis*, *Nitzschia*, some pelagic species of *Thalassiosira*, and *Coscinodiscus* are this size.) Thus a bias may be introduced against the sedimentation of very small diatom frustules by feces.

These predation processes may be of considerable importance in the formation of deep-sea sediments. Off Portugal, west of Porto, zooplankton feces which contain masses of diatom shells were found down to 4000 m deep (approximately two pellets per cubic meter at depths from 3300 to 3600 m). These pellets were packed with diatom species (*Skeletonema*, *Rhizosolenia alata*, *Eucampia*) that would never have settled singly without being completely dissolved before reaching this depth (21, 22). The same is true for silicoflagellates, the skeletons of which were present in large numbers in some pellets; this is somewhat surprising in view of the scarcity of silicoflagellates in the upper water at the time (23).

The fact that diatoms, the basic staple of oceanic herbivores, are packed into fecal pellets, most of which have membranes (15), has the following suggested implications. By virtue of their greater size (50 to 250 μm in diameter), pellets rapidly leave the photic zone, sinking between 40 to 400 m/day (14, 16) and thus depleting upper waters of silica (3) and other nutrients. Shorter settling times provide for a better chance of preservation and, incidentally, for less drift of shells away from their place of origin, thus accounting for the fact that surface water masses can be reflected in sediments below. Preservation is further enhanced in diatoms that are eaten by copepods that pass the skeletons unharmed and encase them in a fecal membrane. Thus, much of the difference between living diatom assemblages and sediment assemblages may come from biological interactions, not simply from differential chemical dissolution favoring robust shells. Sedimentation by pellets allows formation of annual diatomaceous varves (19, 24), since without the accelerated sinking (14) diatoms would take so long to reach the ocean floor that seasonal changes would not be recorded. Sedimentation of pellets may largely provide delivery of an excess supply of silica to the ocean floor, since most silica would otherwise dissolve within the water

column. This excess extraction drives the water toward undersaturation until solution rates on the ocean floor provide the necessary balance for equilibrium of the silica reservoir in the oceans.

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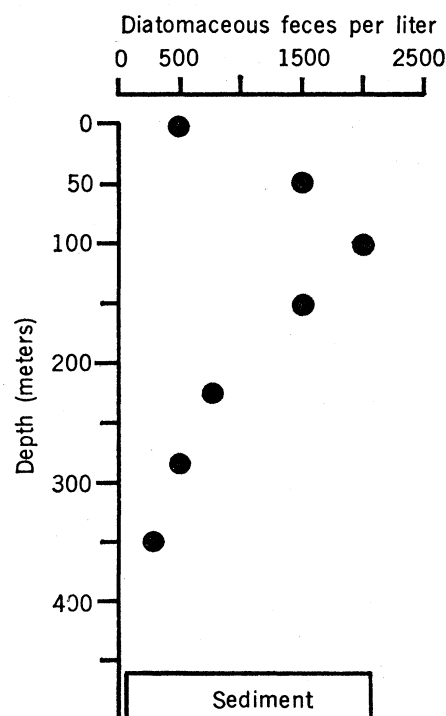


Fig. 4. Concentration of fecal pellets containing diatom shells in waters of the Landsort Basin in the Baltic.