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Characterization of Particulate Matter in the Ocean

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ABSTRACT

Electron micrographs of ocean filtrates collected near the surface at Key West, Block Island, and Chesapeake Bay show three common constituents: diatoms, plant fibers, and amorphous organic matter. In addition, material collected from layers giving strong sonar reflection at Key West and Block Island show numerous smaller iron-rich particles, probably a hydrated iron oxide, in the size range 0.01 to 0.1 micron. The iron particles are too small for x-ray diffraction but can be examined by x-ray fluorescence and electron probe analysis. In addition to iron, the particles show no other elements above atomic number 22, at least not above 1 percent composition.

PROBLEM STATUS

This report is the first and final report by the X-Ray Optics Branch summarizing its part in a study of particulate matter in the ocean. The role of this Branch in this work has been completed.

AUTHORIZATION

This work was performed under funding of the X-Ray Optics Branch at the request of the Sound Division, NRL. The work relates to NRL Problems S01-18 and S01-26 of the Sound Division.

NRL Problem P04-04
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CHARACTERIZATION OF PARTICULATE MATTER IN THE OCEAN

INTRODUCTION

X-ray and electron optical techniques have important capabilities in the characterization of particulate matter in the ocean. Electron microscopy gives better representation of the shape and size of submicron particles than is possible with visible-light microscopy or scattering. X-ray diffraction distinguishes chemical compounds such as clays, carbonates, silicates, etc. X-ray fluorescence allows elemental analysis of a few micrograms of material, and the electron probe allows local elemental analyses of individual particles.

This report is devoted mainly to an electron microscopic investigation of specimens collected in the Key West, Block Island, and Chesapeake Bay areas by A.J. Hiller and colleagues of the Sound Division. In addition, it discusses x-ray fluorescence, electron probe analysis, and x-ray diffraction measurements on material collected from an unusual iron-rich layer at 650-ft depth off Key West.

ELECTRON MICROSCOPY

Specimen Preparation

Specimens collected on Millipore filters are not suitable for direct examination in the transmission electron microscope because the filter is too thick to be penetrated by the electron beam. Therefore, it is necessary to transfer the filtrate to a standard electron microscope support consisting of a transparent, evaporated carbon film on a copper grid base. A faster, more efficient way of doing this was developed for the examination of large numbers of specimens and is shown in Fig. 1.

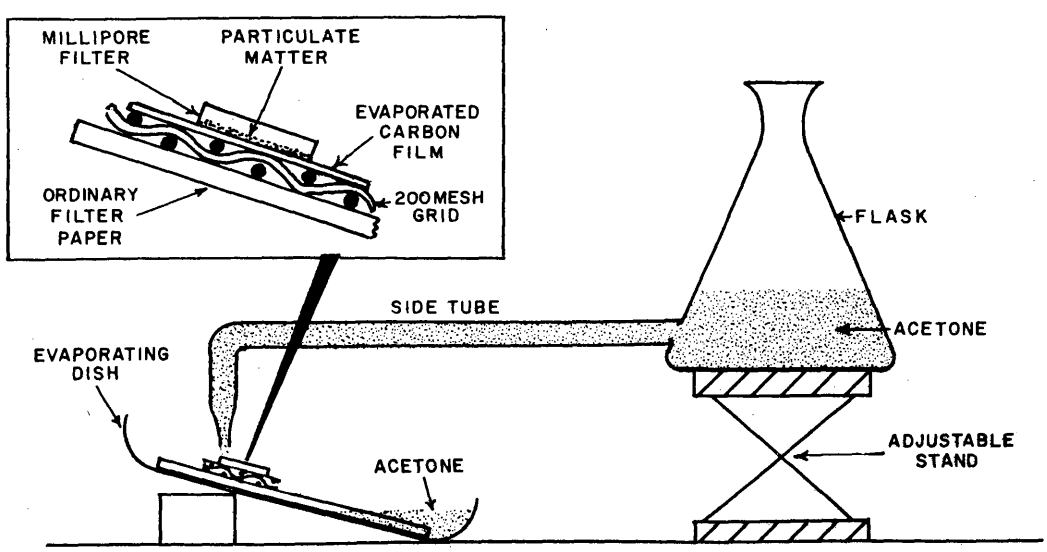

Fig. 1 - Schematic of sample preparation for electron micrographic examination

The evaporating dish is set at an angle with a piece of ordinary filter paper in the bottom. The dish is partly filled with acetone to wet the paper; a carbon-coated electron microscope grid is placed on the paper and is wet by the acetone-soaked paper. Then a 1/8-in. square of the Millipore filter is placed, filtrate side down, on the carbon film and is immediately wet by the acetone. Complete solution of the Millipore material is hastened by acetone from the flask; the side tube is drawn down so that, when not in contact with the specimen, it drips at the rate of about one drop every 5 sec. As the flask is lowered gently on the scissors jack, the drop contacts the specimen and a smooth continuous flow of clean acetone is assured. (About 15 min are required for complete solution.) Figure 2 shows control specimens prepared in this fashion from clean Millipore filters. Figures 2(a), (b), and (d) show no particulate matter whatever and are typical of the general cleanliness of the preparation. Figure 2(c) shows that a few extraneous particles are occasionally introduced in preparing the specimen, but they are not similar in appearance to the ocean filtrates.

Key West Samples

Samples were collected both by air drops and from ships. The amount of water collected and filtered varied from one sample to another; thus the apparent density of particles in the following pictures is not necessarily representative of the actual density in the water.

Figures 3-6 all represent water samples collected near the surface, but by different means and on different dates as stated in the caption. Essentially, these figures all show the same type of particulate matter, namely, the screen-like diatoms, the fiberous plant material, and the filmy or amorphous organic deposits. Figure 7 is completely different in appearance. It was collected at a 650-ft depth from a layer which gave strong sonar scattering (1). The individual particles are in the 0.01 to 0.1 micron size range but tend to agglomerate into groups of particles. It is probably these agglomerates which are measured by the Coulter counter. As later sections of this report will show, the particles seem to be hydrated iron oxide and very little else. In any case, it is very easy by electron microscopy to distinguish these particles from the usual material.

Block Island Samples

Figures 8-11 show samples collected from different depths off Block Island. The zero and 20-ft-depth specimens, Figs. 8 and 9, show the usual diatoms, fibers, and amorphous organic deposit. The 40-ft and 60-ft specimens, Figs. 10 and 11, show in addition many small particles very similar to the iron layer at 650-ft depth off Key West. In the Block Island samples, however, the iron particles are enmeshed in the general organic matrix. There was strong sonar scattering from the 40- to 60-ft layer. It would be much too early to draw conclusions from this meager data, but at least it is consistent that the small iron particles are present in both cases of strong sonar scattering. The rest of the particulate matter is very similar in all samples.

Chesapeake Bay Samples

Figure 12 is a surface sample collected west of Kent Island during rough weather, sea state 3+. There are the usual diatoms and organic matter, plus numerous flakes about 0.2 to 0.3 micron across and very thin; the flakes are probably clays stirred up from the bottom. None of the small iron particles were observed. The sample of Fig. 13 was collected in the same locality but 2 days later in a calm sea, sea state less than 1. There is very little difference in appearance between Figs. 12 and 13. This could mean that the particulate matter is not affected much by sea state or that 2 days are not long enough for the fine clays to settle out.

X-RAY MEASUREMENTS

X-Ray Fluorescence

Quantitative x-ray spectrochemical analysis has become standard practice in industrial chemical analysis of bulk specimens. But small amounts of particulate matter require somewhat different specimen preparation. To reduce background intensity, a disk of the Millipore filter was mounted on a 1/4-mil Mylar membrane. This assembly was supported on an open frame so that the incident x-ray beam which was not absorbed in the filtrate could pass into a beam trap without scattering into the x-ray spectrometer. Standards were prepared by precipitating known quantities of iron or other elements onto similar membranes. The limit of detectability (line intensity greater than three times the standard deviation of the background) was observed to be between 0.05 and 0.5 μg for common elements.

The filtrate from 650-ft depth off Key West, Fig. 7, showed about 15 μg of iron per sq cm. Energy dispersion detected no other elements above atomic number 22. At the sensitivity level established, this would mean that other elements would have to be less than 3 percent of the iron concentration.

Five other specimens were examined by x-ray fluorescence. The sample of Fig. 3 showed no iron or other elements above atomic number 22. Another sample collected in the same location (no micrograph) showed about 1.2 μg of iron per sq cm.

Electron Probe Analysis

Electron probe analysis uses a focused electron beam rather than primary x rays to excite the characteristic x rays in the specimen. The probe is ideally suited for local analysis of micron-sized areas. It is necessary that the specimen be electrically conducting; for particulate matter it is common practice to place the sample on a conducting substrate, such as a pure aluminum block, and to overlay the particles with a few hundred angstroms of evaporated aluminum. An electron probe specimen was prepared from the 650-ft water sample by placing a 1-mm square of the filter, face down, on a polished aluminum block and dissolving the Millipore material in the fashion of electron microscope specimens. Small pieces of Mn, Fe, and Ni were embedded in the aluminum as standards.

Dispersive analysis with crystal spectrometers showed strong Fe lines everywhere on the specimen but no Mn or Ni lines (the limit of detectability would be less than 1 percent for such a specimen). Energy dispersion did not detect any other elements above atomic number 22.

X-Ray Diffraction

Ordinarily, x-ray diffraction would be expected to identify compounds rather than elements present in the filtrate. Japanese scientists (2) have used x-ray diffraction to identify clays, silicon dioxide, and feldspar present in filtrates collected in the China sea and in the Western Pacific. When the 650-ft specimen was examined by powder x-ray diffraction, only a few weak NaCl lines were observed from salt remaining after the washing. This is not too surprising, however, because particles larger than 0.1 micron are required for sharp diffraction lines. Particles as small as 0.01 micron will give weak broad diffraction lines, but only if sufficient quantity of material is available. Future collections should insure several milligrams of filtrate if x-ray diffraction is to be applicable.

CONCLUSION

For future specimens, it would be desirable to collect a thin deposit for electron microscopy or electron probe analysis and a thick deposit for x-ray fluorescence or diffraction. The amount needed should be standardized in either case to aid in quantitative evaluation.

The sensitivity of x-ray fluorescence is good enough for fairly precise quantitative analysis if 10-20 mg of material is available. The electron probe is the only tool capable of identifying individual particles of interest; its application should be pursued to a considerably greater extent.

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2. Ishii, J., and Ishikawa, T., "The Determination of Mineral Components of Suspended Matter in Sea Water by X-ray Diffractometer," in "Studies on Oceanography," Memorial volume to Prof. K. Hidaka of Tokyo University, Tokyo University Press, 1964

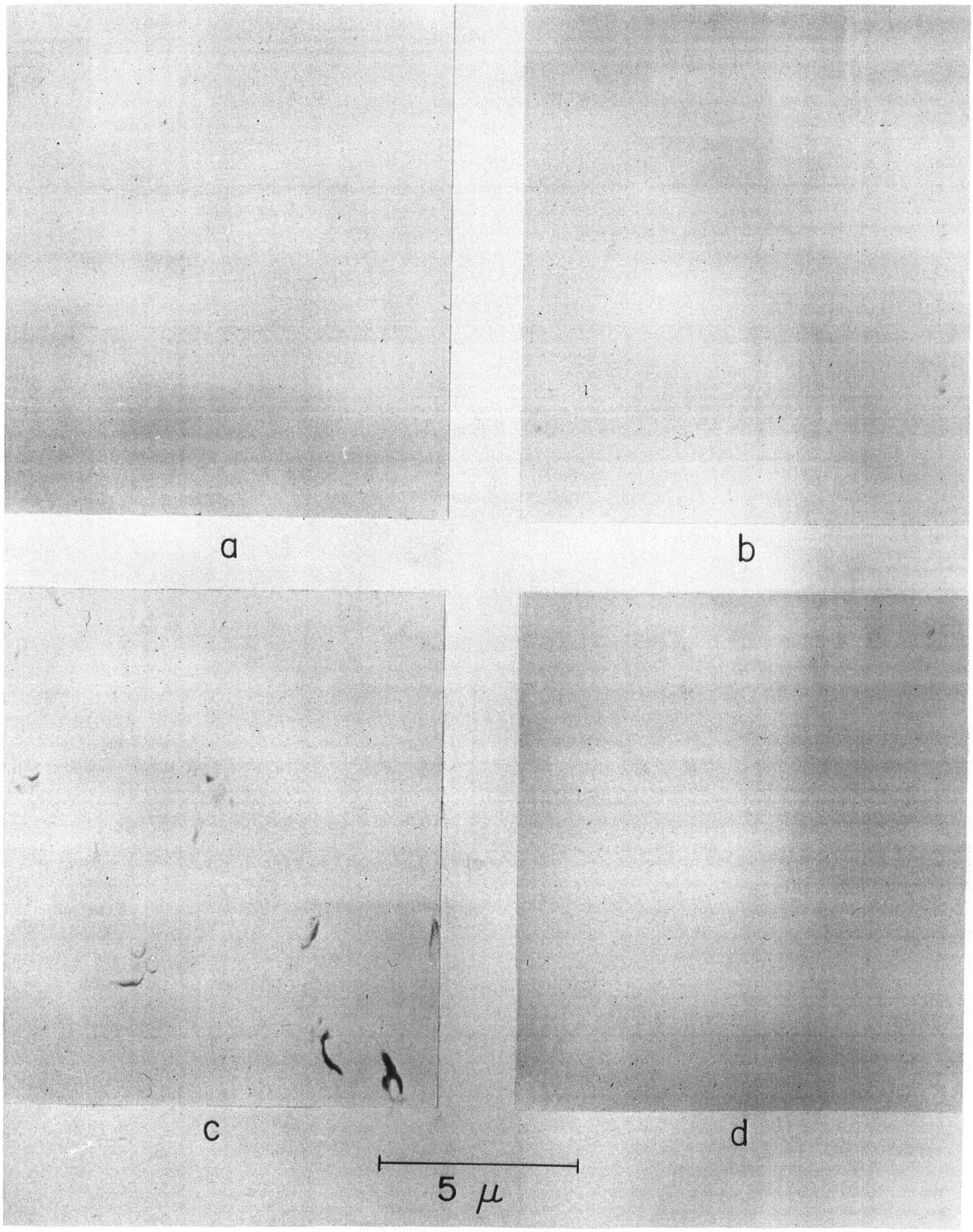

Fig. 2 - Control specimens prepared from clean Millipore filter. A few extraneous particles are shown in Fig. 2(c), but they are not similar to the ocean particles.

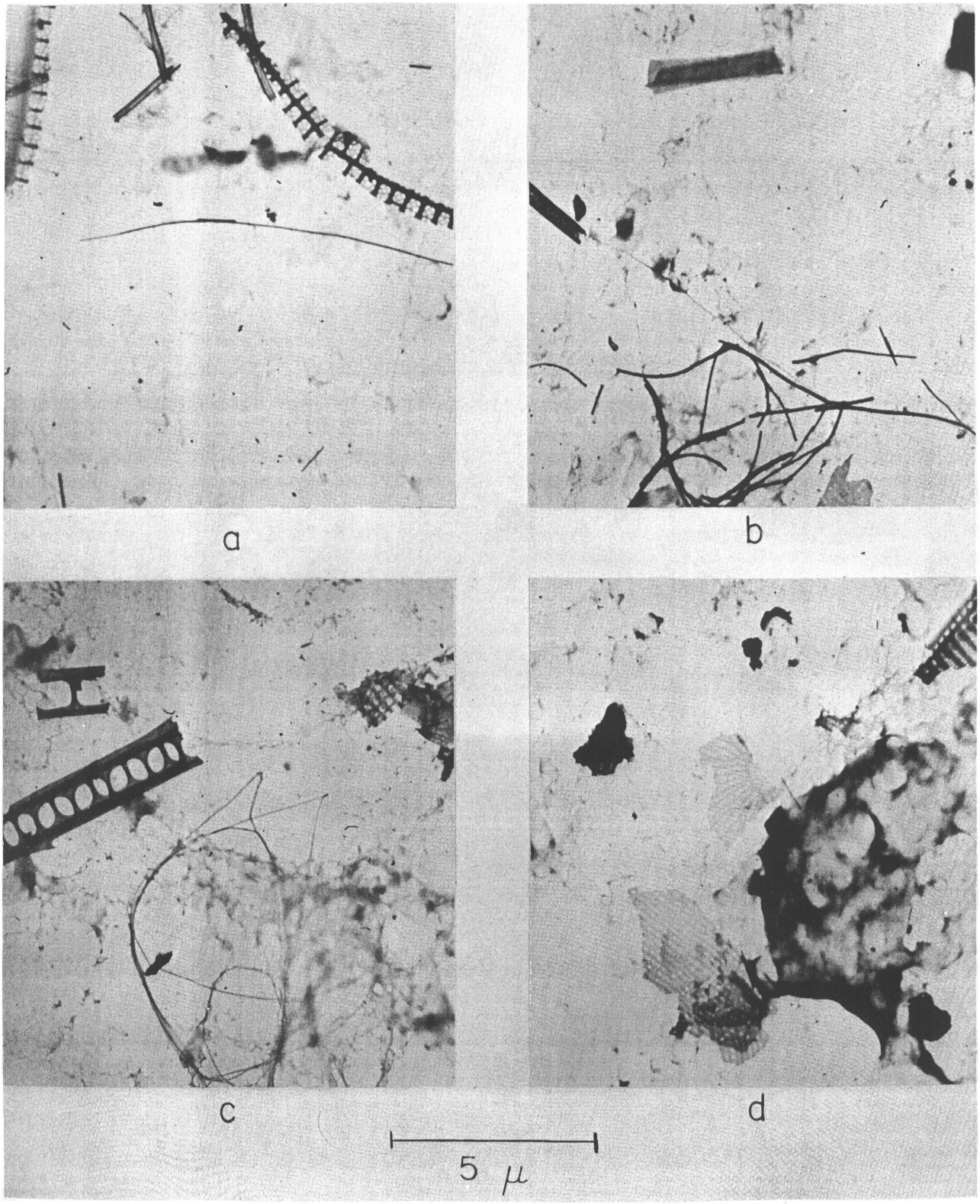

Fig. 3 - Air drop surface water collection W: 2 gal, 20 mi south of Key West, sea state 2, bottom depth 780 ft, collected on 3/24/65

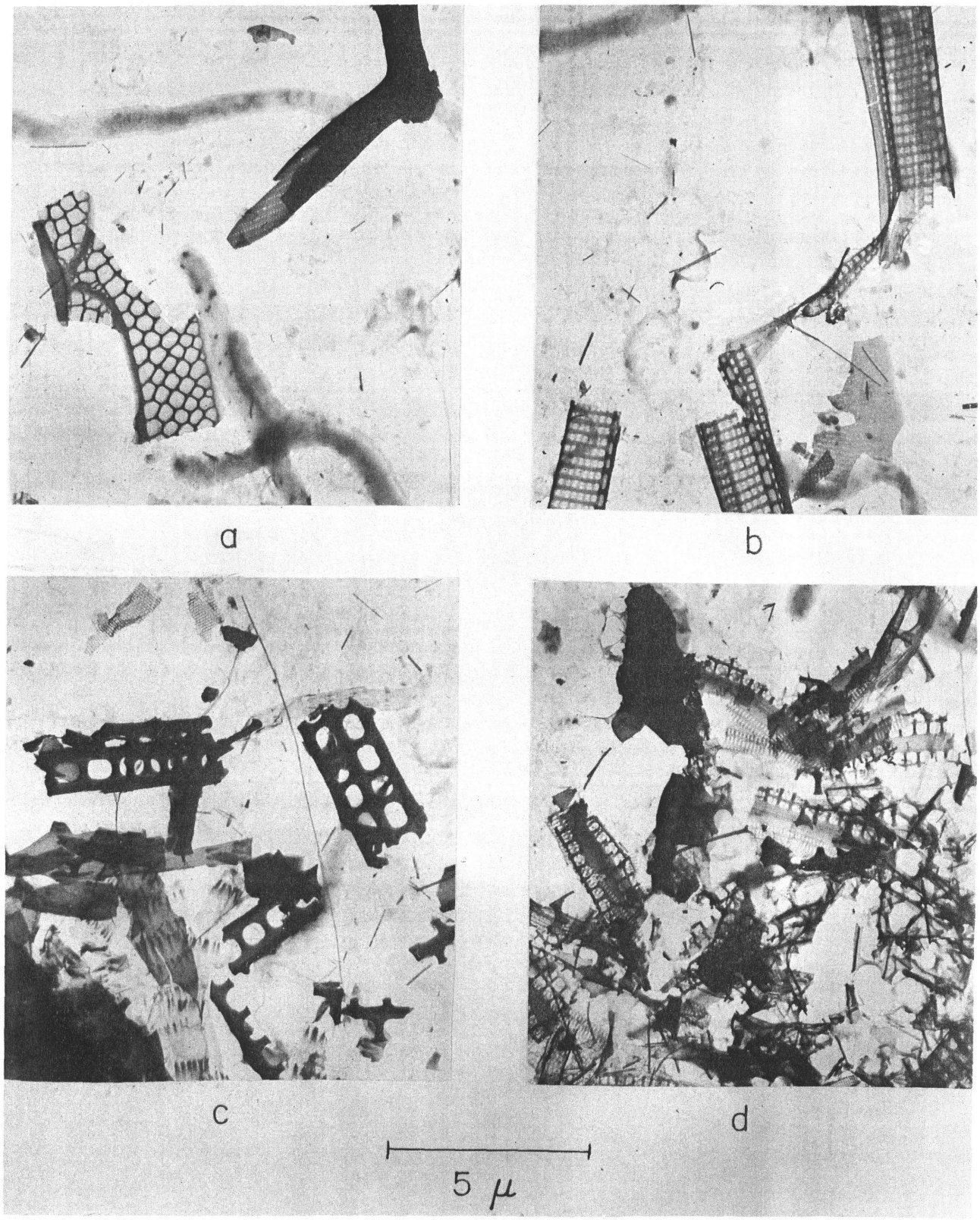

Fig. 4 - Air drop surface water collection A: 2 gal, same conditions as Fig. 3

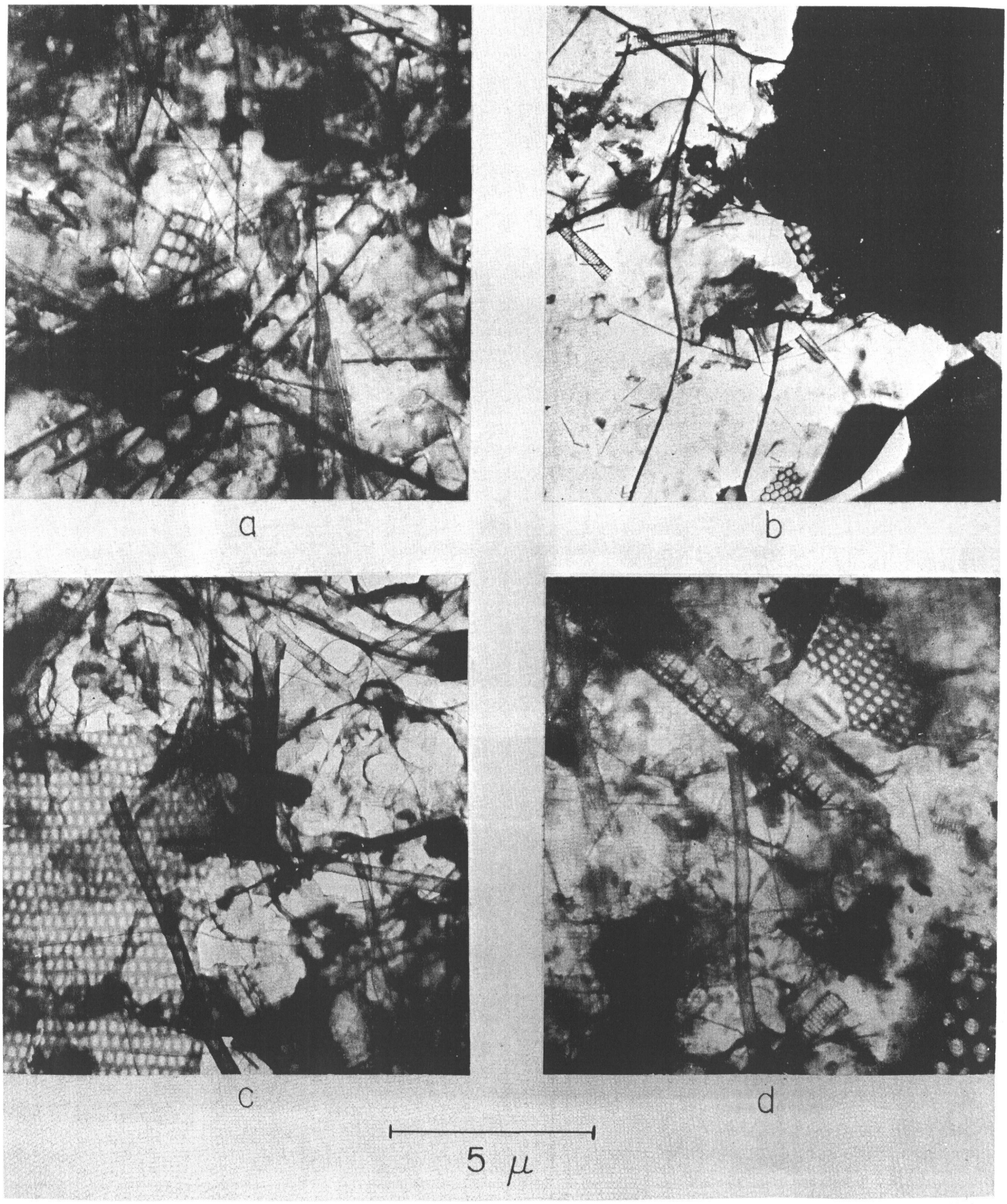

Fig. 5 - Surface water collection from ship: 20 gal, same conditions as Fig. 3

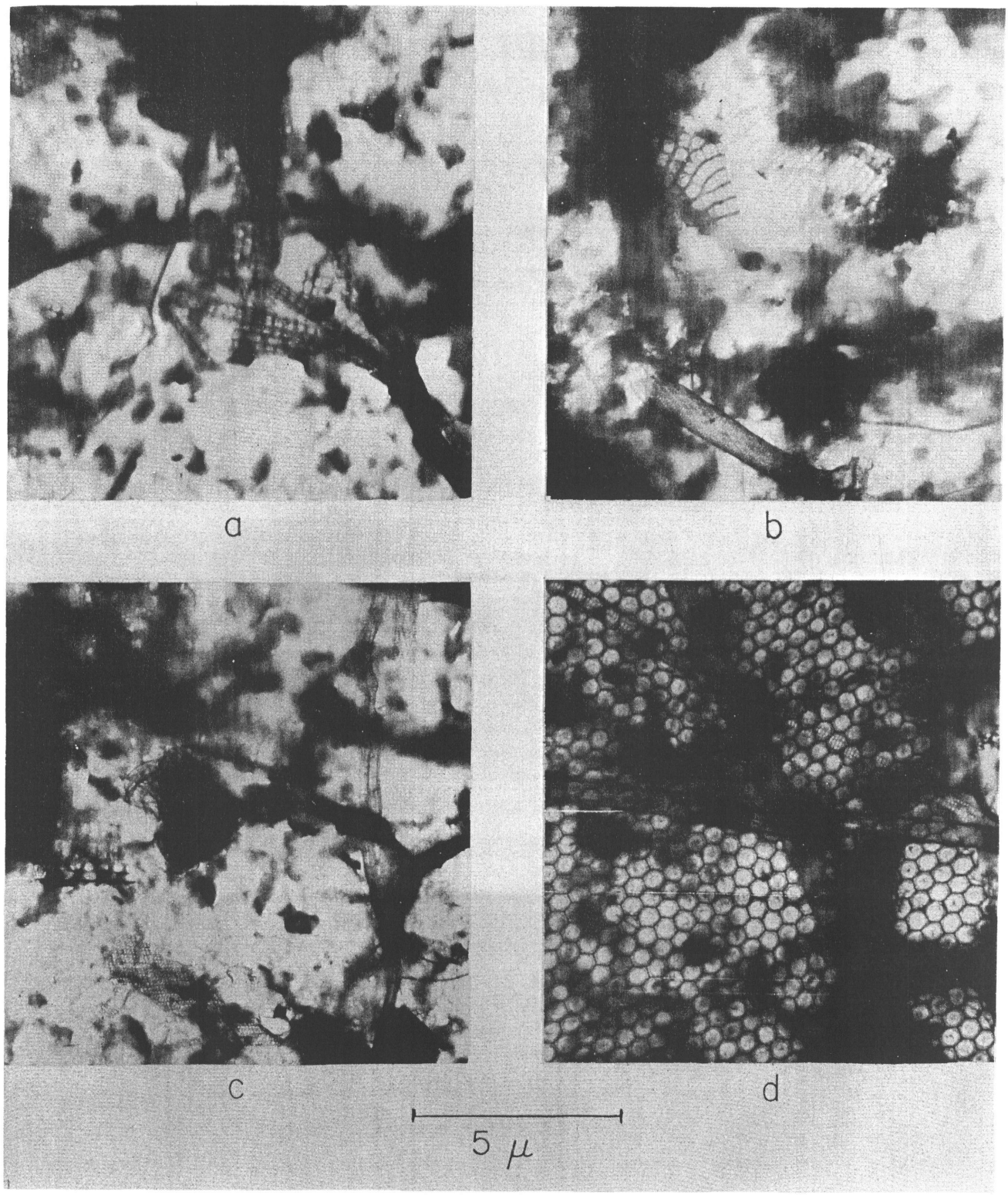

Fig. 6 - Surface water collected from ship: 20 gal, same conditions as Fig. 3, except collected on 3/26/65

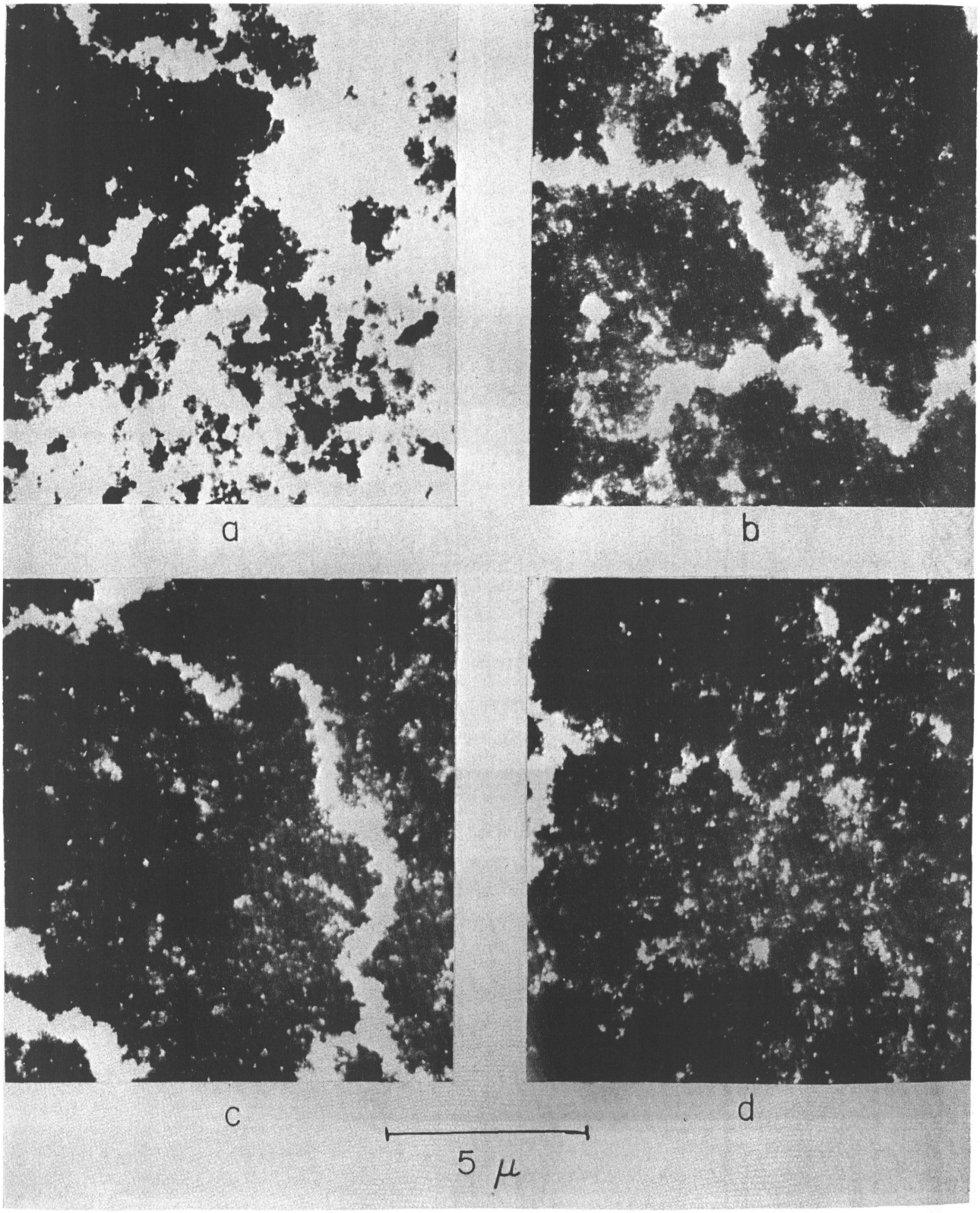

Fig. 7 - Ship collection from 650-ft depth in same area as Fig. 3, collected in January 1965

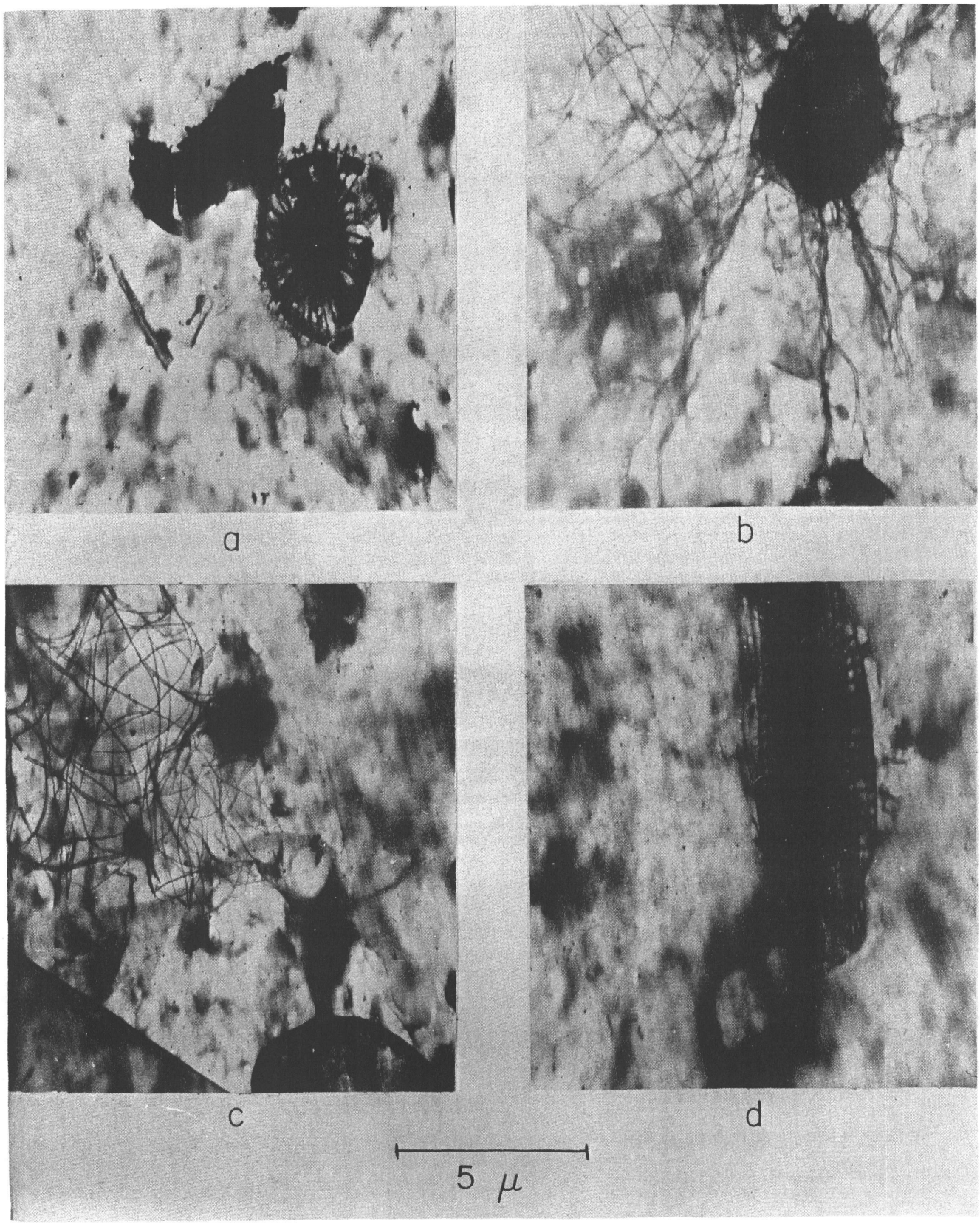

Fig. 8 - Surface water collection, 9 mi south of Block Island, bottom depth 180 ft, collected on 7/30/65

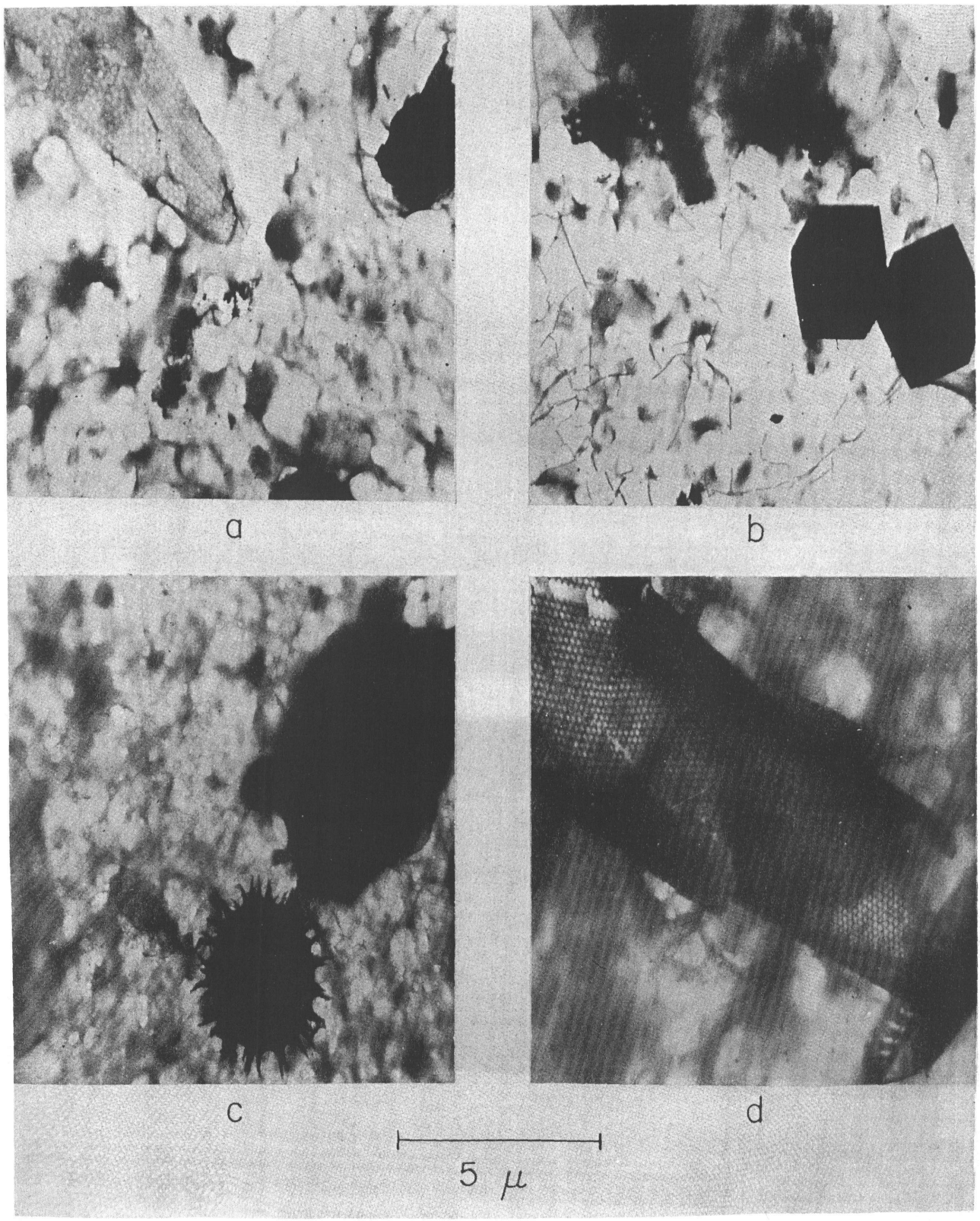

Fig. 9 - Collection from 20-ft depth, same conditions as Fig. 8

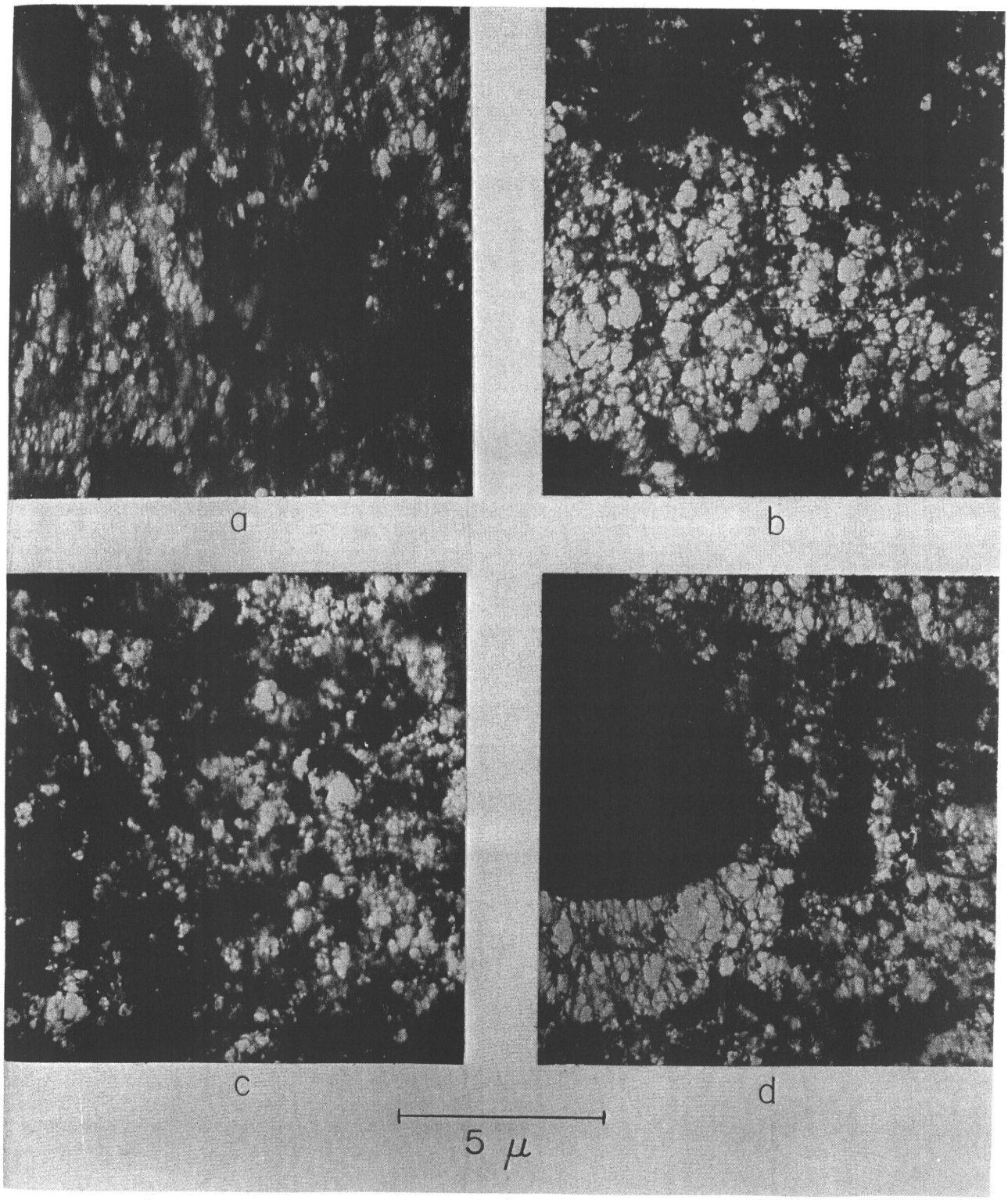

Fig. 10 - Collection from 40-ft depth, same conditions as Fig. 8

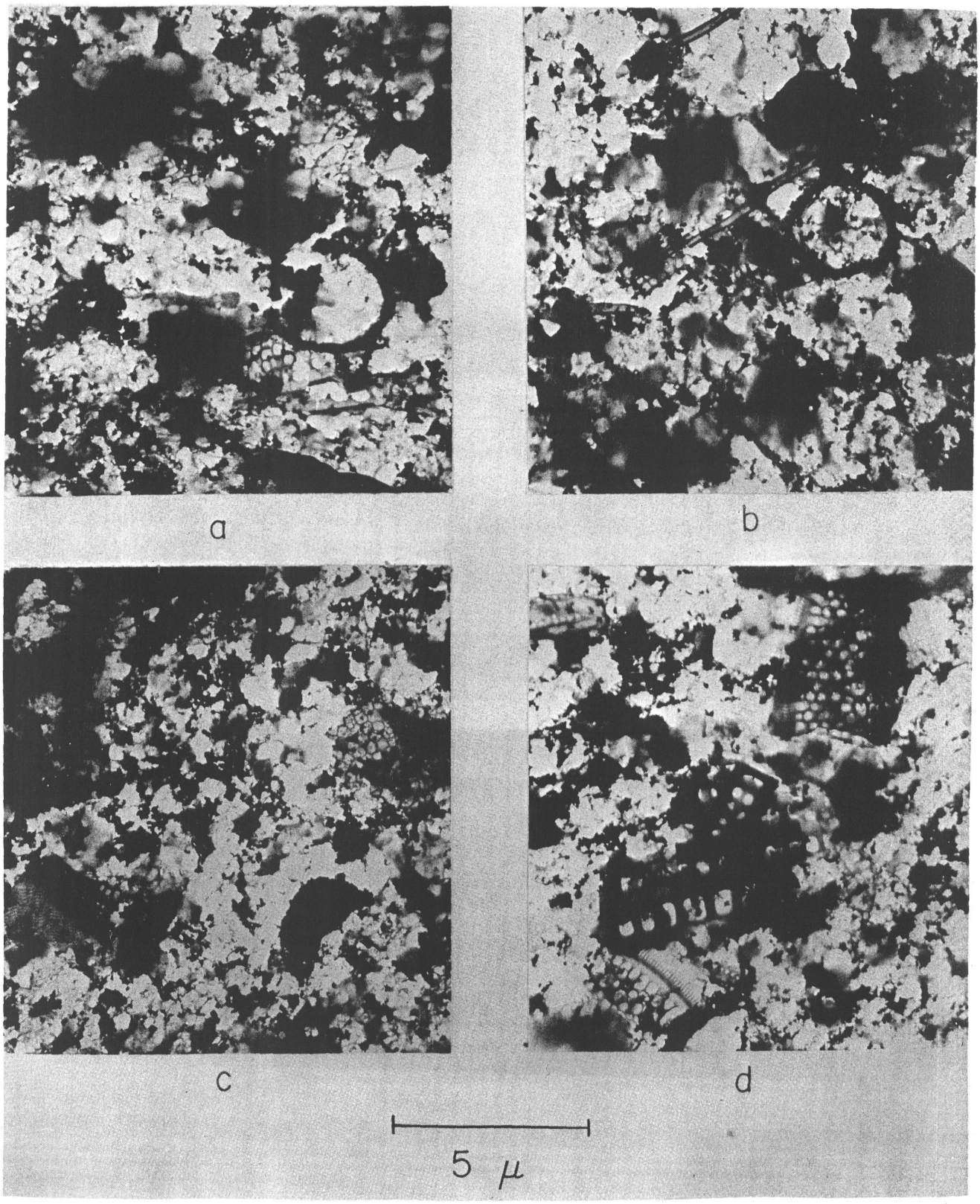

Fig. 11 - Collection from 60-ft depth, same conditions as Fig. 8

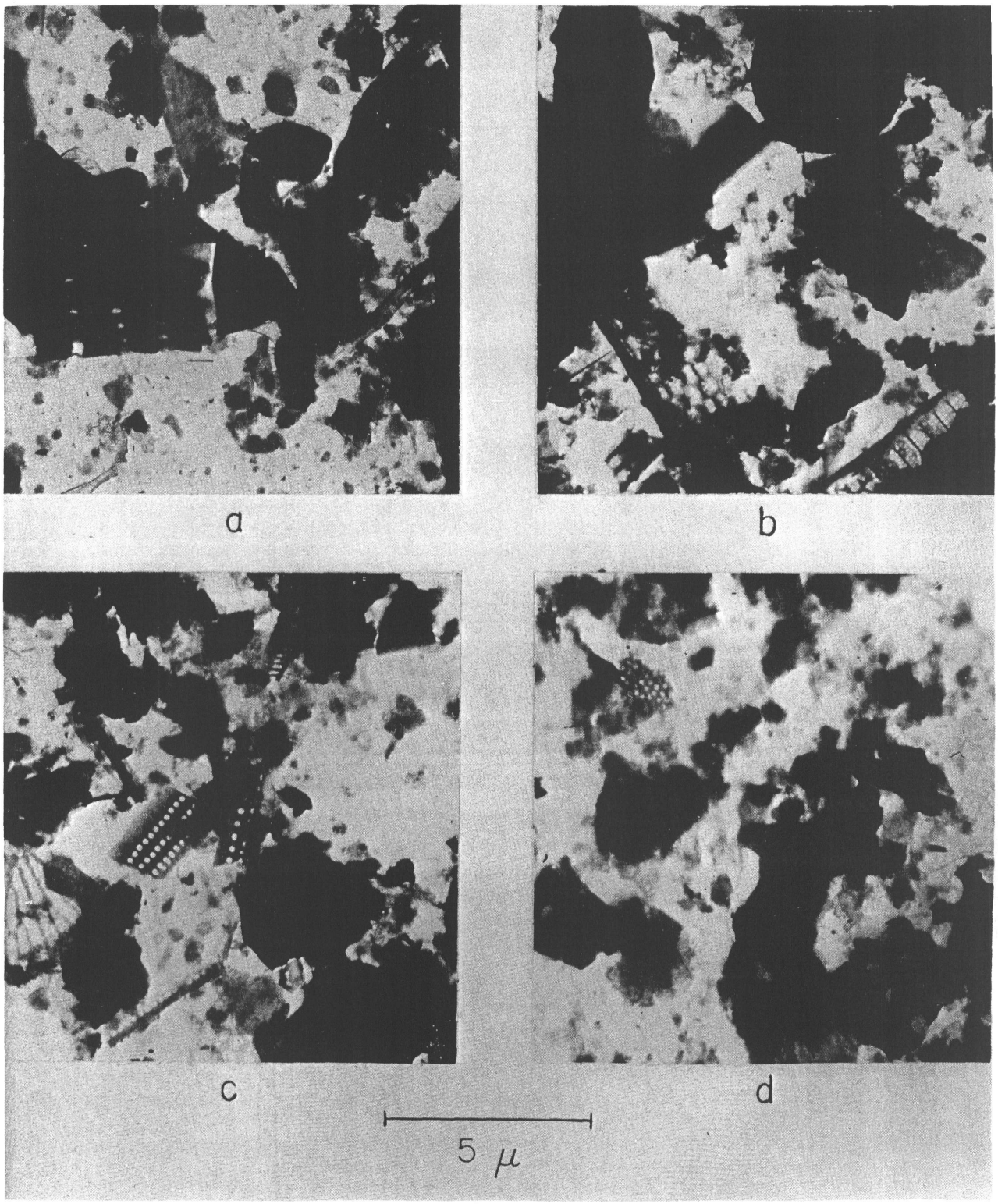

Fig. 12 - Surface water collection, about 1 mi west of Kent Island in the Chesapeake Bay, sea state 3+, bottom depth about 50 ft, collected in October 1965

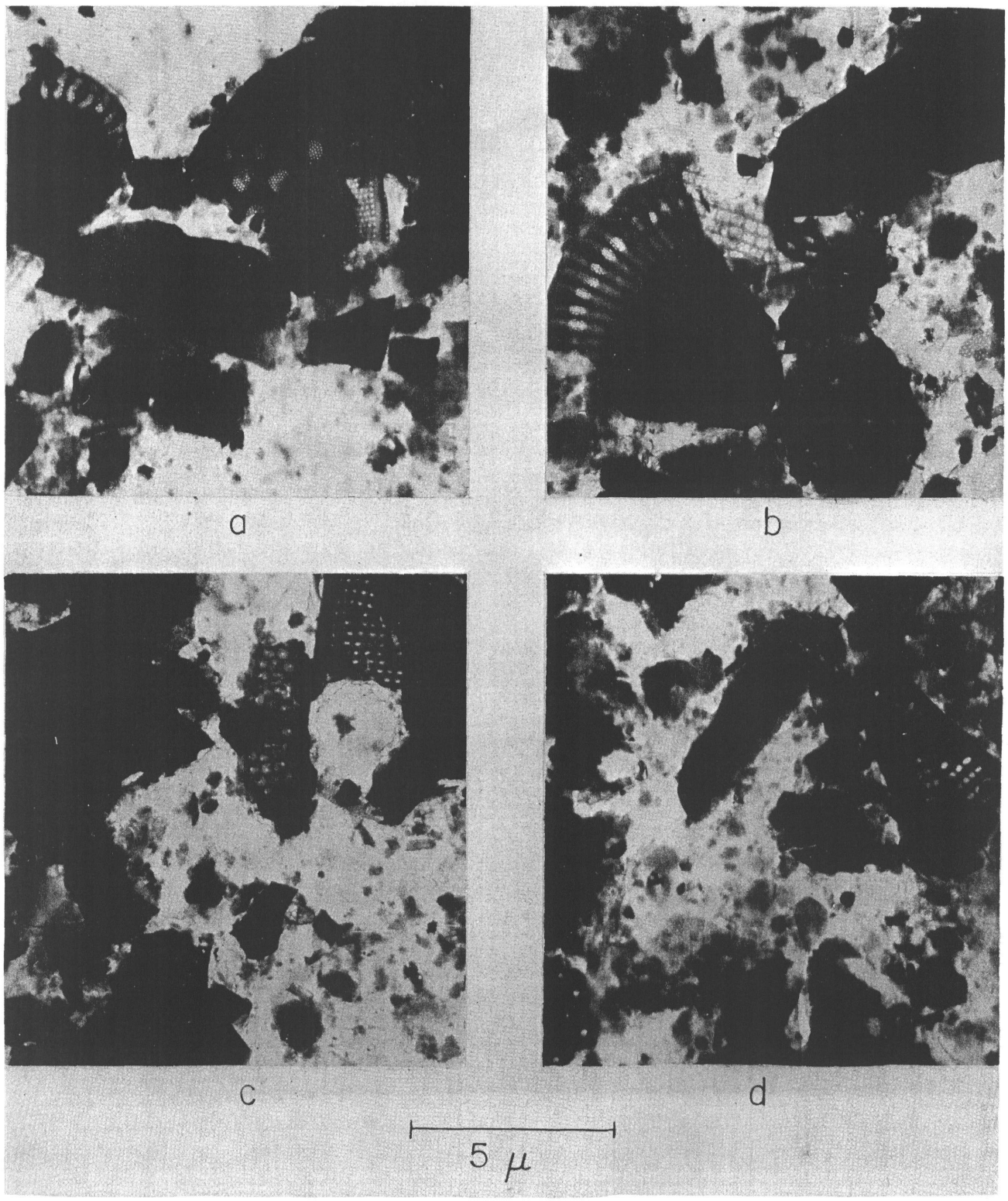

Fig. 13 - Surface water collection, same conditions as Fig. 12 but collected 2 days later and sea state less than 1

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Electron micrographs of ocean filtrates collected near the surface at Key West, Block Island, and Chesapeake Bay show three common constituents: diatoms, plant fibers, and amorphous organic matter. In addition, material collected from layers giving strong sonar reflection at Key West and Block Island show numerous smaller iron-rich particles, probably a hydrated iron oxide, in the size range 0.01 to 0.1 micron. The iron particles are too small for x-ray diffraction but can be examined by x-ray fluorescence and electron probe analysis. In addition to iron, the particles show no other elements above atomic number 22, at least not above 1 percent composition.

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