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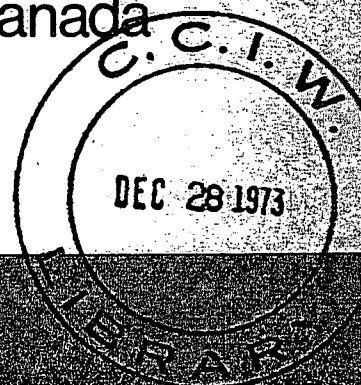
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ASBESTOS FIBRES IN LAKE SUPERIOR  
by

R. W. Durham and T. Pang

Presented at the CIC - CCIW Symposium  
on Water Quality Parameters, November 19-21, 1973

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Canada Centre for Inland Waters,  
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## SUMMARY

The discovery of high concentrations of asbestos fibres in the western arm of Lake Superior prompted the monitoring of the whole lake for fibre concentrations in order to determine the extent of transboundary movement. A description of the electron microscope technique used for fibre analysis and identification is given along with an assessment of the accuracy of the method.

## INTRODUCTION

Asbestos is a commercial product derived from several minerals of the hydrated silicate type which crystallize in an acicular or needle-like fashion. When crushed, these crystals have the property of splitting longitudinally into fibres with great tensile strength and flexibility. A considerable fraction of these fibres can be microscopic in size and enter the atmosphere during the crushing operation as dust. These tiny fibres are the causative agent of the disease asbestosis, a scarring of the lungs by increased fibrous tissue growth, which is an occupational hazard in the asbestos industry. Unfortunately, the widespread use of asbestos materials has lead to the spread of this disease to the general public (1) but a more disturbing finding is that exposure to asbestos causes malignant tumors of the pleura and peritoneum (2). Such exposure is normally considered to occur by way of inhalation of asbestos fibres but there is now concern that minute fibres may be absorbed from drinking water through the gut and into the bloodstream. Pontefract and Cunningham (3) have demonstrated this effect in rats.

The first investigation of asbestos fibres in aqueous suspension was by Biles and Emerson in 1968 (4). They concentrated fibres from beer samples by centrifuging out fibres and sediment, ashing to remove organic matter and then resuspending in water. The fibres in this residue were then scrutinized using a transmission electron microscope. Fibres were similar in size and appearance to a standard sample of chrysotile and electron diffraction patterns of a clump of small fibres confirmed this observation. These fibres were expected to have come from the chrysotile asbestos filters used in beer production.

In 1971, Cunningham and Pontefract (5) used similar techniques to measure the numbers of fibres per litre in beverages and drinking water from several Canadian cities. They found that Canadian beer and tap water contained chrysotile asbestos fibres, mostly less than one  $\mu\text{m}$  in length, at concentrations ranging from 2 to  $10 \times 10^6$  fibres per litre with unfiltered water supplies at the top of the range. Tap water drawn from a lake in the asbestos mining region of Quebec and unfiltered gave a value of  $173 \times 10^6$  fibres per litre.

This report apparently caused the Ontario Ministry of the Environment to assess the water supplies of municipalities in the province drawn from surface waters. Samples from 22 cities and towns were analyzed by Ontario Research Foundation and the results have recently been published (6). Concentrations ranged from  $0.136 \times 10^6$  fibres per litre in Ottawa's tap water to  $3.87 \times 10^6$  in Sarnia's. The mass concentration was calculated from the number of fibres, their size distribution and the density of chrysotile ( $2.4 \text{ g cm}^{-3}$ ). For Thunder Bay with  $0.83 \times 10^6$  fibres per litre, the most probable particle size was 0.1 to 0.2  $\mu\text{m}$  while the estimated mass concentration was 0.235

nanograms per litre.

The U.S. Environmental Protection Agency is concerned over the effect on the Duluth water supply of mine tailings containing the asbestiform mineral cummingtonite (7) being dumped into Lake Superior from mining and milling operations at Silver Bay in Minnesota. The Department of the Environment is naturally interested in determining whether there is any transboundary movement of these fibres, as Lake Superior provides several Canadian municipalities with their drinking water directly as well as flowing out into Lake Huron and thence to Erie and Ontario. In order to evaluate this possibility we are analyzing for asbestos fibres in water samples taken from selected stations during the monitor cruises of Lake Superior undertaken by the Canada Centre for Inland Waters in 1973.

#### ANALYTICAL METHOD

The concentrations of fibres in Lake Superior waters are too low to allow direct observation of a drop with an electron microscope so it is necessary to use a concentration stage in the analysis. The choice is between filtration with the smallest porosity membrane filter and ultracentrifugation. We selected ultracentrifugation after running into difficulty trying to destroy the membrane filter without losing fibres.

In a typical analysis, 250 ml of lake water were spun at 20,000 rpm (about 30,000 g) for two hours to bring down the fibres. These were resuspended ultrasonically in one ml of distilled water without further treatment because the very low concentration of suspended matter in Lake Superior water did not interfere with fibre counting.

One microlitre of this suspension was transferred to a 3 mm carbon-coated grid and dried under a heat-lamp. The grid was mounted in a Siemens 101 transmission electron microscope and scanned at a magnification of 20,000. In order to obtain good counting statistics, the fibres were counted in all the 230 openings of the 200 mesh grid rather than just a fraction of them. This was because of the uneven distribution of fibres on the grid and the fact that the drop did not cover it entirely. The lengths of about 80 fibres on each grid were measured using a calibrated eye-piece in order to determine the size distribution of the fibres in each sample. The shortest fibre detectable was about 0.05  $\mu\text{m}$  in length.

The recovery of fibres in the centrifugation step was checked by centrifuging the supernatant for a further two hours and then counting the fibres and measuring the size distribution. This was done for two samples resulting in recoveries of 86% and 85%. The size distribution of fibres was similar to the original so that the less than complete recovery in one centrifugation was not a fractionation effect. The reproducibility of counting the fibres in the resuspension was determined by counting duplicate one microlitre aliquots after mounting on grids. The difference was 5% which is compatible with the tolerance of  $\pm 1\%$  for the micropipette.

Any contamination of the coated grid by ubiquitous asbestos fibres would be magnified by the concentration factor which was 1000 in this case. We were not able to eliminate contamination completely in preparing the grids but by ultrasonic cleaning of the fresh grids and all glassware, the background contamination averaged 25 fibres per grid. Each grid was scrutinized in the electron microscope before the

sample was evaporated onto it to determine its fibre background level. This value was then subtracted from the total number observed after the sample had been added.

### RESULTS

Figure 1 is a map of the Lake Superior shore-line showing the general location of the sample stations for which results have been obtained. Table 1 shows the results of the analyses of samples from two cruises in early summer of 1973. During cruise 103 two stations only were sampled, 142, between Isle Royale and Thunder Bay and 203, which is about five miles off Silver Bay, Minnesota. The fibre count of the Silver Bay sample was appreciably higher than that of Isle Royale as it was also for cruise 104 although the sample station analysed in that cruise was 138 rather than 142. This station is in Thunder Bay.

Figure 2 is an electron micrograph of an average fibre from station 142 which has the typical hollow cylinder appearance of a chrysotile fibre (8). The fibres shown in Figure 3 are from station 203 and have a very different appearance but are typical of the majority of fibres observed from this sample station. One such fibre shown in Figure 5 was large enough to produce the accompanying electron diffraction pattern. This pattern is identical with that shown in Figure 6 from a fibre in a water suspension of tailings from the taconite milling operation at Silver Bay. We have identified this fibre as cummingtonite by comparing its electron diffraction pattern with that of a standard sample of this mineral.

Figure 4 shows the distribution of the fibres according to length in cruise 103 samples from stations 203 and 142. The distribution of the fibres in the sample from station 203 extends over a much wider range than that of station 142 with about 20% of the fibres being longer than one  $\mu\text{m}$ .

#### DISCUSSION

It is quite clear from the results of both cruises that the mining and milling operation at Silver Bay has a major impact on the asbestos fibre content of the western arm of the lake. The results of the second cruise, 104, however, show that it has little effect if any on the waters of Thunder Bay or those of the eastern lake. The CCIW current monitoring program during 1973 has shown that except for a few early oscillations, there was a steady counter-clockwise flow around the lake (9). Such a flow would tend to move fibres from Silver Bay towards Duluth and then eastwards along the south shore. These currents are slow, averaging a few centimetres per second, so that the fibres will gradually settle out or diffuse into the main body of the lake while the flowing water traverses the immense distances involved.

Except for station 203, the values obtained are consistent with those quoted by Kay (6) for Thunder Bay municipal drinking water which is not filtered. It is unlikely, however, that a standard water filtration system would remove an appreciable fraction of fibres with a mean size of 0.3  $\mu\text{m}$ .



The major difference between the results from the two cruises is the ten-fold higher level found during cruise 103. This may be due to the different sampling techniques as cruise 103 samples were taken by bleeding water into the sample bottle during descent from 15 to 50 metres while cruise 104 samples were taken at discrete depths. However, station 138 was sampled at 1 and 85 metres and the results are not very different. The lake was not yet stratified during cruise 103 so collection of a more concentrated sample through selective layering of fibres at a thermocline could not have occurred.

The higher values obtained during the first cruise, 103, at stations 142 and 203 might be related to the prevailing wind direction during this cruise being offshore. The coastline undergoes severe erosion so that under offshore wind conditions much of this material could move further out into the lake. As the majority of fibres in the station 142 sample were chrysotile, its high value could not be due to a reversal of current flow driving Silver Bay material northeastwards.

We have too few results at the moment to state categorically that Canadian waters of Lake Superior have stable, probably historic levels of asbestos fibres in the  $1$  to  $2 \times 10^6$  per litre range. Also, although the precision of our analytical method is about  $\pm 15\%$ , we need to intercompare samples with other laboratories and agree on the shortest length of fibre to be included before we can claim a particular accuracy and relate our results directly to the work of others.

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(Private communication).

TABLE I

ASBESTOS FIBRE CONCENTRATIONS IN LAKE SUPERIOR

<u>Cruise</u>	<u>Station</u>	<u>Depth</u>	<u>Fibres/litre</u> ( $\times 10^6$ )
103	203	50 to 15 m	87.3
103	142	50 to 15 m	15.5
104	203	1 m	9.5
104	138	1 m	1.4
104	138	85 m	0.76
104	89	1 m	2.2
104	2	1 m	1.7
104	43	1 m	1.4

Cruise 103      June 15 - 28

Cruise 104      July 26 - August 8

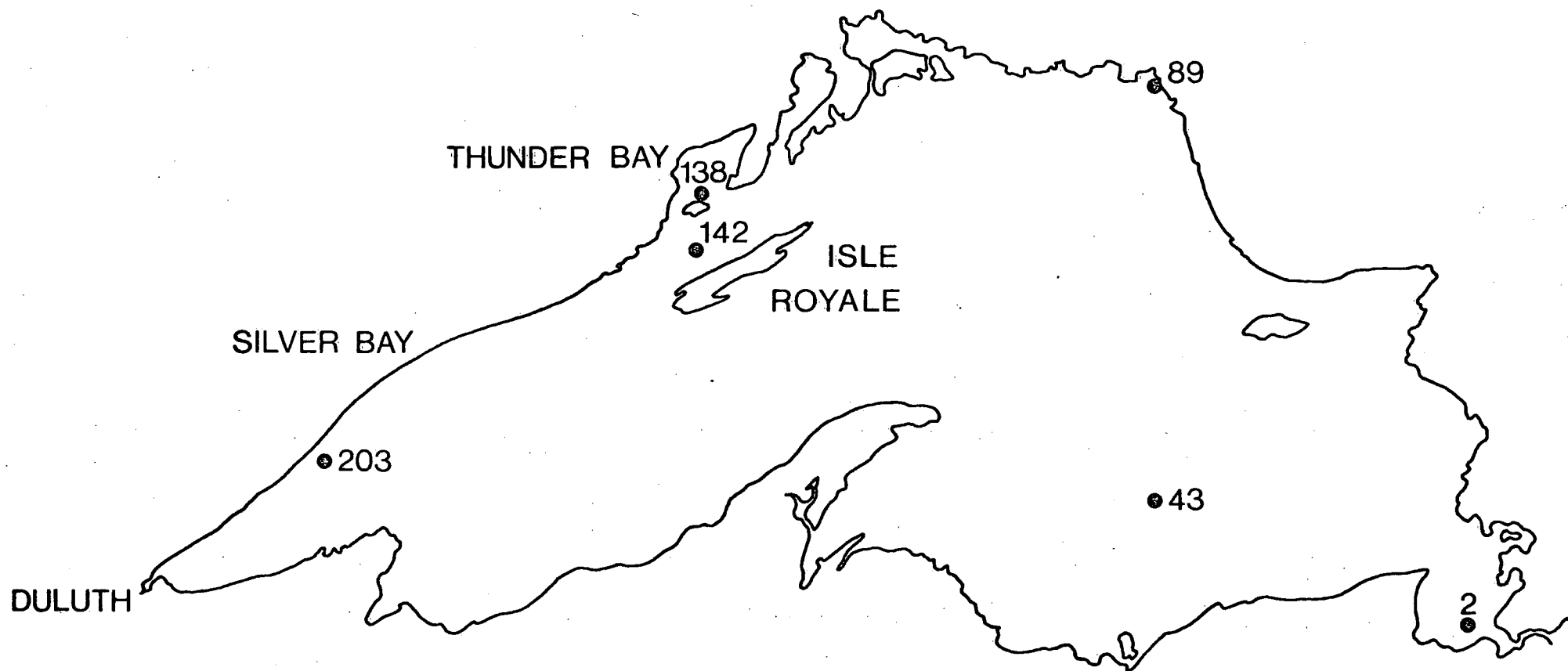


FIGURE 1. Lake Superior showing locations of sample stations.

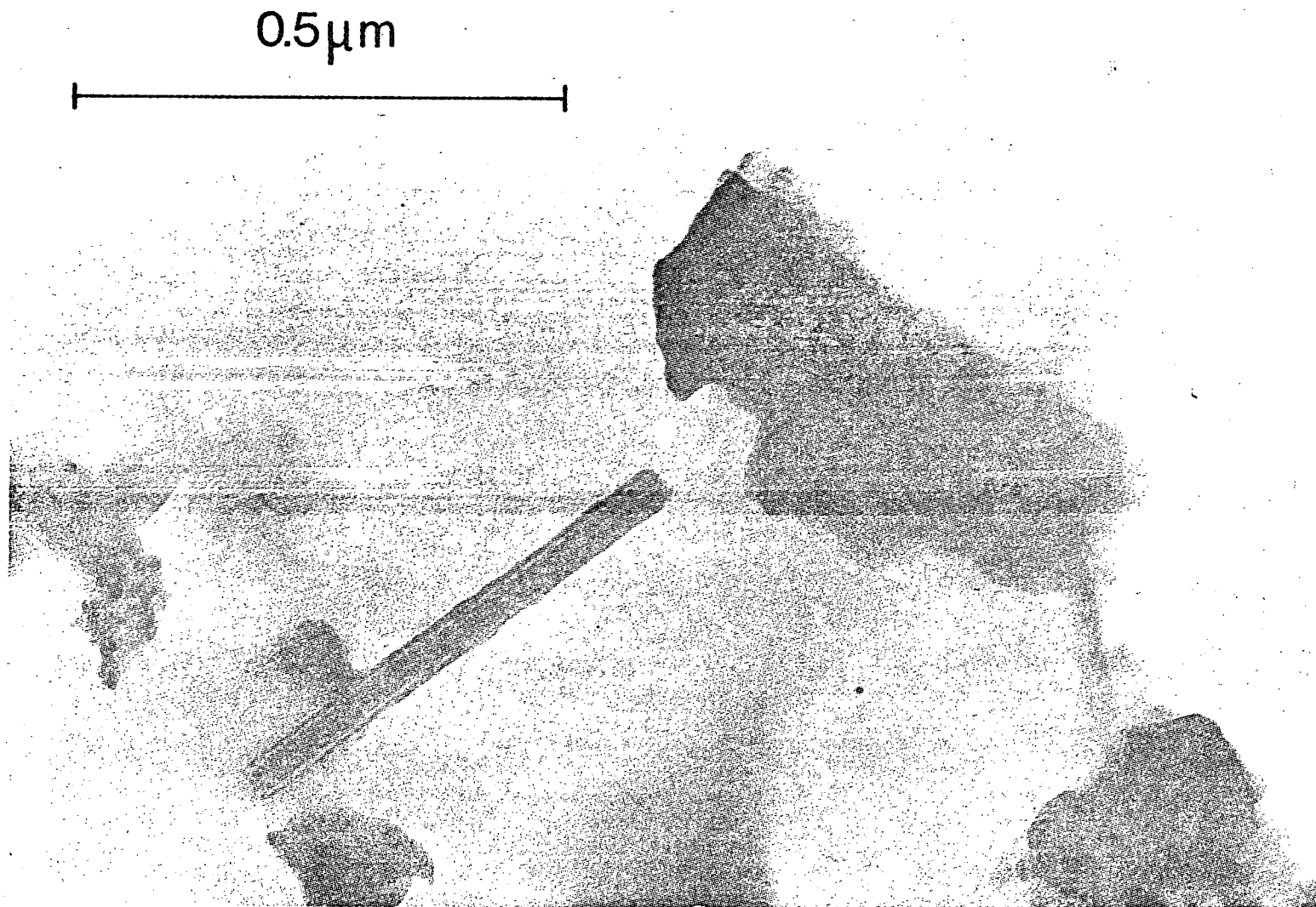


Figure 2. Chrysotile fibres in water sample from near Isle Royale.

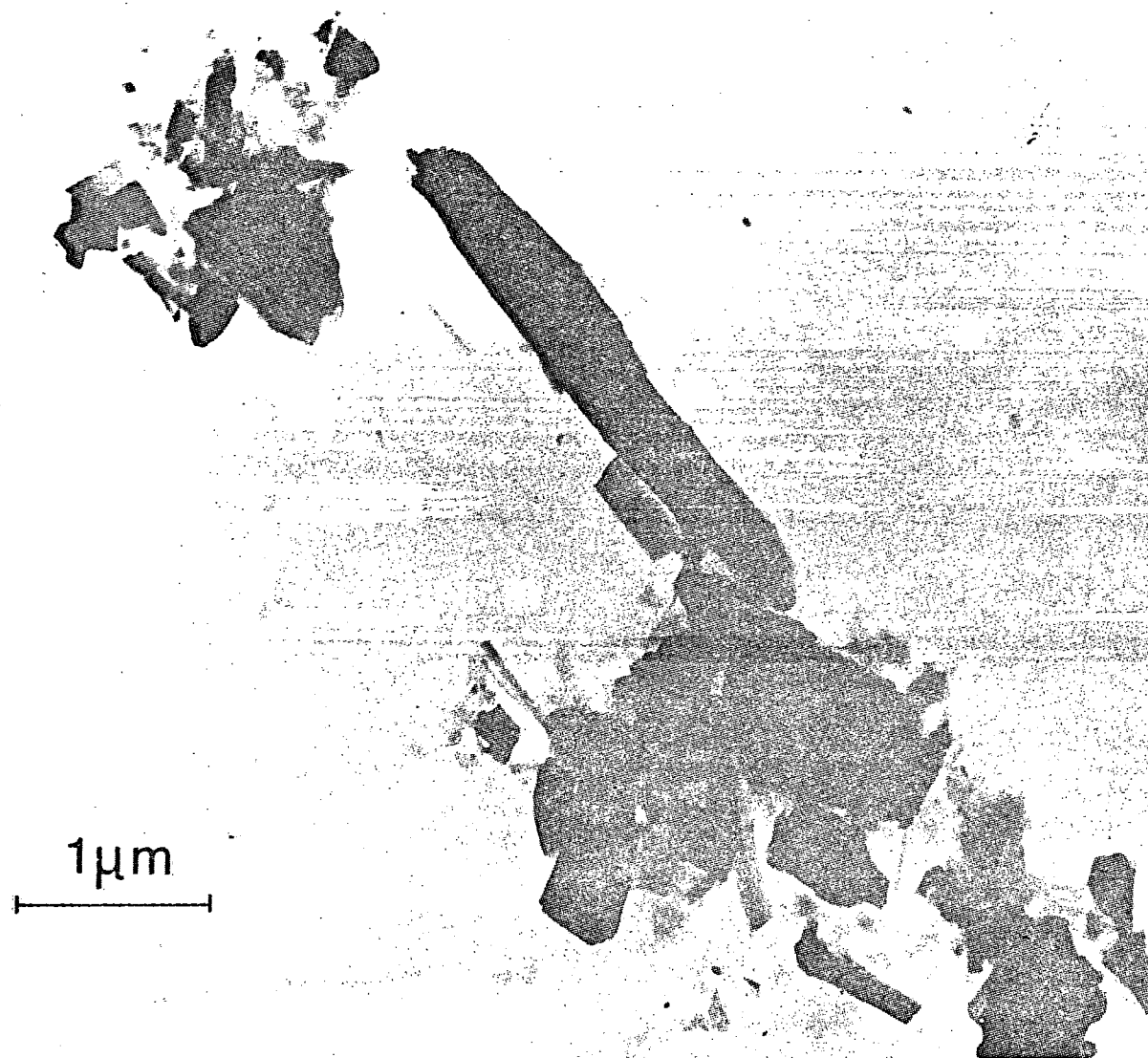


Figure 3. Cummingtonite fibers in water sample near Silver Bay

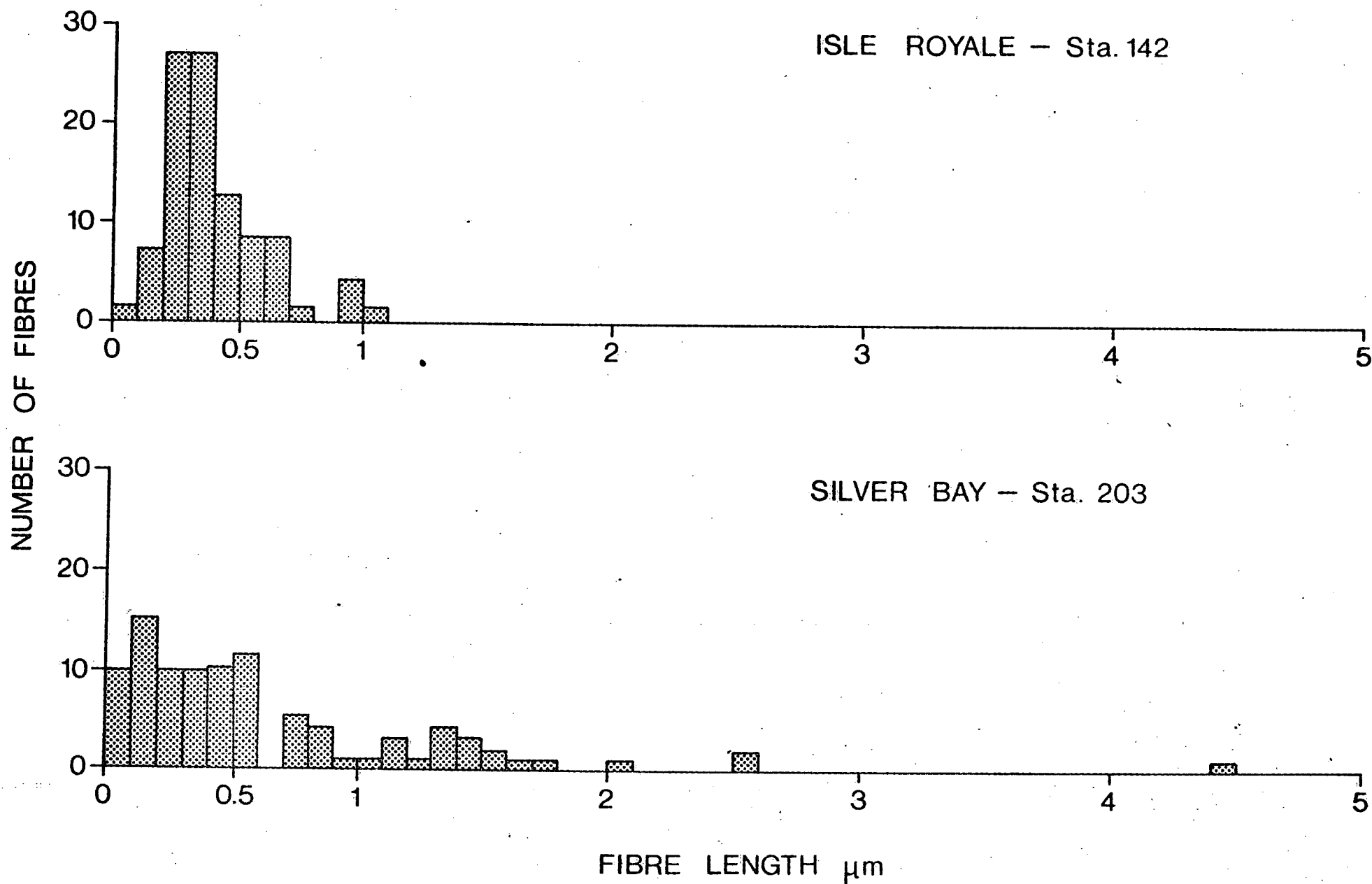


Figure 4. Fibre distributions in water samples from Silver Bay and Isle Royale.

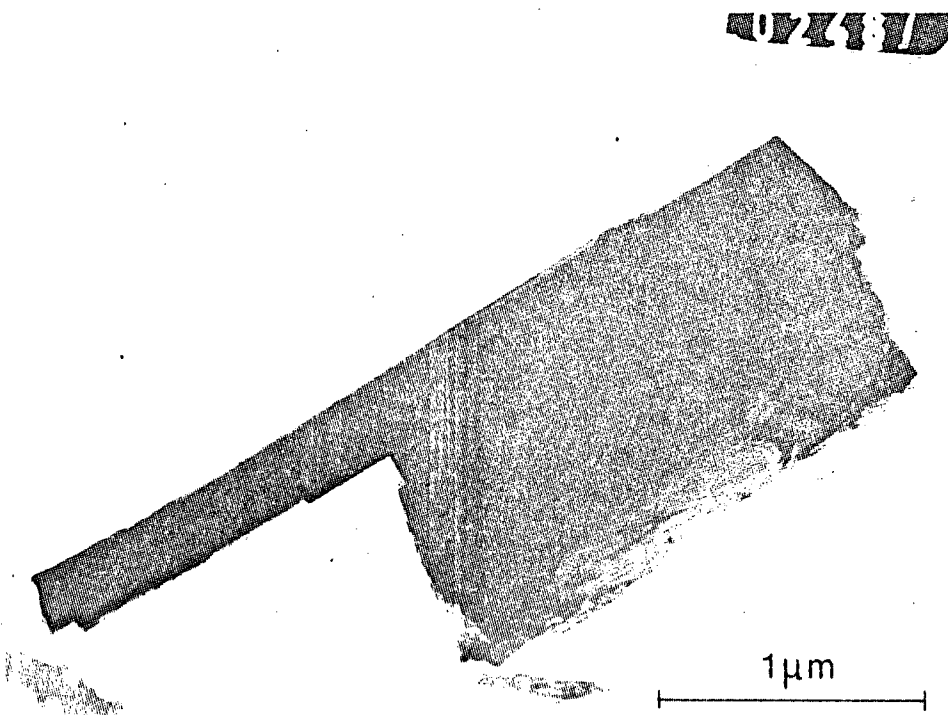
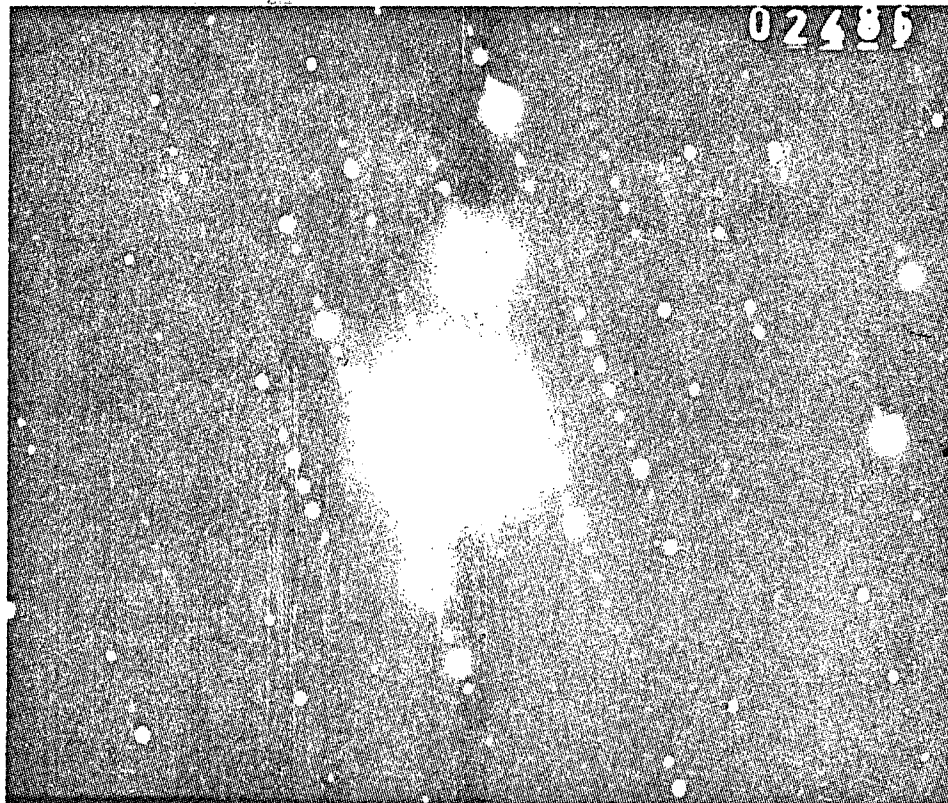


Figure 5. Micrograph and electron diffraction pattern of fibre in water off Silver Bay.



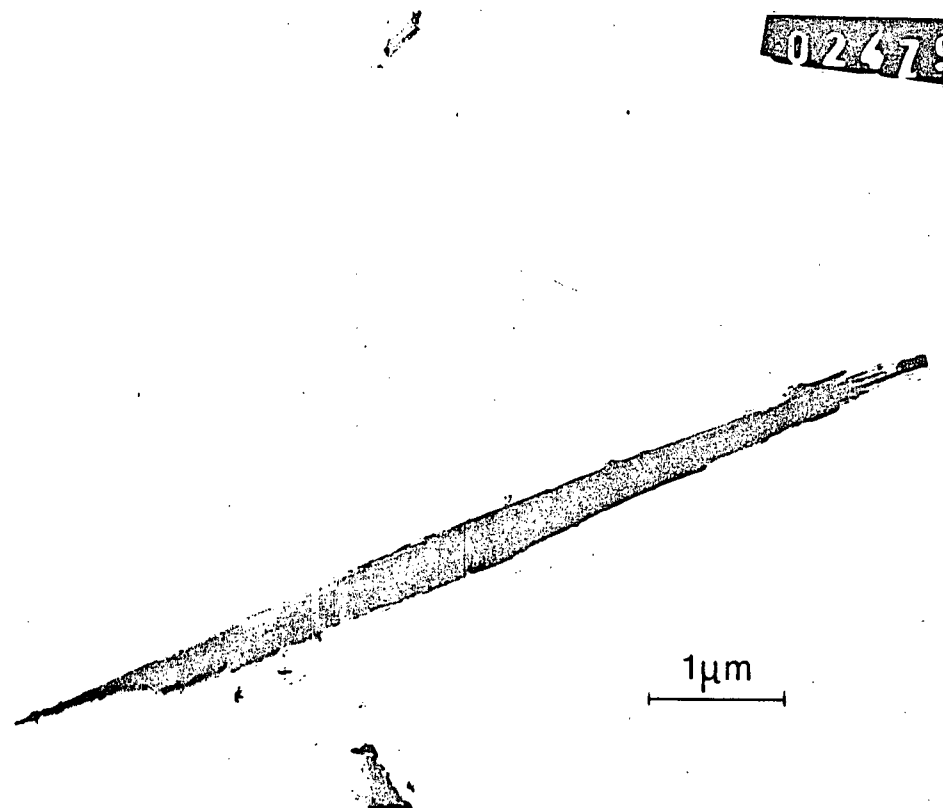
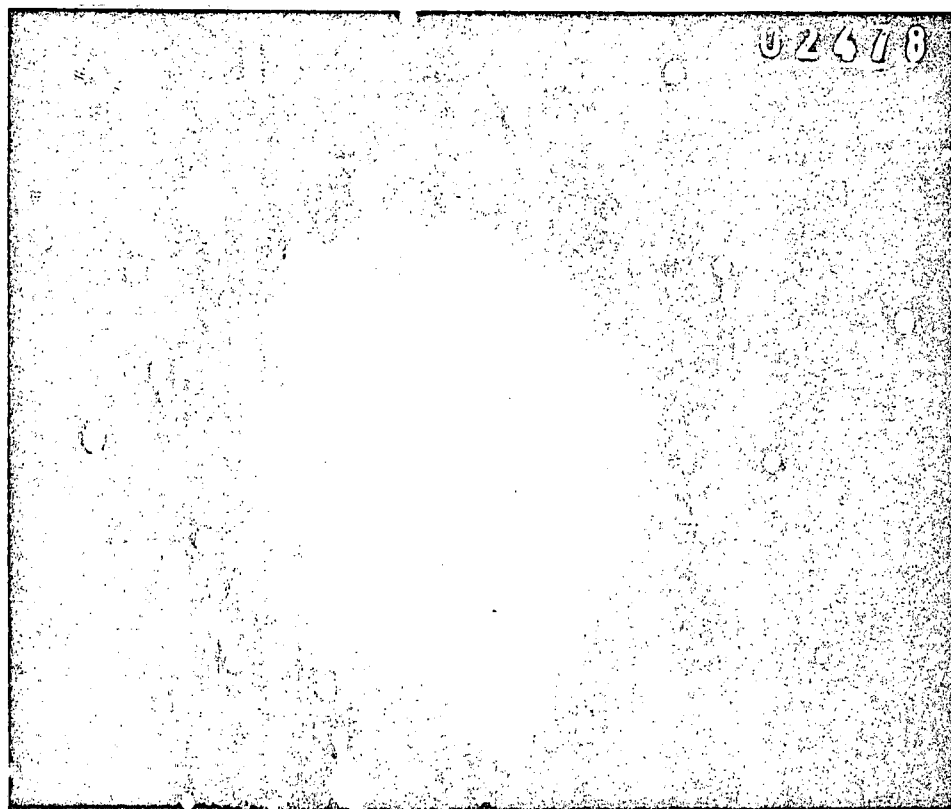


Figure 6. Micrograph and electron diffraction pattern of fibre from tailings of taconite milling operations at Silver Bay

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