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FIBROUS CUMMINGTONITE IN LAKE SUPERIOR

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ABSTRACT

Basic mineralogical and surface-charge data were obtained to elucidate the source and fate of cummingtonite. Fibrous cummingtonite with a mean stoichiometry of $(Fe_5Mg_2)Si_8O_{22}(OH)_2$ and a zeta potential of about –21 mV is added to Lake Superior from taconite tailings. Cummingtonite in suspension and distant from the source increases in Mg to about $(Fe_{3.5}Mg_{3.5})Si_8O_{22}(OH)_2$ and a zeta potential of –31 mV. Cummingtonite in surface lake sediments has a composition approaching the tailings mean and a zeta potential approaching 0 (-11 mV). The gradient in cummingtonite composition is probably due to a mixed compositional source of cummingtonite and preferential coagulation and sedimentation of the Fe-rich variety.

RÉSUMÉ

Des données de base minéralogique et de charge superficielle sont obtenues afin d'expliquer l'origine et le destin de la cummingtonite. De la cummingtonite fibreuse avec une stoïchiométrie moyenne de $(Fe_5Mg_2)Si_8O_{22}(OH)_2$ et un potentiel zéta d'environ –21 mV est ajoutée dans le lac Supérieur par des rejets de taconite. La cummingtonite en suspension et loin de la source augmente son contenu en Mg jusqu'à $(Fe_{3.5}Mg_{3.5})Si_8O_{22}(OH)_2$ et son potentiel zéta jusqu'à –31 mV. La cummingtonite, dans des sédiments de lac superficiels, a une composition approchant la moyenne des sédiments et un potentiel zéta approchant 0 (–11 mV). Le gradient, dans la composition de la cummingtonite, est probablement dû à une source compositionnelle mixte de cummingtonite et une coagulation préférentielle ainsi qu'une sédimentation de la variété riche en Fe.

(Traduit par le journal)

INTRODUCTION

The occurrence and fate of acicular cummingtonite in western Lake Superior is a classic example of the requirement of precise mineralogical, petrographic, and geochemical information, as well as reliance on previous research on amphiboles (Klein 1964; Viswanathan & Ghose 1965; Fischer 1966; Finger 1967; Bonnichsen 1969).

Tailings from taconite mining have been dumped into western Lake Superior at the rate of 60-70,000 metric tonnes/day in a water slurry of about 2.4 × $10^6 m^3$/day. These tailings contain more than 50 wt % quartz and about 40% amphibole, the majority of which is cummingtonite. Acicular cummingtonite has been associated in occupational health studies with respiratory disease as well as pleural cancer (Selikoff 1972), and litigation has been carried out regarding the public health effects in the western lake Superior region (U.S. District Court, 1974). The fate of the acicular cummingtonite in the water is important to this environmental problem, and the fate depends upon the geochemical reactions which, in turn, depend upon the surface chemistry and the detailed mineralogy.

Cummingtonite occurs in fibrous and nonfibrous forms, and is variable in Fe-Mg composition due to the complex igneous and metamorphic history of the region (Bonnichsen 1969). Therefore, one prerequisite to the determination of the ultimate fate of the fibres is to characterize the nature of the tailings. To this end, 1) cell refinement of *x*-ray diffraction data was undertaken; 2) zeta-potential measurements were made; 3) size analyses were compiled, and 4) transmission electron microscopic enumeration of particles accompanied by energy-dispersive fluorescence analysis was carried out.

Sampling

Taconite mining at Silver Bay, Minnesota, consists of wet crushing of ore, washing of quartz and amphibole through a launderer, and transport of tailings to an adjacent delta as well as into Lake Superior. Samples were obtained of mineral extracts, ore, tailings, sediment traps in western Lake Superior, and from two cores of bottom sediments in Lake Superior (Baumgartner *et al.* 1973). Figure 1 shows the locations of tailings samples, sediment-trap samples, and cores. The sequence of samples from the mine pit to the Lake is: pit MM-01067; launderer and tailings MM-01076 and MM-01066; surface land tailings 1-9; sediment-trap samples CRT-01 (nearest), FLT-01, and KLT-02 (farthest); core samples HH-0308 (S0-1 = 0-1 inch, S1-2 = 1-2 inch ——), HH-00711 (S0-1 = 0-1 inch, S1-2 = 1-2 inch ——), and a surface com-

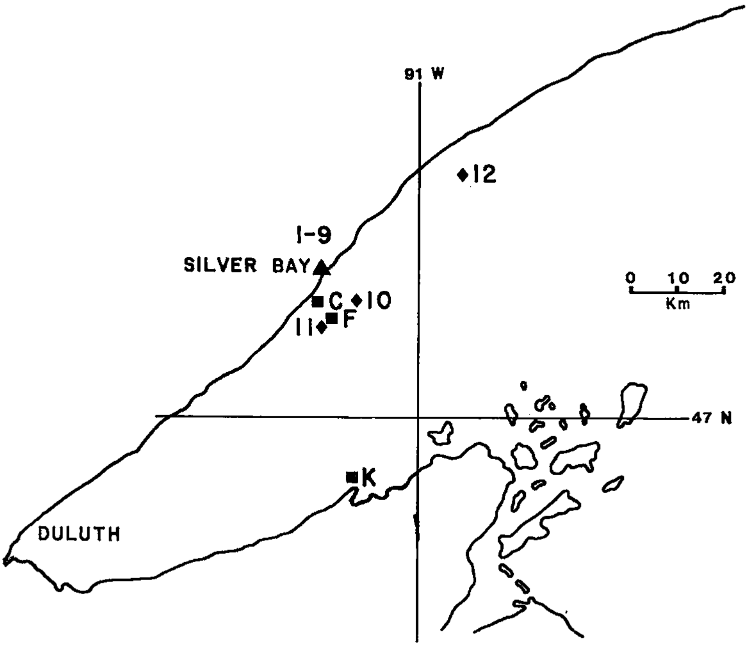

FIG. 1. Location map of samples. Nos. 1-9 are surface samples of tailings delta at Silver Bay; C, F, K are sediment-trap samples CTR 01, FLT 01 and KLT 02, respectively; 10, 11 and 12 are locations of cores 10, HH0030 and HH00711 respectively.

posite core containing a taconite layer 7cm thick. In addition, 11 large-volume surface samples of Lake Superior were obtained between June 16 - June 27, 1973 for fibre analysis (Fig. 3).

Size distribution

Size analyses of the tailings indicate that most amphiboles are <5 μm and, in this size range, the majority of the particles are amphiboles. Therefore, to investigate the details of the amphibole mineralogy and geochemistry, the finer fraction needs to be studied in detail. For particles in the micrometre and sub-micrometre sizes, traditional petrographic and sizing procedures are inadequate. Particles are very small and so are their masses, so that distributions are based upon count, and the enumeration and analysis are carried out using the transmission electron microscope (TEM).

Analyses

Samples for XRD, TEM and zeta-potential measurements are treated to remove the $>10\mu$m fraction. Samples are then dispersed in a measured volume of fibre-free water by mechanical shaking or by ultrasonic vibration.

X-ray diffraction analysis is carried out on a <10 μm size fraction which has been filtered through a membrane filter. Analysis is carried out using either a Guinier camera or *x*-ray diffractometer with quartz as the reference. Refinement of the data to obtain cell constants and volumes is obtained using the computer program PARAM of Stewart (1972). The best fit of data was obtained by inspecting the quality of diffraction peaks that poorly fitted the least-squares analysis, rejecting the individual data set if warranted by examining the peak definition, and carrying out a new least-squares analysis.

TEM analysis is carried out on a Parlodian-coated Cu or Ni grid with 200-mesh squares. One to ten μl of the grid solution are placed on the grid using a micropipette and dried in an upside-down position. Before the sample is placed on the grid, a wetting agent is dried on the grid to enhance wetting and homogeneous deposition of particles during drying.

Typically, sediment samples need no concentration step, but water samples do. A water sample is filtered through a Millipore or Nuclepore 0.45 to 0.01 μm fibre-free filter, to concentrate fine particles. The filter paper or portion thereof is rolled inwards, placed in a vial with 5-15 ml of fibre-free water and the fibres are suspended in the water using a high-intensity ultrasonifying probe at 30,000 Hz for 1-5 minutes. Microlitre aliquots are then transferred to the TEM grid for analysis. Since a comparison of analyses using a mechanical shaker and ultrasonification gave no statistical difference in fibre counts, the amount of breaking and splitting of fibres is probably similar in both techniques.

An optimal concentration on the grid for analysis is 5-30 fibres per square. Greater concentrations obscure other fibres, and lower concentrations approach an ambient average contamination level of slightly less than one fibre per square. All steps of the preparation can contaminate the sample; extreme care must be taken in sample preparation, as fibres are ubiquitous in the modern laboratory environment. In addition, replicate analyses are always carried out on every sample.

An asbestiform mineral is defined as any crystalline substance (giving an electron diffraction pattern) with a viewing length to width ratio of 3 or greater. Therefore, in the general environment, about 40 commonly-occurring minerals can be classified as asbestiform minerals.

Sizing, counting, morphological mineral identification, and electron diffraction analysis are routinely carried out on all samples. Two bull's-eyes on the viewing screen are used as references to measure length and width. In addition, selected grids are carbon-coated for elemental analysis, using energy-dispersive spectrometric analysis. None of these methods gives a positive mineral identification for amphibole and serpentine fibres, but collectively more than 50% of the fibres can be identified mineralogically in the general case, and more than 90% of the fibres can be identified mineralogically in a specific case (Beaman & File 1976).

Counting is carried out on a representative number of grid squares and the statistical distribution between squares is calculated in order to obtain an estimate of counting reproducibility due to the homogeneity of distribution of fibres per square. Counting and sizing is carried out at a magnification between 20-25,000X.

Electron-diffraction analysis is carried out routinely to define whether the sample is crystalline or not. Detailed analysis of an electron diffractogram is not definitive, since the electron-diffraction analysis requires knowledge of the three-dimensional orientation of the particle. Furthermore, the crystalline imperfections in amphiboles often produce very poor patterns or no patterns at all.

Morphological mineral identification of fibres of approximately 1 μm in size can generally be made with assurance for chrysotile, but smaller chrysotile particles and other fibrous minerals are made with much less assurance in the general case. Chrysotile is defined morphologically by its irregular edge and typical appearance of a core which is optically electron dense or light (Clifton *et al.* 1966).

Energy-dispersive spectrometric analysis is carried out on grids after they have been sized and counted. The sample is coated with carbon in vacuum, and the samples are analyzed in the transmission electron microscope, using a Si(Li) detector. Data obtained from the pulse-height analyzer are smoothed using a computer program and elemental intensities and element identification are obtained. Background adjacent to the fibre is subtracted from the analytical curves. Analysis is carried out on an EDAX 707 analyzer attached to a Phillips 300 transmission electron microscope. The analytic beam ranged from 0.3 to 0.5 μm, and channel resolution was 4-40 eV. Results are compared to intensities obtained from fibres of known bulk composition. Although the reproducibility of analyses on the same fibre is good (2-10%), results must be considered semi-quantitative because of backscattering, surface coatings, overlapping grains, and the lack of appropriate standards and calibration curves. Comparison of fibre analysis with bulk chemical analysis on standards deviates by about 20%, but the deviation is certainly much greater for natural samples. Analyses also vary along the length of a fibre. Typically, Si, Al, Mg, Fe (and Mn), Na, K and Ca intensities are used for identification and specification of mineralogy.

The zeta potential gives an indication of the net surface charge on a particle. The zeta potential (ζ), which is the charge at a plane of shear between the bulk solution and the adsorbed water layer can be calculated from the electrophoretic mobility (*Me*), the dielectric constant (ϵ), and viscosity (η) of the solvent:

$$\zeta = \frac{4\pi\eta}{\varepsilon} Me$$

This function is derived assuming that the particle is an insulator whose radius is large relative to the thickness of the double layer. The zeta potential is determined in a zeta meter by measuring the velocity of a particle moving in a known potential field. The zeta potential in general is less than the surface potential because the zeta potential is measured further from the surface than the double-layer thickness.

The zeta potential is interpreted generally in context to a metal-OH bond model where

OH(pH) is the potential determining ion. At negative potentials, positive ions will be adsorbed; at positive potentials, negative ions will be adsorbed, and at the pH of net zero charge, net sedimentation should be maximal for there will be no electrostatic repulsion to prevent coagulation.

Results of Analysis

X-ray diffraction results are shown in Table 1 for cummingtonite, tailings, sediment-trap samples, and two cores at two depths. An estimate of over-all reproducibity is obtainable from comparisons of the results for samples 1, 2, and 3. These are analyses of the same sample using different *x*-ray methods and different personnel. Maximum deviation in cell parameters is a 0.008, b 0.049, c 0.007Å, β 0.10°, V 3.3Å^3.

Assuming that cummingtonite has the stoichiometry $(Mg,Fe)_7Si_8O_{22}(OH)_2$, the atomic proportion of Fe can be obtained from the function of Finger (1967):

$$V = 873.41 + 0.53fe + 0.58mn + 0.97ca \text{ Å}^3$$

where V = volume of the unit cell in Å^3; fe, mn and ca are, respectively, the mole per cent of Fe^{2+}, Mn^{2+} and Ca^{2+} for the octahedral site. The simplification becomes $V = 873.41 + 0.53fe$. Percentages of Fe/(Fe+Mg) are given in Table 1.

Using this technique, cummingtonite at the source has a composition range from 69-81% Fe, or a mineral stoichiometry between $(Fe_{4.8}$-$Mg_{2.2})$. . . to $(Fe_{5.7}Mg_{1.3})$. Proceeding from the tailings into the sediment trap, the composition appears to change towards depletion in Fe. Trap sample C, adjacent to the source, has a composition similar to the tailings but F and K,

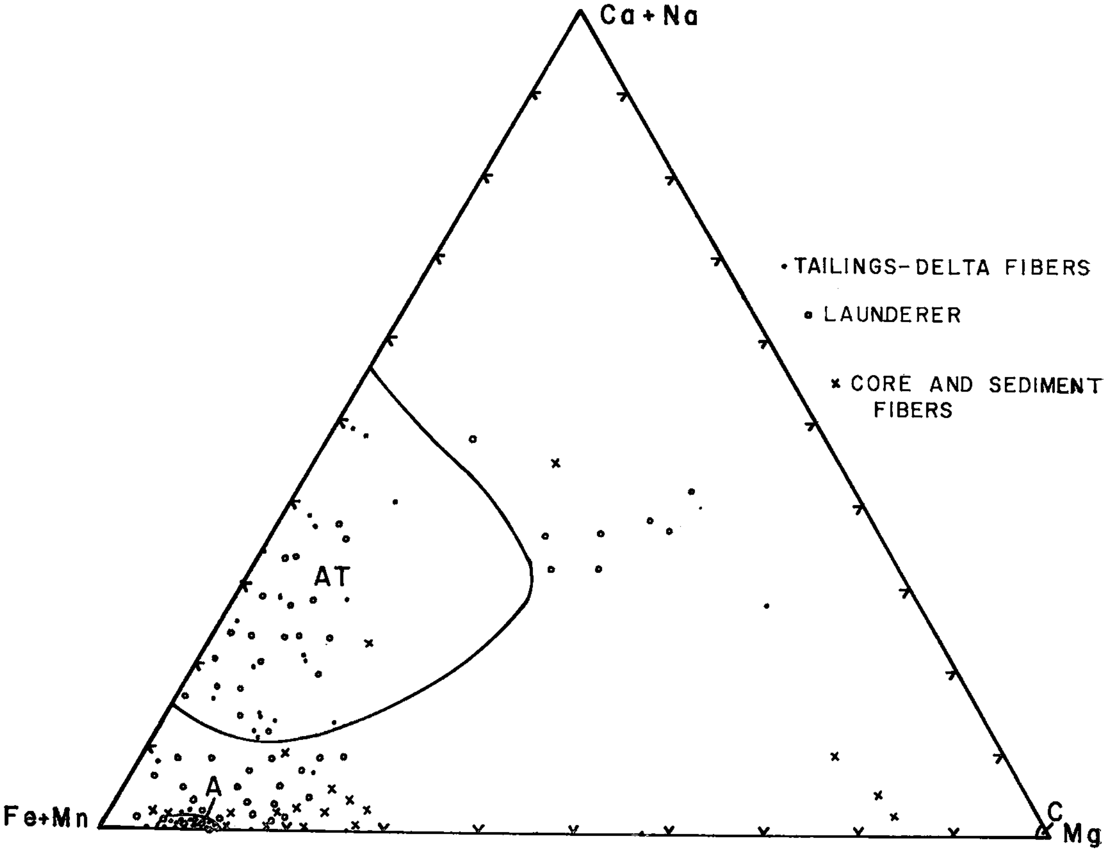

FIG. 2. Composition of individual fibres in samples from western Lake Superior. Values are per cent intensity corrected for background. A is range of analysis for UICC reference sample "amosite", C for UICC chrysotile, and AT is range of results obtained for various samples of actinolite-tremolite. Of 58 fibres analyzed from tailings, 31 fall within the range of analysis of A. Compare results with *x*-ray analysis in Table 1.

TABLE 1. SUMMARY OF CELL PARAMETERS OBTAINED BY REFINEMENT TECHNIQUES USING PARAM

Sample No.	Technique	a(Å)	b(Å)	c(Å)	β(Å)	Volume	Fe/Fe+Mg
1. MM 01067	Diffractometer	9.558±.004	18.354±.012	5.337±.004	101.85±.06	916.3Å^3	81%
2. MM 01067	Diffractometer (2nd instrument)*	9.553±.002	18.319±.005	5.340±.001	101.90±.02	914.4	77
3. MM 01067	Guinier analysis	9.561±.006	18.305±.008	5.333±.003	101.95±.04	913.0	75
4. MM 01066	Diffractometer	9.558±.004	18.296±.010	5.337±.003	101.97±.05	913.0	75
5. MM 101A	Diffractometer	9.542±.008	18.263±.011	5.348±.006	102.04±.08	911.5	72
6. MM 01076	Diffractometer (2nd instrument)*	9.530±.011	18.205±.026	5.353±.010	101.46±.13	910.1	69
7. CTR 01	Diffractometer	9.568±.007	18.236±.013	5.358±.005	102.12±.07	914.0	77
8. FLT 01	Diffractometer	9.541±.007	18.349±.017	5.268±.011	101.64±.13	903.2	56
9. KLT 02	Diffractometer	9.542±.019	18.210±.047	5.291±.022	101.76±.26	900.1	50
10. 308 S0-1	Diffractometer	9.533±.008	18.262±.012	5.317±.010	101.94±.11	905.6	61
11. 308 S1-2	Diffractometer	9.550±.007	18.238±.008	5.344±.003	102.16±.49	909.8	69
12. 711 S0-1	Diffractometer	9.546±.005	18.245±.011	5.343±.004	101.93±.58	910.4	68
13. 711 S1-2	Diffractometer	9.555±.004	18.296±.006	5.339±.002	101.88±.04	913.4	75

1 - 3 are samples of hand-picked cummingtonite-grunerite; 4 - 6 are samplings of tailings from Reserve Mining Company; 7 - 9 are sediment-trap samples; 10 - 13 are samples of cores. The inferred composition of Fe/(Fe+Mg) from the cell volume is obtained from: volume = 873.41+53(Fe/(Fe+Mg)). Error estimate is the standard estimate of error obtained from the least-squares analysis only.

* results obtained with another diffractometer

approximately 10 to 40 km distant, have compositions of 56 and 50% Fe, or $(Fe_{3.9}Mg_{3.1})$ . . . and $(Fe_{3.5}Mg_{3.5})$.

Energy-dispersive analysis

Results of energy-dispersive analyses of individual fibres are shown in Figure 2. Per cent intensities corrected for background are plotted instead of composition, due to lack of calibration curves. For reference, however, U.I.C.C. (International Union Against Cancer) reference amosite fibres from South Africa with a bulk composition of approximately (Fe_5Mg_2) and traces of Al and Ca are plotted (A), along with fibre analyses of actinolite-tremolite from various locations (AT) and Canadian chrysotile (C). The U.I.C.C. reference samples were analyzed in bulk, and intensities of more than 40 fibres were measured.

Results of analysis of the launderer sample show compositional scatter, with a concentration within the compositional range of U.I.C.C. amosite (30 to 70 fibres analyzed). Analyses of land tailings delta fibres show a large concentration of cummingtonite in a narrow range which matches the composition of U.I.C.C. amosite. Samples from the launderer, which carries the tailings to the delta and Lake, appear to have more scatter in analyses of individual cummingtonite fibres, and the fibres in core and sediment-trap samples have an even greater scatter. Tremolite-actinolite fibres are also common to all samples. Assuming surface grab-samples of the large tailings delta are indicative of the delta as a whole, it appears that cummingtonite of about (Fe_5Mg_2) is being preferentially sedimented on the delta, compared to other compositions of cummingtonite.

Zeta-potential measurements

Results of analysis of particles in suspension in Lake Superior water (pH 7.8-8.1) are given in Table 2.

In addition, an aging study was carried out to determine whether the zeta potential of cummingtonite changes with time. There was no statistical difference over one month.

For fibres in the tailings (MM-01066, MM-01076) and hand-picked cummingtonite (MM-01067), zeta-potential values obtained here (-20 to -21 mV) are less negative than those obtained by Iwasaki & Lawver (1970), who obtained -26 mV, although their value for "bottom mud" is in the same range as these results for tops of cores.

The results show that the particles in suspension (sediment-trap data) become more negative with distance from the tailings source (-23 to -31 mV), but the upper inch of cores containing tailings are less negative (-11 mV) than the original tailings. The core samples become more negative and values approach that of the original material with depth (1-2 inches).

TABLE 2. ZETA-POTENTIAL RESULTS OF SAMPLES IN LAKE SUPERIOR WATER

Sample		Zeta Potential
Cummingtonite	MM 01067	- 21 mV
Tailings	MM 01066	- 19.5
Tailings	MM 101A	- 19.8
Sediment trap	CTR 01	- 22.8
	FLT 01	- 24.5
	KLT 02	- 31
Core	308 S0-1	- 10.7
	308 S1-2	- 22
Core	711 S0-1	- 8 to -14
	711 S1-2	- 22.5

The results are reproducible to ±3 mV on replicate analysis. Results shown are for a mean of 6 runs at 300 volts. Dry samples were aged 24 hours in water before analysis.

Although all samples studied contained cummingtonite as ascertained by *x*-ray diffraction analysis, with the exception of MM-01067, one may only infer from a statistical argument that the results given in Table 2 pertain to cummingtonite.

Parks (1967) has shown that the variation in Fe and Mg in silicates can change the surface charge. In addition, any material adsorbed or precipitated on the surface of the fibres changes the surface charge. At a fixed pH as the Fe/Mg of a cummingtonite increases, the surface charge should become more negative, assuming OH is the surface potential determining ion. If Si is preferentially removed, the surface charge should become more positive.

Cummingtonite, $Fe_5Mg_2Si_8O_{22}(OH)_2$, has a zero-point of charge at pH 5.5, whereas amorphous FeOOH has a zero-point of charge at 8.5. The measured zeta potential can be affected by a change in cummingtonite stoichiometry (increasing Fe^{2+} decreases the zeta potential) as well as a change in the surface-adsorbed Fe^{3+} or associaed FeOOH (an increase in Fe^{+3} would decrease the zeta potential).

TEM analysis of Lake Superior water

Large-volume surface samples of Lake Superior, obtained by the Canada Centre for Inland Waters, were enumerated to ascertain the fibre concentrations in suspension. Figure 3 shows the results of the analyses. Concentrations in western Lake Superior are between 5-20$\times 10^6$ fibres/litre and most results from the rest of the lake are between 1 and 3$\times 10^6$ fibres/litre. The reproducibility is generally 100% of the mean. At $>10\times 10^6$ fibres/litre, the reproducibility of analysis is about 50% of the mean.

Fibres in Lake Superior are very small (length averages 0.5 μm) and are difficult to identify mineralogically. The fibres often occur associated with other material in a gelatinous-like, slightly electron-dense medium commonly associated with microbiological material (Kramer & Mudroch 1974). Figure 4 is a photograph of a typical assemblage.

INTERPRETATION OF RESULTS

Chemistry and mineralogy

Bonnichsen (1969), in the study of the Dunka River area, Minnesota, pointed out that there is a range of composition of about $(Fe_{3.5}Mg_{3.5})$ to (Fe_6Mg_1) for cummingtonite from this region. In addition about 0.1 moles Ca, Mn and Al occur in the structure. An approximate composition for a fibrous sample (No. 026C of Bonnichsen) is $(Mg_{1.39}Fe_{5.44}Ca_{.09}Mn_{.08})(Al_{.08}Si_{7.92})O_{21.96}(OH)_2$.

In this study, cell volumes from *x*-ray diffraction studies suggest a composition of $(Fe_{4.8}Mg_{2.2})Si_8O_{22}(OH)_2$ to $(Fe_{5.7}Mg_{1.3})Si_8O_{22}(OH)_2$. Energy-dispersive analyses of individual fibres, although less quantitative, give for the majority of cummingtonite a compositional mean of $(Fe_5Mg_2)Si_8O_{22}(OH)_2$. Analyses of cores and samples suggest a wider spread in composition, as well as an increase in Mg, to approximately $(Fe_{3.5}Mg_{3.5})Si_8O_{22}(OH)_2$.

There is a parallel change in the surface charge, as exhibited by the zeta potential, except that the more negative zeta potential of the sediments and tips of cores suggests that Fe/Mg increases rather than decreases.

Iron-rich silicates do incongruently dissolve in oxidizing waters. Typically, Fe^{2+} is oxidized and a surface coating of FeOOH forms if the

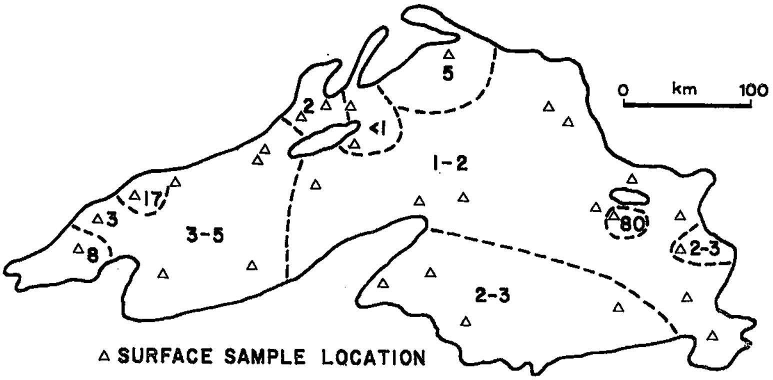

FIG. 3. Estimate of fibre concentration in Lake Superior (10^6 fibre/litre). Values are high in western Lake Superior and near shorelines. There is one anomalously high value in eastern Lake Superior. Streams entering Lake Superior typically have less than 2$\times 10^6$ fibres/litre.

pH is not low and the waters remain oxidizing. Lake Superior has a pH of 8 and is saturated with respect to oxygen, which are almost ideal conditions for this reaction. The following summarizes this reaction:

$$x\mathrm{Mg}^{2+} + (\mathrm{Fe_5Mg_2})\mathrm{Si_8O_{22}(OH)_2} + \frac{x}{4}\mathrm{O_2} + 2.5 \times \mathrm{H_2O} =$$

$$(\mathrm{Fe}_{5-x}\,\mathrm{Mg}_{2+x})\,\mathrm{Si_8O_{22}(OH)_2} + x\mathrm{Fe(OH)_3} + 2x\mathrm{H^+}$$

One would imagine that the value of x would be very small, perhaps in the order of 0.1. But the change in composition suggests that x would be about 1.5 if the above reaction were used to explain the change in cummingtonite composition in the Lake sediments. This change is too large to conceive without a collapse of the mineral structure.

An alternate hypothesis is to assume a range in composition for the cummingtonite at source with a majority of the fibres having a composition near ($\mathrm{Fe_5Mg_2}$). Assuming the ($\mathrm{Fe_5Mg_2}$) fibres deposit first, compared to other Fe compositions, one would find the other compositions in greater concentrations more distant from the tailings. Hence they would be discernible. The range in composition of cummingtonite at the source does exist as noted above.

Surface charge and mineralogy

There is not a clear relationship between the zeta potential and mineralogy. The zeta potential of minerals in this study becomes more negative with distance from the tailings, which can infer an increase in structural Fe in cummingtonite. Yet, according to analyses, the Fe appears to decrease with distance from the source. If the change in zeta potential is due mainly to surface coatings of $\mathrm{Fe^{3+}}$ or other cations, there need be no relationship between mineralogy and zeta potential. The top inch of the lake sediments has a zeta potential approaching zero. This potential may be due to adsorbed cations which would tend to neutralize the surface charge and would result in increased deposition.

Another unresolved aspect concerning the fate of fibrous cummingtonite relates to the longer migration of the more Mg-rich grains. One might argue that the more negative zeta potential would prevent coagulation and sedimentation, yet these particles are typically coated with Fe-oxides and have degraded edges compared to samples adjacent to the tailings delta. Degraded edges suggest reactions which would tend to neutralize the surface charge. Therefore, it is difficult to explain why these fibres tend to have a greater negative charge than fibres with fresh cleavages.

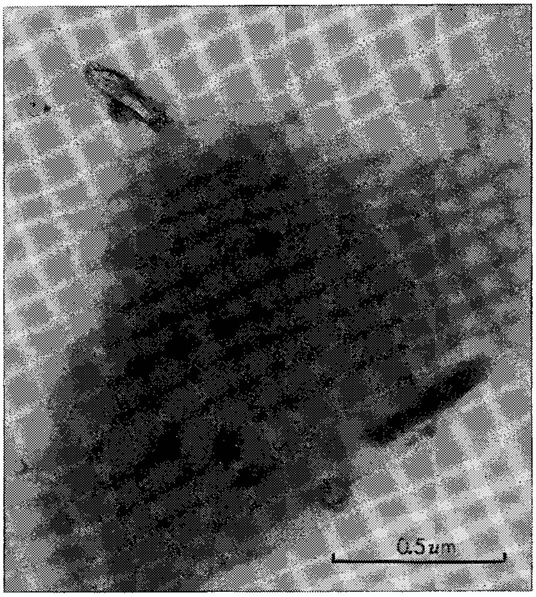

FIG. 4. Electron micrograph of sample of Lake Superior water showing fibrous minerals in an electron-dense gelatinous medium with other microbiological debris. This is a common association in open waters of the Lake.

An alternate hypothesis involves the preferential change in surface silica which would affect the zeta potential and coagulation properties. A decrease in surface silica in these waters would tend to neutralize the surface, increase coagulation and deposition. Unfortunately, there are no definitive data to test this hypothesis.

Fibres are being coagulated and sedimented in western Lake Superior. If this process were not going on, one would expect about 3-5$\times 10^6$ fibres/litre to be distributed evenly throughout the volume of Lake Superior. In comparison, one finds about 1-2$\times 10^6$ fibres/litre, which is slightly higher than input of fibrous minerals from streams. On the other hand, western Lake Superior has higher concentrations of fibres, no doubt due to re-suspension of sediments as well as long-distance movement of fibres. The ultimate fate of the fibres in western Lake Superior depends upon the ability to coagulate the micrometre fibres into larger particles. In turn, this mechanism appears to be related to mineralogy and surface charge.

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REFERENCES

BAUMGARTNER, D. J., HALL, W. F. R., DITSWORTH, G. R. & TEETER, A. M. (1973): Water clarity in relation to fine particulate matter in Lake Superior. Section IV. Particle size analysis. In *Studies Regarding the Effect of Reserve Mining Company Discharge on Lake Superior.* May 2, 1973, U.S. E.P.A., Office of Enforcement and General Counsel, Washington, D.C. 20460.

BEAMAN, D. R. & FILE, D. M. (1976): Quantitative determination of asbestos fiber concentrations. *Anal. Chem.* **48**, 101-109.

BONNICHSEN, B. (1969): Metamorphic pyroxenes and amphiboles in the Biwabik Iron Formation, Dunka River area, Minnesota. *Mineral. Soc. Amer. Spec. Paper* **2**, 314 p.

CLIFTON, R. A. JR., HUGGINS, C. W. & SHELL, H. R. (1966): Hollow chrysotile fibres. *Amer. Mineral.* 51, 508-511.

FINGER, L. W. (1967): *The Crystal Structures and Crystal Chemistry of Ferromagnesian Amphiboles.* Ph.D. thesis, Univ. Minnesota.

FISCHER, K. F. (1966): A further refinement of the crystal structure of cummingtonite $(Mg,Fe)_7Si_8O_{22}(OH)_2$. *Amer. Mineral.* 51, 814-818.

IWASAKI, I. & LAWVER, J. E. (1970): Tailings and natural sediments zeta-potential measurements. Unpublished report to Reserve Mining Co., May 7, 1970.

KLEIN, C. (1964): Cummingtonite-grunerite series: a chemical, optical and x-ray study. *Amer. Mineral.* 49, 963-982.

KRAMER, J. R. & MUDROCH, O. (1974): Asbestos research at McMaster University. *Can. Res. Dev.*, Nov.-Dec. 1974, 31-33.

PARKS, G. A. (1967): Aqueous surface chemistry of oxides and complex oxide minerals: isoelectronic point and zero point of charge. *Amer. Chem. Soc. Adv. in Chem.* 67, 121-160.

SELIKOFF, I. J. (1972): Carcinogenicity of amosite asbestos. *Arch. Environ. Health* 25, 183-188.

STEWART, J. M. (1972): The x-ray system — version of 1972. *Computer Sci. Centre, Univ. Maryland, Tech. Rept.* TR-192.

U.S. DISTRICT COURT, DISTRICT OF MINNESOTA FIFTH DIVISION (1974): Supplemental Memorandum No. 5 — 72 Civil 19, 109 p.

VISWANATHAN, K. & GHOSE, S. (1964): The effect of Mg^{+2}-Fe^{+2} substitution on the cell dimensions of cummingtonites. *Amer. Mineral.* 50, 1106-1112.

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