POSSIBLE GEOLOGIC SOURCES OF LITHIC MATERIAL
FROM THE SPEIGEL SITE, CANADA

In prehistoric North America, trade routes were used to transport people and goods. The most commonly found material used to determine these trade routes is siliceous stone. In geologic studies, X-Ray Fluorescence (or simply XRF) is a popular method of analyzing the major, minor and trace elements in lithic samples. If one determines the proportions of the constituent elements in a lithic artefact, the results can be compared to known proportions in suspected quarrying sites to aid in determination of the source of the artefact. Excavations at the Speigel site [BlHj-1] have uncovered chert (or chert-like) artefacts of an inconclusively determined geologic source. Some of the possible sources of these artefacts include Fossil Hill, Flint Ridge, Onandaga, Hudson Bay Lowland and Knife River. It is also possible that some are mylonite. The intent of this study was to use XRF analysis to help identify the source of these chert artefacts, to help reconstruct ancient trade/social interaction.

Main Point 1: Background on XRF Procedure
A. Description of XRF

X-ray fluorescence is one method of determining the concentrations of elements in a material.[1] There are many uses of XRF analysis, including geological analysis lithic materials.[2] In geological studies, it is often important to analyze and measure the major, minor and trace elements in rock samples.[3] XRF has many advantages in general research and for geological specimens. The relative simplicity of x-ray spectra to optical spectra minimized spectral-line interference. The absorption-enhancement (matrix) effects are predictable and can be readily evaluated. XRF is fast, accurate, versatile and economic.[4] Because it is able to produce very accurate results at extremely high speeds, XRF has been widely applied to research and industry. Analyses can be made in minutes or seconds. This speed is achieved by using computer-controlled equipment.[5] The elements irradiated by the x-rays from boron to uranium can by distinctly identified. By using appropriate standards, qualitative analysis can be done. XRF can cover trace element concentrations from below one part per million (1 ppm) to 100%.[6] XRF has some limitations. It is difficult to analyze elements below

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[1] Physics Department, *XRF Didactic Display Case, Physics Department*, Laurentian University (henceforward: *Physics Department*).

[2] J.A. Anzelmo, J.R. Lindsay, *Topics in Chemical Instrumentation. X-Ray Fluorescence Spectrometric Analysis of Geologic Materials.* Part 1. *Principles and Instrumentation*, in *Journal of Chemical Education*, 64, 9, 1987 (henceforward: Anzelmo, Lindsay, *Topics 1*), p. 181-185.

[3] *Ibidem.*

[4] *Ibidem.*

[5] *Physics Department.*

[6] J.A. Anzelmo, J.R. Lindsay, *Topics in Chemical Instrumentation: X-ray Fluorescence. Spectrometric Analysis of Geologic Materials.* Part 2. *Applications*, in *Journal of Chemical Education*,

sodium. It also has very shallow penetration of solids. It needs standards in the same physical form as the analyte. The equipment used for XRF is initially very expensive.[7]

B. Explanation of How XRF Works

Anzelmo and Lindsay[8] describe the main principles of x-ray fluorescence analysis of geologic materials and also[9] the difficulties, possible sources of error and methods of optimization. The principles of XRF are also detailed by Potts and Webb[10], Williams[11] and Norrish and Chappell.[12] The sample is bombarded with primary radiation from an x-ray tube. This raises the electrons into higher orbitals. When the electrons fall back into their original orbits, they release their excess energy as secondary radiation, or simply fluorescence. This is shown in the top two part of Figure 1. The wavelength of the secondary radiation for each energy transition is inversely proportional to the difference between the initial and final orbitals of the electron.[13]

There are two methods of doing X-ray fluorescence, the "energy dispersion" method (EDXRF) and the "wavelength dispersion" method (WDXRF).[14] In this study, wavelength dispersion x-ray fluorescence was used, so the energy dispersion method will not be detailed.

Wavelength dispersion XRF diffracts the wavelengths of secondary radiation from the sample by directing them onto a crystal with lattice planes parallel to its surface. This process is depicted in the bottom section of Figure 1. In order for diffraction to occur, the distance between the planes (interplanar) (d), the wavelength of the secondary radiation (λ) and the angle at which the secondary radiation hits the crystal (Θ) must all meet Bragg's Law ($n\lambda = 2d\sin\Theta$). The radiation is measured by a detector which converts photons into pulses of electric current that have a height proportional to the photon energy. In order to identify each wavelength, angle Θ is altered. The percentages of each element are calculated based on the intensity of the wavelengths. There are two main types of WDXRF spectrometers, "sequential" and "simultaneous".[15] Both types of WDXRF are shown in Figure 2. These two types of instruments can also be combined by equipping the instrument with both fixed setups and scanning

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64, 9, 1987 (henceforward: Anzelmo, Lindsay, *Topics 2*), p. 200-204; *Physics Department*.

[7] Anzelmo, Lindsay, *Topics 2*.

[8] Anzelmo, Lindsay, *Topics 1*.

[9] Anzelmo, Lindsay, *Topics 2*.

[10] P.J. Potts, P.C. Webb, *X-Ray Fluorescence Spectrometry*, in *Journal of Geochemical Exploration*, 44, 1992 (henceforward: Potts, Webb, *X-Ray Fluorescence*), p. 251-296.

[11] K.L. Williams, *An Introduction to X-Ray Spectrometry: X-Ray Fluorescence and Electron Microprobe Analysis*, Boston, Massachusetts, Allen & Unwin, 1987.

[12] K. Norrish, B.W. Chappell, *X-Ray Fluorescence Spectrography*, in *Physical Methods in Determinative Mineralogy*, edited by J. Zussman, New York, Academic Press New York, 1967 (henceforward: Norrish, Chappell, *X-Ray Fluorescence*), p. 161-214.

[13] *Physics Department*.

[14] Anzelmo, Lindsay, *Topics 1*.

[15] *Ibidem*; *Physics Department*.

setups, or simple by fitting a scanning setup in place of one or two fixed setups, thus combining the advantages of both in one instrument.

In a simultaneous spectrometer, more than one element is determined at the same time. For each element to be identified, there is a crystal and detector which are preset to the correct wavelength. This type of spectrometer is quick and also reliable for a specific group of elements. Because the geometry of the system does not change, logarithmically curved crystals can be used.[16] All of the secondary radiation that goes through the entrance slit will strike the crystal at the same angle Θ. Intensities can be maximized for optimum sensitivity because of the accurate focussing.[17] The operating conditions remain more nearly constant with this system[18].

A sequential spectrometer determines the constituent elements one at a time. A single crystal is rotated through $\Theta°$ while the detector is moved $2\Theta°$. This keeps the proper geometry needed for the detector to receive the radiation at the various angles.[19] This type of spectrometer is able to identify any combinations of elements. By using various instrument parameters, it is possible to optimize the analysis and identification of each individual element.[20] The advantage of a sequential spectrometer is versatility. The disadvantage is that analysis of samples for many elements requires more time. This is because each x-ray line must be detected and processes individually.[21]

C. Procedure for Doing the Analysis

The procedure for preparing the sample for analysis is relatively easy, but it must be carried out carefully. It is important for the sample to be homogeneous and easily reproduced form.[22] Often, the samples are ground to a powder and pressed into a pellet to be analyzed for trace elements.[23] In this study, a flux and fusing were added and the sample was melted into a glass disk. Doing this can remove errors that are caused by some mineralogical effects. Although the sample preparation in this study was done manually, there do exist machines which serve this function.[24]

Main Point 2: Discussion of Results
A. Descriptions of Possible Sources

In the Great Lakes region, during the time period that Killarney was in use, materials were traded and transported over long distances. The primary

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[16] Anzelmo, Lindsay, *Topics 1*; *Physics Department*.
[17] *Physics Department*.
[18] Anzelmo, Lindsay, *Topics 1*; *Physics Department*.
[19] *Physics Department*.
[20] Anzelmo, Lindsay, *Topics 1*; *Physics Department*.
[21] Anzelmo, Lindsay, *Topics 1*.
[22] *Physics Department*.
[23] Norrish, Chappell, *X-Ray Fluorescence*, p. 161-214; Potts, Webb, *X-Ray Fluorescence*; *Physics Department*.
[24] *Physics Department*.

(and often times the only) record left of the trade routes are non-perishable items such as metals, shells and lithic materials. Siliceous material, such as chert, which was used as tools is the most common evidence of prehistoric trade found on archaeological excavation.[25] Traded items are often found in the form of the finished product which were most likely exchanged among members of adjacent groups as the various groups moved to their seasonal occupation sites. Before being finally deposited where the archaeologist finds it, an artefact might have changed hands many times and thereby been transported a long distance. In prehistoric times, trade was an integral part of local economies and very likely provided people with many of subsistence needs.[26] The presence at the Speigel site of the grave goods associated with the Adena culture suggests that it was part of a large trade network involving various materials, including cherts, particularly those from the Ohio Valley.[27]

Most of the lithic artefacts found at the Spiegel site from Hudson's Bay Lowland (HBL) and Fossil Hill Formation (FH). Both of these sources are in close proximity to the site. The Fossil Hill Formation is on Manitoulin Island in the southeastern are. Hudson's Bay Lowland is a general area throughout northern Ontario, and this material is often found in the form of pebbles or cobbles. There have also been some artefacts found that were visually identified as Flint Ridge (FR) chert.[28] Artefacts found included finished products, debitage and partially manufactured tools. This suggests that the materials themselves were being imported, either through trade or direct procurement, and not just the finished products.[29] The location of the various geologic sources are shown in relation to the Speigel site in Figure 3.

The Mylonite studied in this sample is from the Killarney area slightly north of the Speigel site. Mylonite is not chert, but can be mistaken for chert. During the nineteenth century, the geologist and amateur archaeologist Robert Bell briefly mentioned in his reports that he had located a large band of material which he described as chert. He speculated that it was the same material being excavated from the burial mounds of what is now the Speigel site. The location of this band is on the north shore of Lamarandier Bay, but the precise location is not known. In Figure 4, the general area of the mylonite is show in relation to the Speigel site. It is now known that there are no chert formation in that area. Bell's description of the 'chert' band he located do match the description of some mylonite found in that area. The geologic sample obtained for this study was from the vicinity noted by Bell, although it should be noted that there was considerable uncertainty as to whether the geologic sample obtained was from

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[25] J.V. Wright, R.L. Carlson, *Prehistoric Trade*, in *Historical Atlas of Canada*. Volume I. *From the Beginning to 1800*, ed. R. Cole Harris and Geoffrey J. Matthews, cartographer and designer, Toronto, University of Toronto, 1987, Plate 14.

[26] *Ibidem*.

[27] *Ibidem*.

[28] K.T. Buchanan, *The Spiegel (BlHj-1) Survey 1982*, in *Report No. 16 of the Archaeological Survey of Laurentian University*, 1990, p. 102.

[29] *Ibidem*.

the same band mentioned by Bell. Mylonite is formed along a fault. The two sides are pressed together and as they rub against each other, they often form fine particles that are subsequently fused together. Mylonite can sometimes be visually identified by small pieces of mica with similar alignment within the lithic material. The approximate location of the fault line is shown in Figure 4.

The artefacts analyzed in this study were compared to samples of known geological material. The XRF analysis done for this study was performed on twenty seven samples. Five of the samples were known Mylonite (MY) from a geologic site. Five were known Flint Ridge (FR) samples. Five were known Fossil Hill (FH) samples. Six were known Onandaga (ON) samples. Six of the samples were from artefacts found at the Speigel site. Possible sources of the artefacts were hypothesized based on visual characteristics prior to chemical analysis (see Appendix 1: "Description of Samples Prior to Grinding"). To this information, was later added the results of previous chemical analyses done by P. Julig. One of these samples was an artefact from the ElHv-& archaeological site and was suspected to be of HBL origin. Ten samples were known Onandaga (ON) samples. Seven samples were known Knife River Flint (KRF) samples. Twenty were from Hudson's Bay Lowland (HBL). Of the twenty HBL samples, seven were from Stooping River Formation (SRF), two were from Ekwan River (EK) and the remaining eleven were general HBL from glacial deposits. The location of the geologic sources are shown on Figures 3 and 4.

B. Observations from Output and SPSS Results

This study attempted to correlate artefacts and known geologic sources. The proportions of elements obtained through XRF analysis of the artefacts were compared directly to the proportions obtained for several known geologic sources. The geologic sites chosen were those suspected of being the possible original source of the artefact material. Initially, visual attributes were used to identify the artefacts. This was compared to the identification made using the chemical analysis and the Statistics Program for Social Science (SPSS). For x-ray fluorescence analysis to be useful, the results must have high precision and low analytical uncertainty. The proportions of elements must exhibit low uncertainty and little variation within sites. There must also by distinguishable variability between sites. "Diagnostic" elements are elements which allow the simplest geochemical distinctions between sources. "Trace" elements refer to elements that are present in less than about one thousand parts per million ('ppm' for short). In this study, in order to simplify terminology, the term 'trace' element is used synonymously with 'major' and 'minor' elements which are often present in larger quantities.

In many sourcing studies, visual attributes alone are used to assign sources of chert (and other lithic material) artefacts. Eley and Bitter[30] discuss and describe the characteristics of cherts from southern Ontario. As some of the

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[30] E.B. Eley, P.H. von Bitter, *Cherts of Southern Ontario*, Toronto, University of Toronto Press, 1989.

cherts in this study were from southern Ontario, this was of use in visually identifying the source of the cherts. Eley and Bitter[31] discuss both microscopic and macroscopic characteristics, and also the use of thin sections to visually identify the cherts. Lack of both time and access to equipment prevented the use of thin section identification. The visual method was also not done in detail because the intent of this study was to determine the geologic source by chemical analysis. It is easy to mistake sources using the visual method by itself. In keeping with the focus of this study, to identify artefact sources based on their chemistry, visual attributes were used only to corroborate the source assignments.

This study used the Statistics Program for Social Science (SPSS) to attempt to identify the sources of the artefacts. The statistical analysis was performed using a dataset comprised of percents of the element oxides and also a dataset comprised of the parts per million of the elements. Both datasets produced relatively similar outputs. Two command files were used. The first command files considered all of the HBL geologic samples together as one source. The second command file divided the HBL samples into General HBL, Stooping River Formation and Ekwan River. The commands were the same for both files. The samples HBL samples were simply divided for the second statistical analysis. The two command files produced slightly different output. Five main functions were carried out in the statistical analysis. These included a description of the component elements for each source; principal component analysis (factor analysis) of the variables; cluster analysis of the sources and artefacts; discriminant analysis of the sources and artefacts; and mean element proportions by source. The statistical output was used to attempt to source the artefacts.

A description of the component elements for each source, and the means of the elements listed by source were both examined. The component elements of each of the artefacts were compared to the range and averages of the sources to see if they could match. This was a brief comparison. Most of the artefacts were able to fit within, or close to, the ranges of most of the geologic sources.

A principal component analysis (also known as factor analysis) of the variables was done. The number of principal components was equal to the number of geologic sources. This was an attempt to determine which variables rate high or low with other variables, or in other words, how the proportions of the elements are related to one another. It was found that when Potassium content was high, so was Aluminum and Titanium. This is very common of the mylonite samples. To a lesser, it was evident in Onandaga chert. It is also very characteristic of artefact sample PJ-23 (more similar to the levels found in the mylonite samples) which was visually classified as mylonite. It was also found that when calcium content was high, silica was low. This is very characteristic of Onandaga chert. This characteristic is not readily evident in any of the artefact samples. The final relation identified was that when iron content is high, so is

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[31] *Ibidem*.

sodium content. This was only identified in the first statistical output (the one which grouped all HBL as a single group). This is very common in the mylonite samples and also to a lesser degree in the Fossil Hill samples and the Flint Ridge samples. None of the artefact samples are readily sourced by this characteristic though.

The known geologic sources were compared using cluster analysis. Cluster analysis showed that there is a lot of intra-source variability and a lot of inter-source similarity. This means that each site is diverse and none of the sites is very unique. When cluster analysis was done on the geologic samples and the artefact together, the group the artefacts were assigned to did not correspond to any particular geologic source, except for one artefact. Artefact sample PJ-23 was placed into the group which corresponded only to the mylonite samples.

Discriminant analysis was also used to help identify the geologic source of the artefacts. The samples (both geologic and artefact) were placed into six groups based on those assigned to them from the cluster analysis and then by their known geologic sources (grouping all of the HBL samples together). Each of these groups was analyzed based on the first two principal components and then also based on the ten component elements. This produced four lists of groupings. Lists of groups based on the principal components, did not contain artefacts because the artefacts were not used in the original principal component analysis, and therefore had no value for any of the principal components. When the artefacts were sorted by the groups from the previous cluster analysis, none of the artefacts could be positively linked to any specific geologic source. When the artefacts were sorted by geologic sources, artefacts PJ-22, PJ-24, PJ-25, PJ-26 and PJ-27 were identified as most likely being Fossil Hill chert or possibly Onandaga chert; artefact PJ-23 was identified as most likely being Onandaga chert or possibly Fossil Hill chert; and the artefact from EiHv-7 was identified as most likely being Knife River Flint or possibly Fossil Hill chert.

In the output from the second command file, discriminant analysis produced slightly different results. There were eight groups used with the second command file because the HBL group was divided into specific locations. This produced slightly different groups in the cluster analysis and also caused the artefacts to by identified differently in the discriminant analysis. As with the first output, when the artefacts were sorted by the groups from the previous cluster analysis, none of the artefacts could by easily linked to any specific geologic source. Although, artefact PJ-23 was identified as possibly belonging to the group characteristic of Onandaga chert, Stooping River Formation chert or general HBL. The artefact from EiHv-7 was identified as possibly belonging to the group characteristic of mylonite. When the artefacts were sorted by geologic sources, artefacts PJ-22, PJ-23, PJ-24, PJ-25 and PJ-27 were identified as most likely being Fossil Hill chert or possibly Onandaga chert; artefact PJ-26 was identified as most likely being Fossil Hill chert or possibly general HBL; and the artefact from EiHv-7 was identified as most likely being Ekwan River chert or possibly Knife River Flint.

In this study, there was a very low number of cases. The sample population (the number of samples of each of the geologic sources) was too small and possibly not representative of the statistical population (all possible samples from each of the geological sources). To do statistics, the sample population is supposed to be at least 30 samples. The fewer the number of samples, the less reliable the analysis will be. In this study, there were five to twenty samples for the geologic sources, most only having about six. The reason for the low number of samples was due to limited access to the equipment required to do the analysis. Future studies like this one should have larger sample sizes.

Conclusion

There were very few results from this study from which to draw any strong conclusions. It appears that the mylonite which Robert Bell refers to as "chert" was being used. A future line of inquiry might be "Where was the quarrying site of the mylonite?" and "Where exactly is the band which Bell mentioned?". The chemical analysis also seems to confirm the visual identification of some of the artefacts as being from the Fossil Hill chert formation. The chemical analysis of the artefacts in this study is insufficient to reconstruct ancient trade or social interactions. Both the mylonite and the Fossil Hill chert are both local formations and would have been directly procured.

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POSIBILE SURSE GEOLOGICE ALE MATERIALELOR LITICE DIN SITUL
SPEIGEL, CANADA
Rezumat

În America de Nord preistorică drumurile comerciale erau folosite pentru transportul persoanelor şi bunurilor. Cel mai răspândit material utilizat pentru determinarea acestor drumuri comerciale este piatra silicată. În studiile geologice, fluorescenţa razelor X (sau pe scurt XRF) este o metodă populară pentru analizarea elementelor majore, minore şi a urmelor din mostrele litice. Dacă se determină proporţiile elementelor constitutive ale unui artefact litic, rezultatele pot fi comparate pentru a cunoaşte proporţiile din siturile de carieră bănuite pentru a contribui la determinarea sursei artefactului. Excavaţiile de la situl Speigel [BlHj-1] au scos la iveală artefacte din cremene (sau de tip cremene), dintr-o sursă geologică nedeterminată în mod concludent. Unele dintre sursele posibile ale acestor artefacte includ Fossil Hill, Flint Ridge, Onandaga, Hudson Bay Lowland şi Knife River. Este de asemenea posibil ca unele să fie milonite. Scopul acestui studiu este de a utiliza analiza XRF pentru a contribui la

identificarea surselor acestor artefacte din cremene şi de a contribui la reconstruirea contactelor comerciale şi sociale.

LISTA FIGURILOR

Fig. 1. Stânga sus: Orbitele unui atom care manifestă transferuri de energie. Dreapta sus: orbite (sau niveluri de energie) ale unui atom. Jos: Radiaţie secundară şi cristal în spectometru.

Fig. 2. Diagramă reprezentând dispersia lungimilor de undă simultane (deasupra) şi secvenţiale (dedesubt) la spectometre cu fluorescenţă a razelor X.

Fig. 3. Harta Marilor Lacuri şi a împrejurimilor înfăţişând locaţia sitului Speigel şi sursele geologice discutate în acest studiu.

Fig. 4. Harta zonei golfului Killarney înfăţişând situl Speigel şi locaţia benzii milonite.

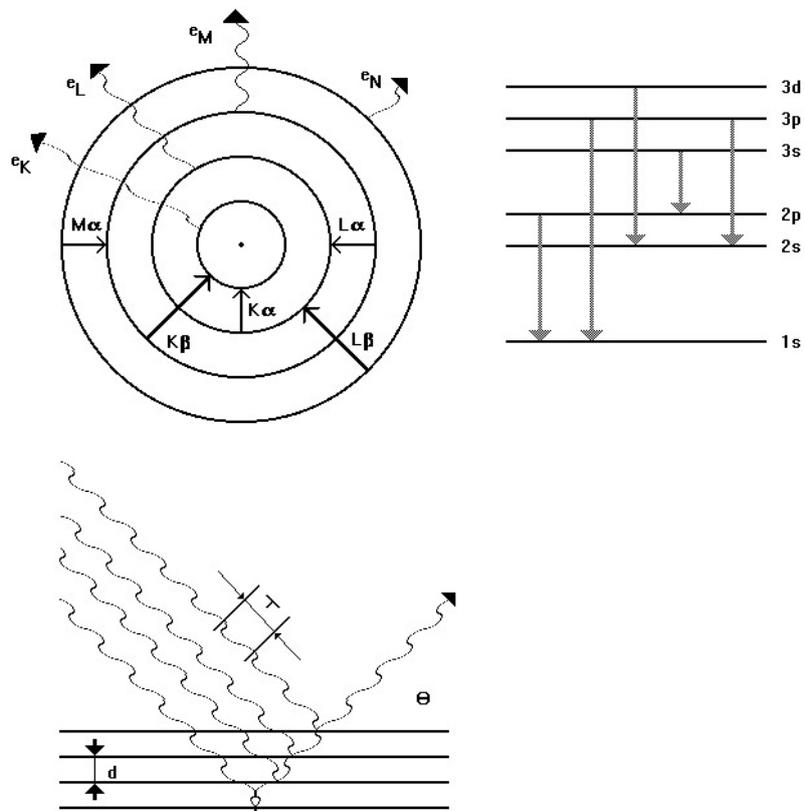Appendix 1. Descrierile mostrelor anterioare măcinării.

Fig. 1. Top left: Orbitals of an atom showing energy transfers. Top right: Orbitals (or energy levels) of an atom. Bottom: Secondary radiation and crystal in the spectrometer.
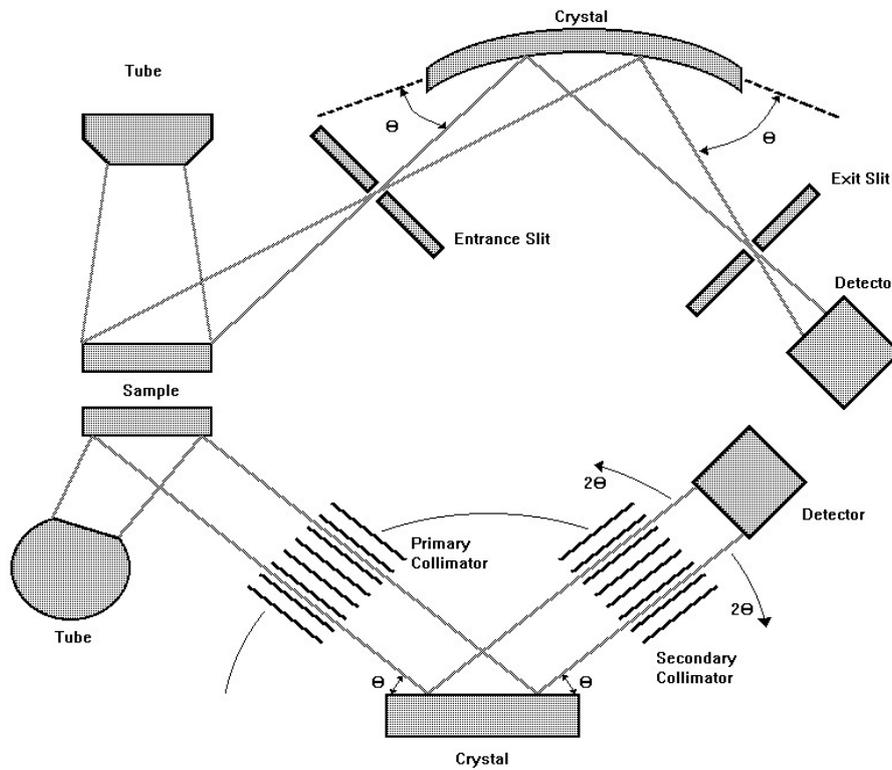
15

Fig. 2. Diagram showing the simultaneous (above) and sequential (below)
wavelength dispersion x-ray fluorescence spectrometers

Fig. 3. Map of the Great Lakes and surrounding area showing the location of the Speigel site and the geologic sources discussed in this study
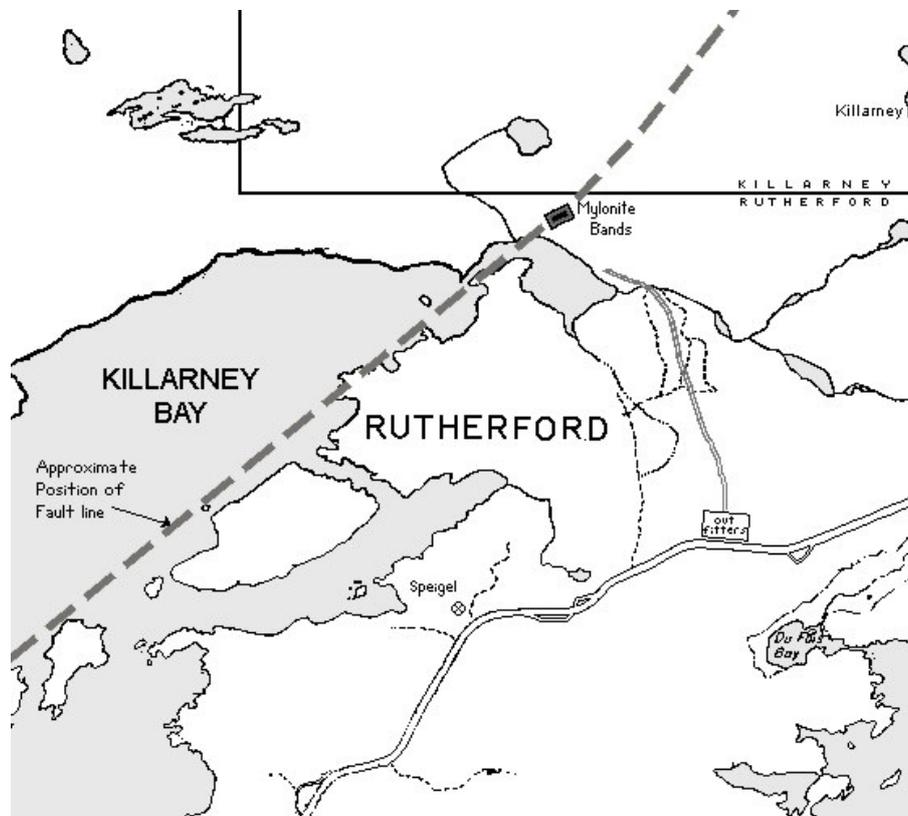
Fig. 4. Map of the Killarney Bay area showing the Speigel site and the location of the mylonite bands

Sample#	Original Description of Sample	Source (Cat. #)	Powder Wt. (g)	+Vial
M1	Dark brown and black	No Cat. # (mine)		
M2	Light brown	129		
M3	Pink with red lines	137		
M4	Medium brown	139		
M5	Pink/orange	139		
FR6	Off-white and light brown with black flecks	120		
FR7	Light brown	120	3.3	24.8
FR8	Light brown	120	3.7	25.2
FR9	Light brown	120	5.6	27.1
FR10	Light brown	120	5.3	26.8
FH11	Off-white with medium brown blobs	96	4.5	26.0
FH12	White with brown	96	5.0	26.5
FH13	Medium brown/orange with some white	96	3.4	24.9
FH14	White with dark and light brown	96	5.45	26.95
FH15	Off-white with dark brown blobs	96	3.95	25.45
ON16	Brown	ON-1	3.4	24.9
ON17	Light and dark brown bands	ON-5	3.35	24.85
ON18	Brown	ON-8	3.6	25.1
ON19	Light and dark brown	ON-9	2.7	24.2
ON20	Brown/grey	ON-10	3.85	25.35
ON21	Brown	Onandaga #122	1.9	23.4
X22	Medium brown; possible ON or FR	BlHj-1 N5W9L4-5; hand axe	4.8	26.3
X23	Pink and white; possible mylonite	BlHj-1 N10W14L2 Tray 2 84	4.55	26.05
X24	White; possible FH	BlHj-1 N10W14L2 Tray 2 84	3.6	25.1
X25	Light brown; possible FR	BlHj-1 N12W13 Chert Tray 10	1.75	23.25
X26	Clear, light brown, light lines running through it; possible FR or FH	BlHj-1 N6 & N7 1984 bag Tray 2	1.2	22.7
X27	Various shades of pink, looks like chert; possible mylonite	BlHj-1 N7W6L3	0.95	22.45

Appendix 1. Descriptions of Samples Prior to Grinding