CHERT ANALYSIS BY INFRARED SPECTROSCOPY

Darrel G. F. Long, Brenda Silveira and Pat Julig

Abstract

Visual identification of chert sources for lithic artifacts is complicated by the similar appearance of many potential sources, hence methods must be devised to allow rapid accurate identification with minimal destruction of cultural artifacts. While petrographic analysis of thin sections, INAA, XRF and ICP-MS, and palynology can be used to resolve these problems they are in many cases not practical for low-cost analysis of numerous samples and in some cases may require destruction of large quantities of archaeological material. Fourier transform IR spectroscopy provides a potentially rapid method of relatively non-destructive analysis which can be used to establish a database on the crystallinity and trace mineral components in cherts which may form the basis for future analysis of artifact trade patterns. Direct examination of geological samples of chert from Hudson Bay Lowlands, Southern Ontario and Syria, using a Perkin Elmer FT-IR Spectrometer were at first unsuccessful due to overabundance of sample and irregular reflectance characteristics of the cherts. An alternate method was developed by trial and error in which 0.004 g of ground chert was diluted with progressive amounts of potassium bromide (KBr) in order to generate distinctive reproducible results. Best results were obtained using pellets made up to a total weight of 0.1 g by addition of KBr. This technique appears to be successful in identifying different groups of chert based largely on the presence of distinctive sets of peaks for trace mineral components. Limited analysis suggests that this technique may be used to successfully fingerprint samples of chert from different formations, and possibly from different localities within the same formation.

Résumé

L'identification visuelle des sources de chert exploitées pour la fabrication d'objets lithiques est d'autant plus compliquée que de nombreuses sources possibles ont un aspect semblable; il faut donc imaginer des méthodes qui nous permettent une identification exacte et rapide en détruisant le moins possible les objets culturels. Si l'on peut faire appel à l'analyse pétrographique de coupes minces, à l'analyse instrumentale par activation neutronique, à la fluorescence X, à la spectrométrie de masse avec plasma induit par haute fréquence (SM-PIHF) et aux microfossiles pour résoudre ces problèmes, ces méthodes sont bien souvent impraticables si l'on veut analyser à faible coût de nombreux spécimens et d'ailleurs, elles exigent parfois la destruction d'une grande quantité de matériel. La spectrographie infrarouge à transformée de Fourier (FTIR) offre un moyen parfois plus rapide de procéder à une analyse relativement non destructive qui nous permet de créer, sur le caractère cristallin des cherts et les oligo-éléments qu'ils contiennent, une base de données sur laquelle on peut s'appuyer pour analyser ultérieurement les structures de troc/échange d'objets. L'examen d'échantillons géologiques de chert en provenance des Basses-Terres de la baie d'Hudson, du Sud de l'Ontario et de la Syrie à l'aide d'un spectromètre Perkin Elmer à infrarouge et transformées de Fourier (FTIR) n'a rien donné d'utile pour commencer en raison de la surabondance de l'échantillon et des caractéristiques de réflectance des cherts. Une méthode de rechange a été mise au point par tâtonnement; elle consiste à diluer 40 milligrammes de chert broyé dans une quantité de plus en plus grande de KBr afin de générer des résultats distinctifs et reproductibles. Les meilleurs résultats ont été obtenus avec des granules d'un poids total de 0,1 g auxquels on a ajouté du bromure de potassium (KBr). Il semble que cette technique permette d'identifier différents groupes de chert, en grande partie à la présence d'ensembles distinctifs de pics correspondant aux oligo-éléments. Quoique limitée, l'analyse nous pousse à conclure que cette technique pourrait être utilisée pour caractériser des échantillons de chert issus de différentes formations, voire même de différentes localités au sein d'une même formation.

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Introduction

A characteristic of early Palaeo-Indian (ca. 12,000 - 10,000 BP) cultures in the Great Lakes Region of North America is their common use of high quality, often non-local or exotic cherts, and the similarities of their lithic assemblages across broad regions (Mason 1981, 1986; Goodyear 1989). These may have been made from chert collected directly from *in situ* geological sources, from superficial, often glacially transported material, or from chert obtained by trade or other forms of cultural exchange. As many artifacts in archaeological collections of cryptocrystalline lithic material are superficially similar it is essential that rapid, minimally destructive methods be devised, to develop, verify or refute models of cultural interaction based on "expert" visual identification of potential sources. While petrographic analysis of thin sections, Instrumental Neutron Activation Analysis (INAA), X-Ray Fluorescence (XRF), ICP-MS, oxygen isotope analysis and palynology can be used to resolve these problems (Long *et al*.,1998, 1999; Tankersley *et al*.,1988; Eley and von Bitter, 1989; Julig *et al*.,1998, 2000; Julig and Long in press), they are in many cases not practical for low-cost analysis of numerous samples and in some cases may require destruction of large quantities of sensitive archeological material. While non-destructive techniques, such as cathodoluminescence (CL) microscopy can been used to identify specific quartz-rich lithic sources, such as the Hixton Silicified Sandstone (Julig *et al.*,1998; Long *et al.*,1998, 1999) and some cryptocrystalline volcanic rocks (McEachen *et al.*,1999) they are of little use in distinguishing specific chert sources. We decided to test the efficiency of Fourier Transform Infrared Spectroscopy (FT-IR) in distinguishing chert types from the Great Lakes region, the Hudson Platform, and Syria, as Voner (1990) had indicated that for most samples preparation is minimal and spectra are sufficiently distinct and reproducible, and a Perkin-Elmer Paragon 1000, FT-IR device was available in the Central Analytical Facility at Laurentian University. Initial results were presented by Silveira and Long (1999) based on an undergraduate thesis by Silveira (1999).

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy is based upon the principle that spectral information can be obtained using optical interference phenomena: this occurs as bonds within a molecule can only absorb or emit light of an energy equivalent to the spacing between two energy levels, these being either one level higher or lower then the primary state (Kronenberg and Wolf, 1990). Central to the FT-IR instrument is a beam splitter, which diverts light from an infrared source into two beams. One of these beams is reflected by a fixed mirror, while the other beam is reflected by an oscillating mirror. The beams are recombined at the beam splitter resulting in constructive and destructive interference, depending on the instantaneous optical path difference of the two beams (Kronenberg and Wolf 1990). The transmission spectrum measured with the sample in the optical path is then compared to the spectrum measured with the sample removed, and resultant spectrum is extracted using Fourier transformation (Kronenberg and Wolf, 1990). Vibrations from bonds within a molecule are each associated with a set of specific energy levels, which correspond to individual peaks in the FT-IR spectra. Individual (dipolar) bonds are most easily detected at frequencies between 1350 and 4000 cm-1, while group characteristics are best seen in the "fingerprint" region between 200 and 1400 cm-1 (Voner, 1990; Jones and Jackson 1993). These energy levels and peak positions have been determined for numerous minerals by Lippincott et al (1958), Kodama (1985), Salisbury *et al*. (1991), Jones and Jackson (1993), and others. In theory trace component peaks can be detected by mathematically removing the principal mineral spectra (in this case quartz) and comparing the results with a target library of reference spectra. Unfortunately this was not possible on the dedicated computer attached to FT-IR device at Laurentian University, hence thin sections, and existing XRD and

INAA analysis were used to help determine which minerals were responsible for peaks not present on the reference alpha-quartz spectra.

Geological Materials

The majority of samples used in this study are replacement cherts (Hesse 1990), from the Ordovician, Silurian, and Devonian of Southern Ontario, which have previously been examined both petrographical and palaeotologically by Eley and von Bitter (1989). Additional samples of (reworked) Hudson Bay Lowland Chert (probably derived from the Devonian Stooping River Formation) from Pleistocene deposits along the north shore of Lake Superior (Julig *et al.*,1992), were used, as were visually similar samples of Knife River Flint (Tertiary) from western North Dakota (Julig *et al*.,1991), and Lower Eocene (Tertiary: Late Ypresian), black and brown flints from Syria (Krasheninnikov *et al*., 1996; Julig *et al*., in press).

Chert is a stable microcrystalline variety of quartz, composed of silica and oxygen with minor impurities (Eley and von Bitter 1989; Hesse 1990). Most secondary (replacement) cherts include remnants of the host carbonate rock (calcite, dolomite) and may include trace amounts of clay, organic material, iron and manganese oxide, iron sulphide and/or phosphate. Most of these are present at the part per million level. Structural water may be present in immature cherts, such as Opal CT (Rice *et al*.,1995) but is largely absent from older cherts. Silica polymorphs and their trace mineral components have been documented using infrared techniques (Cherster and Iderfield 1968; Langer and Florke 1974) including FT-IR (Rice *et al.*,1995), but no previous systematic studies on geological sources have been made.

Methodology

We first tested the capacity of the FT-IR equipment at Laurentian University to analyze whole samples, powdered samples, slabs and thin sections of chert (Silveira, 1999). Unfortunately this approach gave non-reproducible results due both to the large amount of sample involved, and the masking effects of the glass slide, and was abandoned. We then attempted to use small amounts of powdered sample, diluted with potassium bromide or cesium iodide (CsI), and compressed into flat discs so that they could be placed directly in the light path. Discs prepared by grinding 0.0005 g of sample and 0.0995 g of KBr were opaque, hence the technique was modified, using CsI, mixed together and ground in an agate mortar and pestle, then compressed in a die for 1.5 minutes under vacuum to produce clear pellets. The modified technique produced reproducible quartz peaks, but spectra of cherts samples failed to show marked secondary peaks (above background noise) indicative of trace mineral components.

Silveira (1999) subsequently experimented with varying amounts of sample, KBr and CsI to obtain reproducible results for both quartz and chert. She found the best results were obtained from pellets made by re-grinding 0.004 g of previously ground sample, made up to a total weight of 0.1 g by addition of pre-ground KBr. This technique appears to be successful in producing spectra in which different groups of chert can be distinguished from each other in the "fingerprint" region between 200 and 1600 cm-1 due to the presence of distinctive peaks of their trace mineral components. We found no noticeable differences in spectra produced from bulk powders and micro-samples produced by grinding the surface of solid samples with a diamond-tipped burr, providing that the burr was used no more than two times.

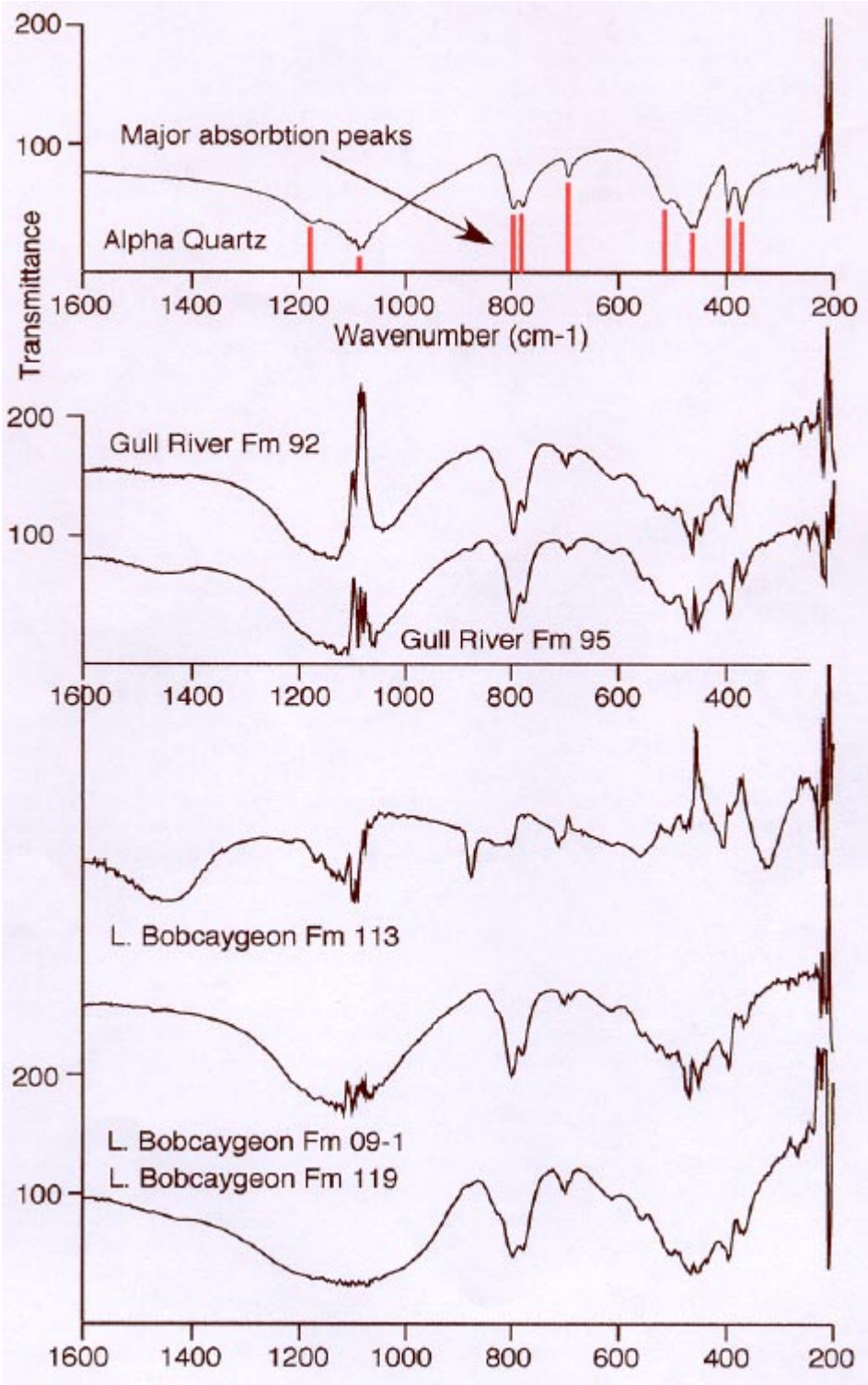

Figure 1. FT-IR spectra of quartz and chert from the Gull River and Bobcaygeon Formations. Low points on curves indicate maximum absorption.

Results

Using the method outlined above, reproducible FT-IR spectra were obtained for alpha-quartz (Fig. 1, top) and chert samples from the Gull River (Fig. 1, middle), Lower Bobcaygeon (Fig. 1, bottom), Fossil Hill (Fig. 2, top), Manitoulin (Fig. 13), Lockport (Fig. 2, middle) Amabel (Fig. 2, bottom), Bois Blanc (Fig. 3,

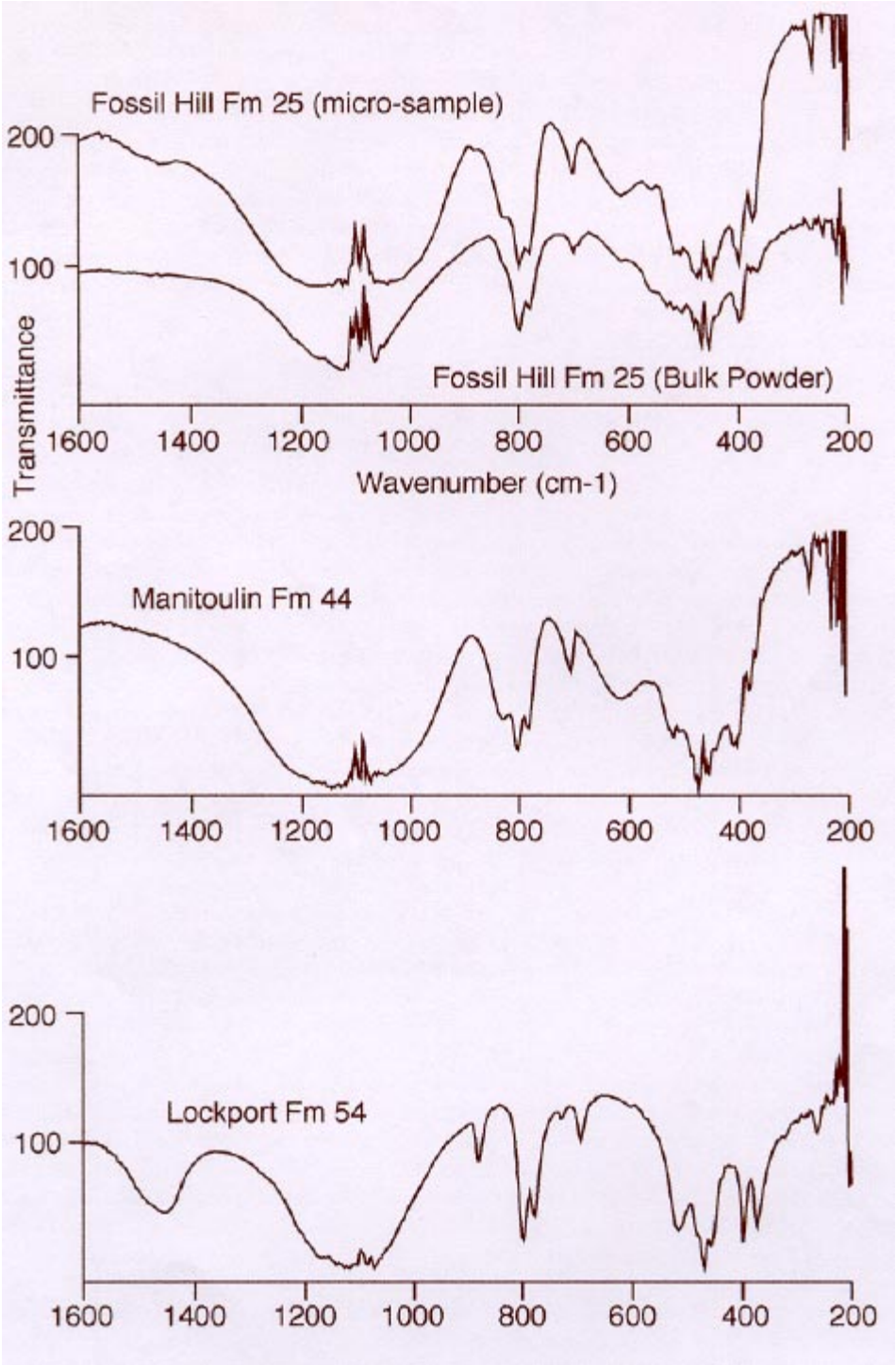

Figure 2. FT-IR spectra of chert from the Fossil Hill, Manitoulin and Lockport Formations.

top), Onodanga (Fig. 3, middle), Dundee (Fig. 3, bottom), Kettle Point (Fig. 4, top), Hudson Bay Lowlands (Fig. 4, middle), Knife River Flint (Fig. 4, bottom), and Syrian cherts (Fig. 5).

In all of the spectra obtained the dominant peaks correspond to the known spectra of quartz (Fig. 1, top), although the exact position of the dominant absorbtion peaks (low points on the curves) did not always correspond to previously documented peaks at 368, 393*, 460*, 509*, 692*, 778, 797, 1080 and 1168 cm-1. Minor off-set may be related to interference effects of trace minerals, and reflection of specific wave-

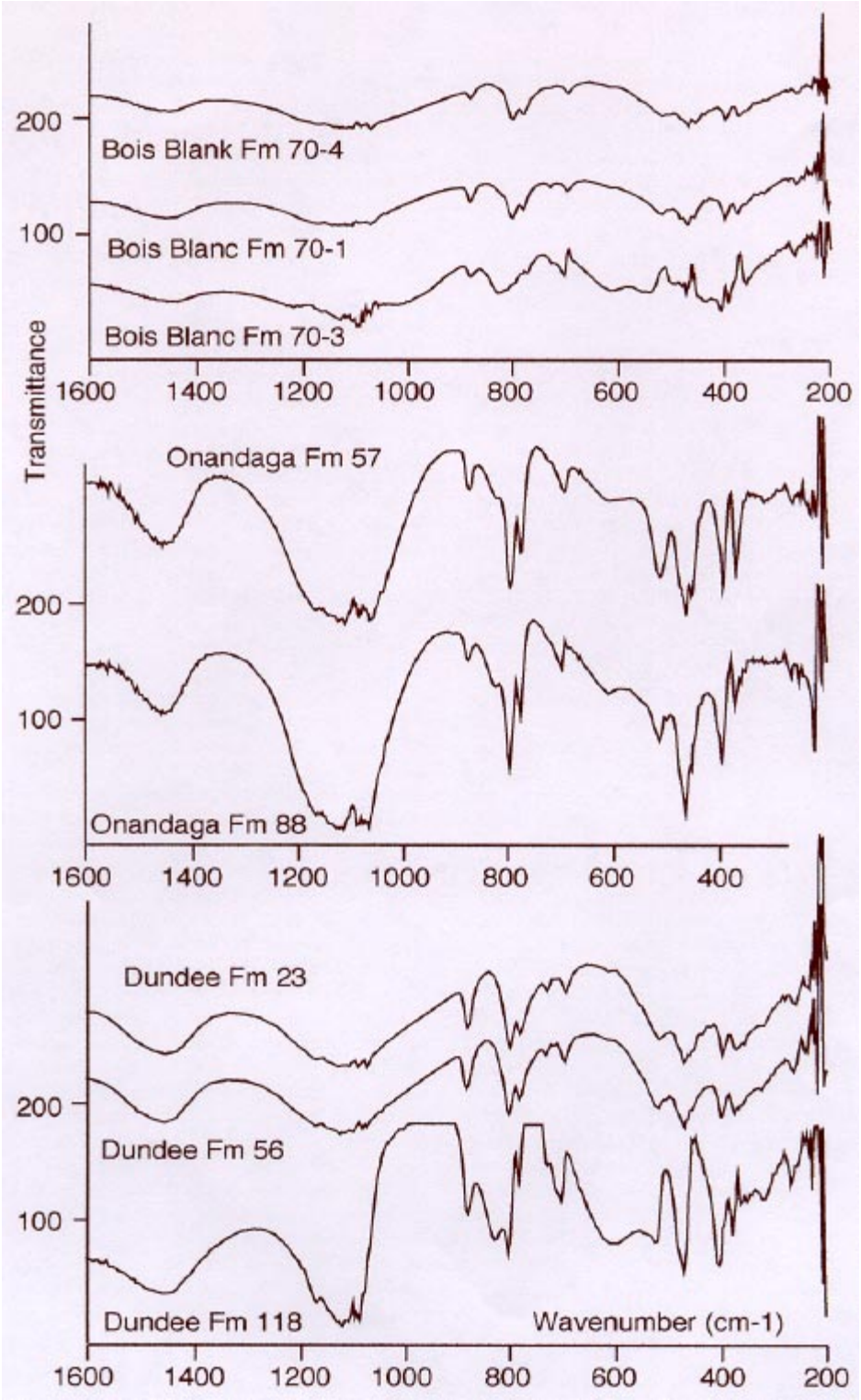

Figure 3. FT-IR spectra of chert from the Bois Blank, Onandaga and Dundee Formations.

lengths by non-quartz components (i.e the large spike at ~1100 cm-1 in the Gull River, Fossil Hill, Manitoulin, and one of the Syrian samples). Quartz peaks at 692 to 368 cm-1 are not always readily apparent, but at least one can usually be found in the chert spectra.

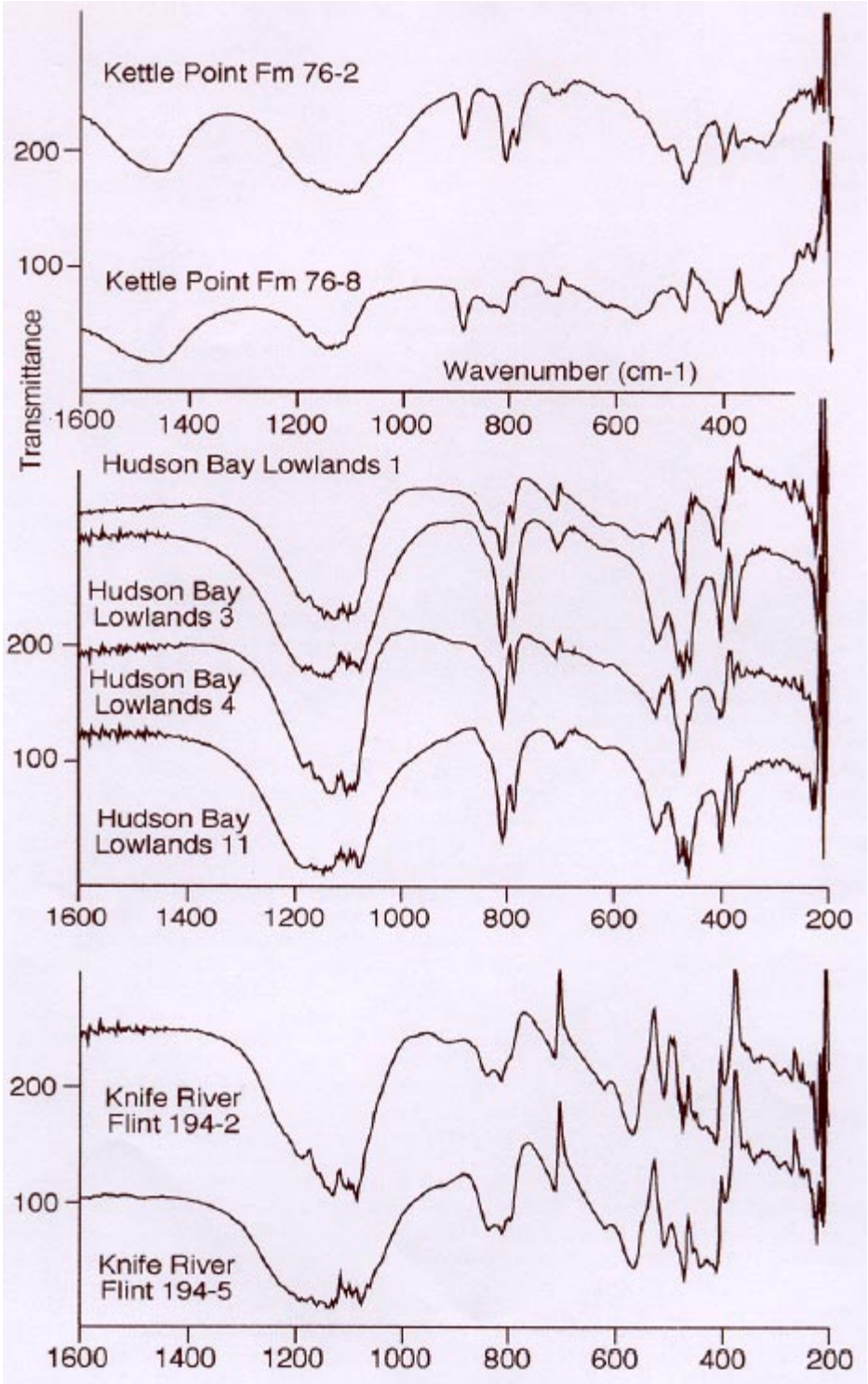

Figure 4. FT-IR spectra of chert samples from the Kettle Point Formation, Hudson Bay Lowlands and Knife River Flint.

Close examination of the chert spectra indicate several small peaks that do not correspond to the standard alpha-quartz spectra. These additional peaks were identified as belonging to the trace mineral components, which are predominantly calcite, dolomite, goethite, glauconite and hematite (Fig. 6). As the quartz spectra could not be readily subtracted from the chert spectra, it was not possible to isolate the exact residual spectral component caused by individual trace components. Positive identification of major trace minerals was made when two or more secondary peaks matched the reference spectra of suspected

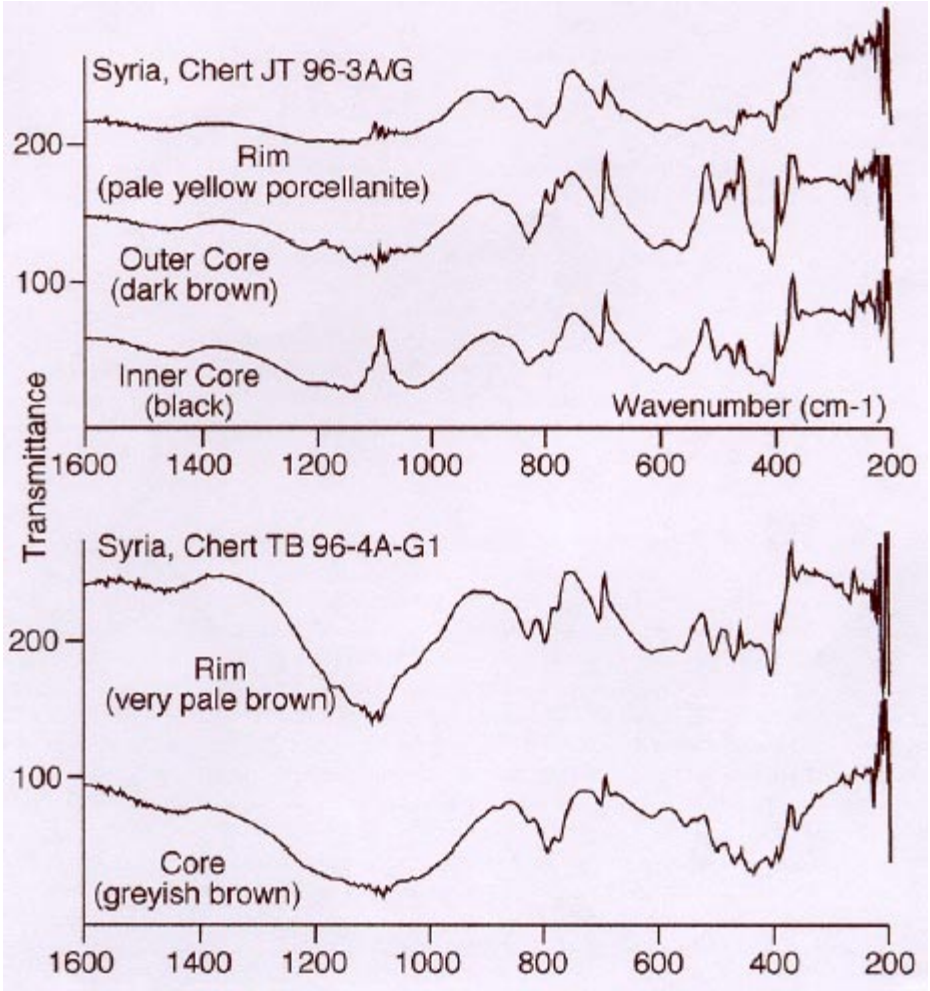

Figure 5. FT-IR spectra of Syrian cherts.

trace components (vertical bars on Fig. 6), after primary quartz peaks (Fig. 1, top) had been excluded (Table 1).

After identification of quartz peaks we sought peaks associated with calcite, as most cherts are known from previous studies to contain this or dolomite (Eley and von Bitter 1989; Hesse 1990). Calcite and dolomite spectra are very similar (Fig. 6). Both have a broad peak at 1429 (calcite) to 1441(dolomite) cm-1: the calcite peak typically has a width of about 200 cm-1, while dolomite has a width of about 600 cm-1. All but five of the chert samples examined contained trace amounts of calcite. Most had a secondary peak at around 877 which corresponds to a known calcite peak at 877cm-1. The only exception is in the spectra from the Amabel Fm, which contains a small peak at 831 cm-1, which may correspond to the calcite reference peak at 848 cm-1. The expected calcite peak at 320 cm-1 is not universally present.

Dolomite peaks are apparent in samples from the Lockport, Amabel, Bois Blanc, Dundee and Kettle Point Formations at around 729, 350 and 326 cm-1. These peaks are difficult to distinguish from calcite. Goethite is identified in some of the cherts based on peaks at peaks around 605 and 400 cm-1. The latter correspond to a merged triple peak in the reference spectra (fig. 6). Goethite peaks are not prominent: this may be due to low transmittance, combined with low primary concentration. Organic material in the Lower Bobcaygeon, Manitoulin and Kettle Point Formations (Table 1) is more difficult to determine since it is not easily identifiable in thin section, and there are numerous spectra for known organic material. We used a peak for a simple organic compound at about 600 cm-1 to determine organic material. It is possible that

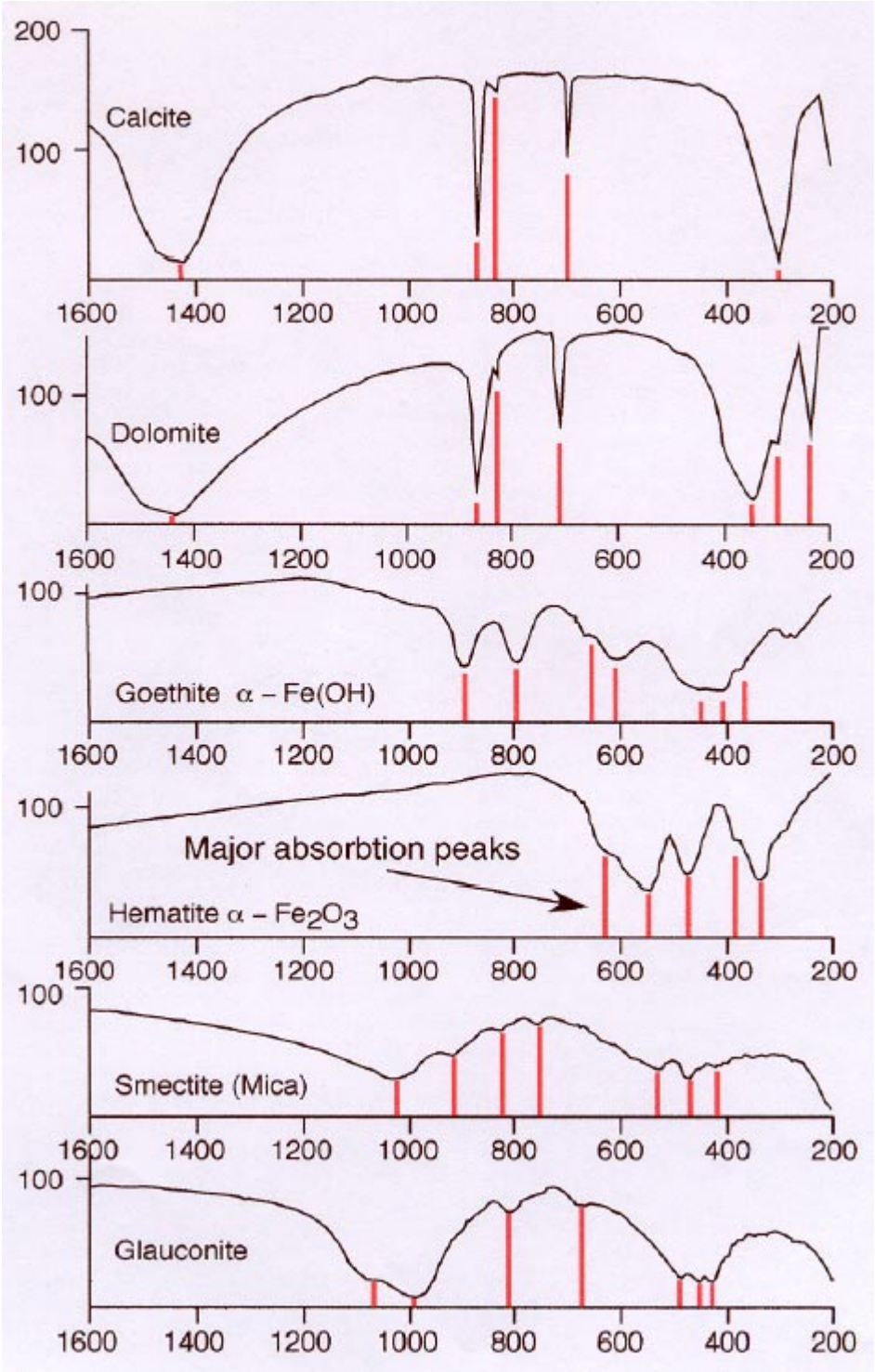

Figure 6. FT-IR spectra of minerals which are found as common trace components of chert.

other unidentified peaks in the chert spectra could belong to organic material since they do not match known common trace mineral spectra.

Clay minerals are present in samples from the Fossil Hill Formation (Fig. 2) confirming optical observations by Eley and von Bitter (1989). They are identified here using peaks at 909, 523, 466 and 413 cm-1, which are apparent as small peaks in the smectite spectra (Fig 6) as well as other clay minerals.

Table 1. FT-IR spectra of common trace components found in cherts. These are identified in chert spectra by matching sets of major absorption peaks (indicated by vertical lines).

Sample	Quartz	Calcite	Dolomite	Goethite	Hematite	Glauconite	Clay	Phosphate	Orgaincs
Gull River Fm , 92	x	x		x	x				
Gull River Fm, 95	x	x		x	x				
L. Bobcaygeon, 91-1	x				x				
L. Bobcaygeon, 113	x	x		x					x
L. Bobcaygeon, 119	x	x							x
Fossil Hill Fm, 25	x	x			x		x		
Fossil Hill Fm, 17	x	x			x		x		
Manitoulin Fm, 44	x	x		x	x				
Lockport Fm, 54	x	x	x	x					x
Amabel Fm, 27	x	x		x					
Amabel Fm, 70-1	x	x	x	x					
Bois Blanc Fm, 70-1	x	x	x	x					
Bois Blanc Fm, 70-3	x	x	x	x		x			
Bois Blanc Fm, 70-4	x	x	x	x		x			
Onodaga Fm, 57	x	x		x	x				
Onodaga Fm, 88	x	x		x	x				
Dundee Fm, 23	x	x	x						
Dundee Fm, 56	x	x	x						
Dundee Fm, 118	x	x	x						
Kettle Point Fm, 76-2	x	x	x		x				x
Kettle Point Fm, 76-8	x	x	x	x	x				
Hudson Bay Lowlands 1	x	x							
Hudson Bay Lowlands 3	x	x		x	x	x			
Hudson Bay Lowlands 4	x			x	x	x			
Hudson Bay Lowlands 11	x			x	x	x			
Knife River Flint 194-2	x								
Knife River Flint 194-5	x								
Syria JT 96-3A/G, core	x	x			x	x		x	
Syria JT 96-4A/G1, core	x	x			x	x		x	

After elimination of peaks for quartz, calcite, glauconite and hematite, the spectra of the two Syrian cherts examined (fig 5) where found to have unidentified peaks at about 780, 435, 408 and 393 cm-1. The presence of phosphatic material in the thin sections (? Fish scales) suggests that these may be useful for identification of phosphatic material (as no appropriate spectra were found). Examination of the spectra for the core, and inner and outer rims of these cherts showed little difference in peak characteristics, suggesting that the presence of a mineral component may be more important than its absolute abundance. The cause of the peak at around 700 cm-1 in the Knife River Flints is as yet unknown.

Conclusions

This study demonstrates that FT-IR can be used to distinguish between selected sets of cherts, from known geological sources, given the limited number of samples examined, and is a cost effective alternative to XRF, INNA and petrographic analysis. The presence of major trace mineral components can be identified using peak matching and elimination. In addition, examination of spectra in Figures 1 to 5 indicates that with minor exceptions (Amabel 27 and L. Bobcaygeon 113) samples from individual formations have similar yet distinct spectra. More important is that the shape of the curves (as opposed to the position of major peaks) are distinct and hence provide a rapid method to "fingerprint" each formation. We need to examine a larger number of geological sample to determine if the spectral signature differs for specific horizons within each formation, or if along-strike changes are significant. As FT-IR is inexpensive, and spectra can be obtained using only 0.004 g of sample (a minor scar which is easily hidden beneath a label), it is readily applicable to the analysis of large collections of cryptocrystalline cultural artifacts (chert, flint), both to verify "expert" visual identification of sources, and to expand models of cultural interaction.

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Darrel G. F. Long, Brenda Silveira (Dept. of Earth Sciences) and Pat Julig (Dept. of Anthropology) Laurentian University, Sudbury, Ontario P3E 2C6