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*J.B. Percival, R.D. Knight, and P. Hunt*

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# Mineralogical investigations of Canadian till and lake- and stream-sediment reference materials: part 2. A comparison of four methods to determine semiquantitative mineralogy<sup>1</sup>

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**Abstract:** Four methods to determine modal mineralogy were compared for three reference materials, STSD-1, LKSD-4, and TILL-1. These methods include ModAn, a normative calculation based on bulk chemical and mineralogical composition, X-ray diffraction analysis, and two scanning electron microscope techniques: feature image analysis and X-ray mapping. Results from each of the methods are reasonable and comparable; however, the choice of method must take into consideration their limitations such as need of bulk composition and mineralogy data to run ModAn; a detection limit of 2–3% of a mineral for XRD; automated X-ray beam positioning in feature image analysis; and extended processing time for X-ray mapping.

**Résumé :** Quatre méthodes de détermination de la minéralogie modale ont été appliquées, à des fins comparatives, à trois matériaux de référence : STSD-1, LKSD-4 et TILL-1. Il s'agit des méthodes suivantes : la méthode ModAn comportant un calcul normatif basé sur la composition chimique globale et la composition minéralogique, l'analyse par diffraction X et deux méthodes de microscopie électronique à balayage, soit l'analyse par spectre d'éléments ponctuels et la cartographie de rayons X. Les résultats obtenus à l'aide de ces quatre méthodes sont intéressants et comparables. Cependant, le choix d'une méthode devra tenir compte des limites de chacune : la nécessité de connaître la composition globale et de posséder des données minéralogiques en ce qui a trait à la méthode ModAn; un seuil de détection de 2 à 3 % pour un minéral donné dans le cas de l'analyse par diffraction X; le positionnement automatisé du faisceau de rayons X en ce qui concerne l'analyse par spectre; et la lenteur du traitement pour ce qui est de la cartographie de rayons X.

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<sup>1</sup> Contribution to the Metals in the Environment Program

## INTRODUCTION

In any project where mineralogical analyses is desirable, it is important to be able to identify, either qualitatively or quantitatively, the major and trace mineral components in a soil, sediment, till, or rock sample. X-ray diffraction analyses as a routine method provides information of this nature but detection of minerals present in amounts less than 2–3 weight per cent can be difficult. Fine-grained materials (i.e.  $<5\ \mu\text{m}$ ) cannot be studied easily under a binocular or petrographic microscope, therefore, the scanning electron microscope (SEM) is the tool of choice. Several questions remain: 1) how can we maximize the amount of information derived from SEM analyses with a minimum amount of user time; 2) are the methods comparable; and 3) how accurate are the results? This paper compares four different methods to determine quantitative mineralogy using reference materials. The methods examined include a mathematical calculation, ModAn, based on bulk chemical and mineralogical compositions (Paktunc, 1998, in press); whole-rock X-ray diffraction analyses; automated SEM feature image analysis; and automated SEM X-ray mapping. This forms part of a Metals in the Environment (MITE) project aimed at developing a standard protocol of mineralogical analyses for MITE-related samples (Percival et al., 2001).

## SAMPLE PREPARATION

Three geochemical reference materials (obtained from Canada Centre for Mineral and Energy Technology (CANMET)) were selected for detailed analysis: LKSD-1, STSD-4, and TILL-1 (Table 1). Sample LKSD-1 is a composite of sediment collected from the central bottom area of Joe Lake (NTS 31 F) and Brady Lake (NTS 31 M). The stream-sediment sample, STSD-4, is derived from combining composite sample 5 (NTS 31 F) and composite sample 4 (NTS 93 A, 93 B) of Lynch (1990, 1996). TILL-1 is a soil sample collected from B and C horizons at Joe Lake near Lanark, Ontario (NTS 31 F). Details concerning their preparation as geochemical reference materials are given by Lynch (1990, 1996).

For XRD analysis, the bulk powdered sample was packed into an aluminum holder. For SEM analyses, polished thin sections were prepared at Vancouver Petrographics. These sections contain only sparse amounts of material evenly distributed within epoxy.

## METHODS

### *ModAn calculation*

ModAn is a computer-based program developed by Paktunc (1998, in press) which estimates mineral quantities from bulk chemical and mineralogical compositions (available from <http://www.iamg.org>). In this mathematical code, mineral modes are estimated through Gaussian elimination and multiple linear regression techniques to solve simultaneous mass-balance equations (Paktunc, in press). The bulk compositional data is entered in weight per cent oxides and minerals expected are selected from a list of 95 minerals. The program recalculates the bulk and mineralogical compositions and several iterations may be necessary in order to determine the best fit (i.e. the smallest residual sum of squares). If negative numbers appear in the estimated mineral modes, then the selected mineral may be incompatible with other minerals.

### *X-ray diffraction analysis*

A Philips PW1710 automated powder diffractometer equipped with a graphite monochromator, Co  $K\alpha$  radiation at 40 kV and 30 mA was used for whole-rock analyses. Data was digitally captured and then processed using JADE™ (v. 3.1; Materials Data, Inc.), a PC-based program that enables manipulation of X-ray patterns for optimization (e.g. correction for background, instrument error) in identification of mineral species. Semiquantitative analyses were possible through comparison with a set of reference standards using a predetermined reference intensity ratio (RIR). The RIRs used at the X-ray laboratory have been, in many cases, recalculated using quartz as the internal standard. Error could be as high as  $\pm 20\text{--}25\%$ .

### *Scanning electron microscopy*

Polished thin sections were examined under the Leica Cambridge Stereoscan S360 SEM and the Cambridge S200 scanning electron microscopes. The S360, used for feature image analysis, is equipped with an Oxford/Link eXL-II energy-dispersion X-ray analyzer (EDS), Oxford/Link Pentafet Be window/light element detector, and an Oxford/Link Tetra backscattered electron detector. The SEM was operated at an accelerating voltage of 20 keV, beam current of 2 nA, and the EDS at 30% dead time. The SEM images were digitally captured at 768 x 576 pixels and 256 greyscale and stored for further processing. The S200 is interfaced to an

**Table 1.** Sample collection location for reference materials (Lynch, 1990, 1996).

Sample	Composition	Location	NTS designation
LKSD-1	Sediment	Joe Lake, Ontario Brady Lake, Ontario	31 F 31 M
STSD-4	Composite sample 5 Composite sample 4		31 F 93 A, 93 B
TILL-1	Composite soil, B + C horizons	Joe Lake, Ontario	31 F

Oxford-Link XP2 energy-dispersive X-ray spectrometer (EDS) with a 4PI operating system for obtaining EDS X-ray maps. Operating conditions were 20 keV accelerating voltage, beam current of 1.3 nA, and a working distance of 25 mm. Digital X-ray maps (512 x 512 pixels) were captured using a dwell time of 50 ms per pixel at a magnification of 132x. This magnification was selected so that 50–300 particles are in the field of view. Over a 4–5 hour period, seventeen elements (Si, Al, K, Fe, Mn, Mg, Ca, Na, Ti, P, S, As, Ba, Cr, Cu, Ni, Zn) were mapped using automated EDS data capture.

### *SEM feature image analysis*

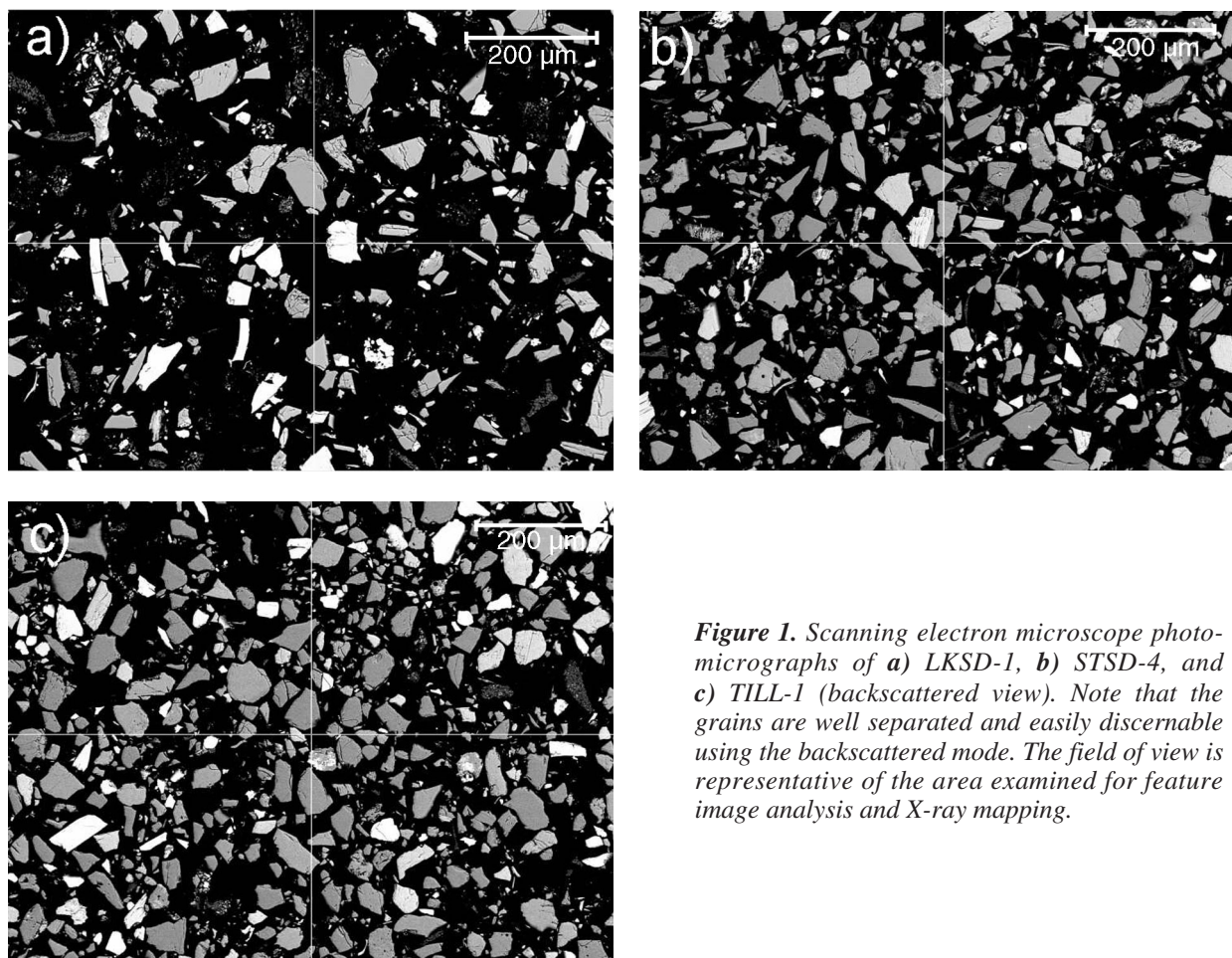
Featurescan™ is a package available from Oxford Instruments for the detection, measurement, and analysis of features in an image. This software package is well suited for particulate mineral analysis. Images were captured live on the SEM in backscatter mode. The primary basis of detection is the threshold range of signal intensity and, in this study, the backscattered electron signal was used to detect features of grey levels higher than the epoxy (Fig. 1). Particle size was also used as a limiting factor. Any feature less than 100 pixels in size was excluded from this study. Once the grain was identified, X-ray counts for the 17 elements listed above were simultaneously collected from the geometric centre of the grains.

Following detection of the required phases, a series of morphological and analytical measurements per feature were performed. The analysis point is defined as the centre of the longest chord to ensure that the measurement is made somewhere on the feature. Once the analysis point is determined, an X-ray count for 5 seconds was initiated. This data file was brought into a spread-sheet application and the results were then tabulated and plotted.

The advantage of using feature image analysis in this mode is that the process can be run fully automated. Each feature can be detected very quickly, typically about 30 seconds per field of view and then the collection of X-ray data takes about 5 seconds per grain. A disadvantage is that each feature is assumed to be homogenous and that the centre of the feature is typical of the whole grain composition.

### *EDS X-ray mapping*

X-ray mapping using EDS is comprised of four steps: 1) acquisition; 2) processing and enhancement; 3) image analyses; and 4) mineral analyses (Petruk, 1989; Tovey and Krinsley, 1991; Krinsley et al., 1998). Post-image capture analysis was carried out using Adobe Photoshop™ (v5.5) to edit electronic images and Fovea Pro™ (v1.0; Reindeer Games Inc. Asheville, North Carolina) to add analytical



*Figure 1. Scanning electron microscope photomicrographs of a) LKSD-1, b) STSD-4, and c) TILL-1 (backscattered view). Note that the grains are well separated and easily discernible using the backscattered mode. The field of view is representative of the area examined for feature image analysis and X-ray mapping.*

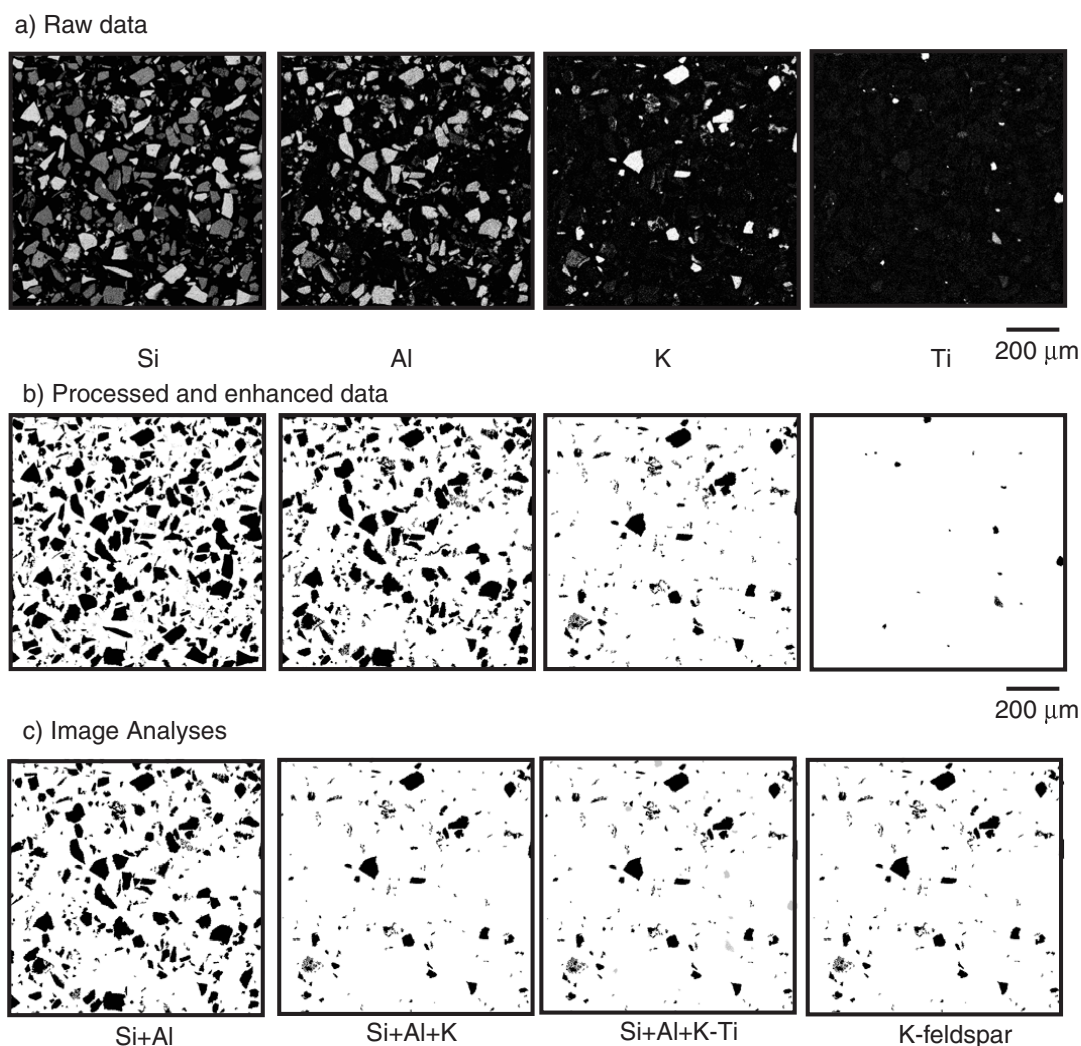
features to the Adobe™ platform. Both programs are compatible with PCs and Macintosh computers and are widely available and relatively inexpensive.

### Acquisition

Digital images of 512 x 512 pixels were generated using automated EDS data capture. Each element map is saved as a TIFF image with greyscale intensity of 0–255, representing a 200 Kb to 800 Kb file size. Figure 2a displays X-ray maps of Si, Al, K, and Ti data. Brighter areas correspond to higher concentrations of the element.

### Processing and enhancement

Image processing includes conversion of greyscale images to false RGB colour setting in order to take full advantage of the analytical features offered in Fovea Pro™ 1.0. The relative abundance of an element is qualitatively established using the image brightness scale and setting threshold levels followed by saturation of the features into binary images, and setting cutoff values to about 5 pixels in order to remove background noise. Image enhancement addresses several concerns that are inherent in EDS maps. They include eliminating aberration related to surface imperfection on the thin section, the manipulation of grain-edge effects by standard erosion, and



**Figure 2.** Scanning electron microscope photomicrographs of **a)** raw EDS maps for Si, Al, K, and Ti; **b)** maps of the same elements after setting the threshold, converting into binary images, and applying a cutoff value to eliminate background noise; **c)** maps showing how K-feldspar is derived. The first image in **c)** is the result of adding overlapping areas from the Si and Al maps of **b)**. The Si+Al +K map of **c)** is derived by adding the overlapping areas from the Si+Al map of **c)** to the K map of **b)**. The third image of **c)**, Si+Al+K-Ti, illustrates the areas of Ti to be subtracted in grey. Subtracting the Ti file helps reduce the possibility of the final map containing grains of biotite. The field of view is representative of the area examined for feature image analysis and X-ray mapping.

**Table 2.** List of minerals identified by combining elemental analysis as in feature image analysis and EDS X-ray mapping methods.

Mineral	Feature image analysis	X-ray mapping	
		Addition elements	Subtraction elements
Quartz	Si	Si	Al, K, Mg, Na, Ca, Fe, Ti
Plagioclase	Si, Al, Na, Ca	Si, Al, Na (albite) Si, Al, Ca (anorthite)	K, Fe, Ti K, Fe, Ti
K-feldspar	Si, Al, K	Si, Al, K	Ti
Orthopyroxene	Si, Mg, Fe	Mg, Fe	Ca (Al)
Clinopyroxene/ amphibole	Si, Mg, Ca, Fe Si, Ca, Mg, Fe, Al Si, Ca, Mg (tremolite)	Ca, Mg, (Fe) Al, Ca, Na, Mg, Fe	(Al)
Epidote	Si, Al, Ca, Fe	Al, Ca, Fe	K, Na
Garnet	Al, Si, Mg		
Chlorite	Si, Al, Mg, Fe	Mg, Al, Fe	Ca
Mica	Al, Si, K (muscovite) Si, Al, K, Mg, Fe (biotite)	Si, Al, K, Mg (Fe)	
Titanite	Ti, Ca, Si	Ti, Ca	Fe
Ilmenite	Ti, Fe	Ti, Fe	Si, Al, Mg
Rutile	Ti	Ti	Si, Al, Mg, Ca, Fe
Fe-oxide	Fe	Fe	Si, Al, Ca, Mg, Ti
Sulphide	Fe, S	S	Si, Al, Ca, Mg, K, Mn, Ti
Carbonate	Ca (calcite) Ca, Mg (dolomite)	Ca	Si, Al, K, Mn, Ti
Apatite	P, Ca	P, Ca	Si, Mg, Na, Mn, Fe, Ti

dilation procedures. During processing and enhancement, caution must be taken to minimize loss of information, especially related to filling of holes that may have resulted from decomposition of the main mineral to secondary minerals or inclusions of different composition. Examples of processed and enhanced X-ray maps are displayed in Figure 2b. Corresponding raw images are shown in Figure 2a.

### Image analyses

Image analyses of EDS element maps uses Boolean algebra and mathematical manipulation of two or more images to obtain a third image that is representative of a specific mineral. Common Boolean operations consist of 'And', 'Or', and 'Exclusive Or'. Mathematical operations consist of 'Add' and 'Subtract'. Fovea Pro™ also includes an extensive group of measurement capabilities such as area, perimeter, morphological features, and location and orientation.

For a single-element mineral such as quartz, the processed Al, K, Mg, Na, Ca, Fe, and Ti maps are subtracted from the processed Si map to identify those grains that are characterized by high concentrations of Si only. Similarly, rutile is based on grains containing high Ti, but lacking Si, Mg, Al, Ca, and Fe. Multi-element minerals are identified through both addition and subtraction of element maps. For example, to map K-feldspar in sample STSD-4, the first step was to produce an image of grains where Si and Al occur together (Fig. 2c). The K map is then added to this image resulting in a map of Si+Al+K. Often, to further define a mineral, one or more of the element maps must be subtracted from the Si+Al+K map to produce a final map of K-feldspar. Areas where Ti occur in the Si+Al+K map are identified by grey fill in the Si+Al+K-Ti map. None of the grains containing Ti overlap with any of the Si+Al+K grains (Fig. 2c). After

subtracting Ti, the resulting image is displayed as a map of K-feldspar (Fig. 2c). In the case of K-feldspar, the map must be compared to a muscovite map to ensure no mineralogical overlap. A similar procedure is carried out to identify the minerals listed in Table 2. Elements listed in parentheses may occur in such low concentrations that adding or subtracting the element map results in a loss of mineralogical information. These elements must be examined from the original data file and possibly adjusted using a different threshold value or not be included at all to ensure a reasonable mineralogical identification.

### Quantitative mineralogical analyses

Quantitative mineralogical analyses can be achieved by EDS mapping through calculation of the area occupied by individual minerals and normalizing the value to the total area occupied by all minerals. The calculated normalized mineralogy corresponds to the percentage of area occupied by a specific mineral. This value can be converted to weight per cent by assuming that area per cent is equal to volume per cent and multiplying the volume per cent by the specific gravity of the mineral and normalizing the results. Results of area per cent to weight per cent conversion will change for those minerals of high specific gravity that occur in amounts greater than about 5% of the normalized value. This conversion was not carried out during this study as grains of high specific gravity occur in small amounts.

## RESULTS AND DISCUSSION

A classical method to compare presence and percentage of minerals in igneous rocks was to use a normative classification such as CIPW (Cross, Iddings, Pirsson, and Washington)

**Table 3.** Summary of major elements (expressed as weight per cent oxide) for three reference materials. Analyses by XRF as reported in Lynch (1990, 1996); FeO by titration; H<sub>2</sub>O<sup>+</sup>, CO<sub>2T</sub>, and S<sub>T</sub> by combustion and infrared; H<sub>2</sub>O<sup>-</sup> by gravimetric method; C<sub>T</sub>, C<sub>org</sub>, C<sub>inorg</sub> by LECO method (model CR-412).

Element	LKSD-1	STSD-4	TILL-1
SiO <sub>2</sub> (wt %)	40.1	58.9	60.9
TiO <sub>2</sub>	0.5	0.8	0.98
Al <sub>2</sub> O <sub>3</sub>	7.8	12.1	13.7
Fe <sub>2</sub> O <sub>3T</sub>	4.1	5.7	6.82
MnO	0.1	0.2	0.18
MgO	1.7	2.1	2.15
CaO	10.8	4.0	2.72
Na <sub>2</sub> O	2.0	2.7	2.71
K <sub>2</sub> O	1.1	1.6	2.22
H <sub>2</sub> O <sup>+</sup>	-	5.5	4.4
H <sub>2</sub> O <sup>-</sup>	2.5	1.6	1.3
P <sub>2</sub> O <sub>5</sub>	0.2	0.2	0.22
LOI (1000 C)	29.9	11.6	7.3
Sum	99.9	99.9	99.9
FeO*			2.6
CO <sub>2T</sub>	48.2	15.6	7.3
C <sub>T</sub>	12.6	4.2	2.0
C <sub>org</sub>	10.3	4.0	2.0
C <sub>inorg</sub>	2.3	0.25	0
S <sub>T</sub>	1.67	0.10	0.02

\* not able to determine FeO due to high organic content  
- not analyzed

**Table 4.** Quantitative mineralogical results of LKSD-1 based on ModAn XRD, and both SEM methods, feature image analysis and X-ray mapping. For feature image analysis the percentage is based on number of grains given in parenthesis. Note that for X-ray mapping, clinopyroxene includes amphibole.

Mineral	ModAn	XRD	Feature image analysis	X-ray mapping
	wt %	wt %	modal %	area %
Quartz	22	26	33 (31)	27
Plagioclase	27	27	34 (32)	35
K-feldspar	10	10	7 (6)	14
Orthopyroxene			2 (2)	2
Clinopyroxene			10 (9)	3
Amphibole	7	4	2 (2)	
Tremolite				
Garnet				
Muscovite				
Biotite				1
Chlorite	7	2		
Epidote			3 (3)	
Titanite				
Ilmenite			2 (2)	tr
Rutile				tr
Fe-oxide				4
Pyrite	3	12	1 (1)	2
Calcite	21	18	3 (3)	
Dolomite	3		2 (2)	4
Apatite				0
Total	100	100	99 (93)	101

tr = trace

(Hyndman, 1972). Cohen and Ward (1991) have developed an equivalent program called Sednorm for sedimentary rocks. Both these methods are based on bulk chemical analyses. More recently, a program, NORMA, has been developed to calculate normative mineralogy of glacial tills and rocks in Finland (Räisänen et al., 1995; Tarvainen et al., 1996). In NORMA, mineralogical composition is calculated from the proportions of soluble and insoluble constituents determined in hot aqua regia and total concentrations as determined by X-ray fluorescence methods. This enables determination of the primary hydrous minerals such as micas and secondary hydroxides (Räisänen et al., 1995).

In this study, ModAn was used to estimate mineral quantities based on both mineralogical (as determined by XRD) and bulk chemical composition. Major-element chemistry for each of the reference materials is shown in Table 3. These data represent analyses from at least 35 different laboratories (Lynch, 1990, 1996). Measurement of ferrous iron as FeO, CO<sub>2</sub>, H<sub>2</sub>O<sup>+</sup>, and H<sub>2</sub>O<sup>-</sup> were carried out in the analytical laboratories in Mineral Resources Division; total C, organic C and inorganic C in the Sedimentology laboratory of Terrain Sciences Division. The data indicate that LKSD-1 is organic-rich, with a organic C content of 10.3 weight per cent and a total CO<sub>2</sub> content about 48 weight per cent. Reference material LKSD-1 also contains a higher concentration of total S than the others. Silica content is high for all three samples

reflecting contribution from quartz and other silicate minerals. For samples with high organic content, FeO analyses were not possible, hence it was only determined on TILL-1.

Results of the calculation are given in Tables 4, 5, and 6 for LKSD-1, STSD-4, and TILL-1, respectively. In general, the three materials contain comparable amounts of quartz, plagioclase, and K-feldspar. Sample LKSD-1 contains abundant calcite and minor to trace pyrite, whereas only a minor to trace amount of calcite and pyrite is estimated for STSD-4. In STSD-4, there is more amphibole than in the other two, and in TILL-1, more chlorite.

Results of whole-rock XRD analyses are shown in Tables 4–6. All three samples are dominated by quartz and plagioclase feldspar. K-feldspar and amphibole occur in minor amounts and chlorite, mica (illite), and smectite in trace amounts. Sample LKSD-1 also contains minor calcite and pyrite, consistent with its geochemical signature. Pyroxene was detectable in trace amounts in TILL-1, but not in the other two samples. Overlapping X-ray peaks can limit identification of trace quantities of some minerals.

Backscatter images of each of the three reference materials are shown in Figure 1. Differences in mean atomic numbers of the minerals are reflected in the relative brightness of the grains on the backscattered electron images. The samples consist of subrounded to subangular and silt- to sand-sized (up to 100 µm) particles that are evenly distributed and well



**Table 5.** Quantitative mineralogical results of STSD-4 based on ModAn, XRD, and both SEM methods, feature image analysis and X-ray mapping. For feature image analysis, the percentage is based on number of grains given in parenthesis. Note that for X-ray mapping, clinopyroxene includes amphibole.

Mineral	ModAn	XRD	Feature image analysis	X-ray mapping
	wt %	wt %	modal %	area %
Quartz	26	45	32 (55)	35
Plagioclase	32	30	36 (62)	43
K-feldspar	13	13	12 (20)	16
Orthopyroxene			4 (6)	3
Clinopyroxene			<1 (1)	5
Amphibole	15	5	6 (11)	
Tremolite			1 (2)	
Garnet			<1 (1)	
Muscovite		tr	1 (2)	
Biotite			3 (5)	
Chlorite	10	4		
Epidote				1
Titanite			<1 (1)	1
Ilmenite			2 (3)	1
Rutile	1			tr
Fe-oxide		3	1 (2)	1
Pyrite	tr			tr
Calcite	3			tr
Dolomite				
Apatite				1
Total	100	100	100 (171)	102

tr = trace

separated in the thin sections. Both STSD-4 and TILL-1 contain a small number of rock fragments that would not be readily identified using feature image analysis (Fig. 1b, 1c) because the X-ray counts are collected in the centre of the grains.

Figure 3 illustrates how feature image analysis processes the SEM backscatter images for sample STSD-4. The program discriminates between features by measuring the levels of greyscale. In this case, the threshold range is set to separate particles from the background. The box outline defines discrete grains or features detected. If two grains are touching, they are identified as one feature (arrowed in Fig. 3). The number of discrete grains detected in each sample and their calculated percentage is summarized in Tables 4–6. For each sample, the total number of grains in the field of view varied with STSD-4 and TILL-1 having more than 150 grains and LKSD-1 less than 100 grains.

Based on feature image analysis, all three samples are dominated by quartz and plagioclase feldspar, which occur in subequal amounts. All other minerals occur in minor to trace amounts. Only LKSD-1 contains carbonates and sulphides; STSD-4 has orthopyroxene, mica, and garnet; and TILL-1 contains a trace amount of apatite. No chlorite or rutile were detected in any of the samples. These three reference samples have similar characteristics if based solely on the dominant minerals.

Quantitative mineralogy results derived from SEM X-ray mapping are presented in Tables 4–6. All three samples are dominated by feldspars with plagioclase being predominant. TILL-1 contains equal amounts of quartz and feldspars whereas LKSD-1 and STSD-4 contain lesser amounts of quartz compared to feldspars. All three samples contain up to 5% clinopyroxene and/or amphibole; LKSD-1 and STSD-4 also contain up to 3% orthopyroxene. Small amounts of mica (1%), Fe-oxide (4%), chlorite (9%), sulphide (2%), and carbonates (4%) occur in sample LKSD-1. These minerals occur in trace amounts or not at all in samples STSD-4 and TILL-1. Only trace amounts of epidote were detected in TILL-1 (3%) and STSD-4 (1%) and none in LKSD-1.

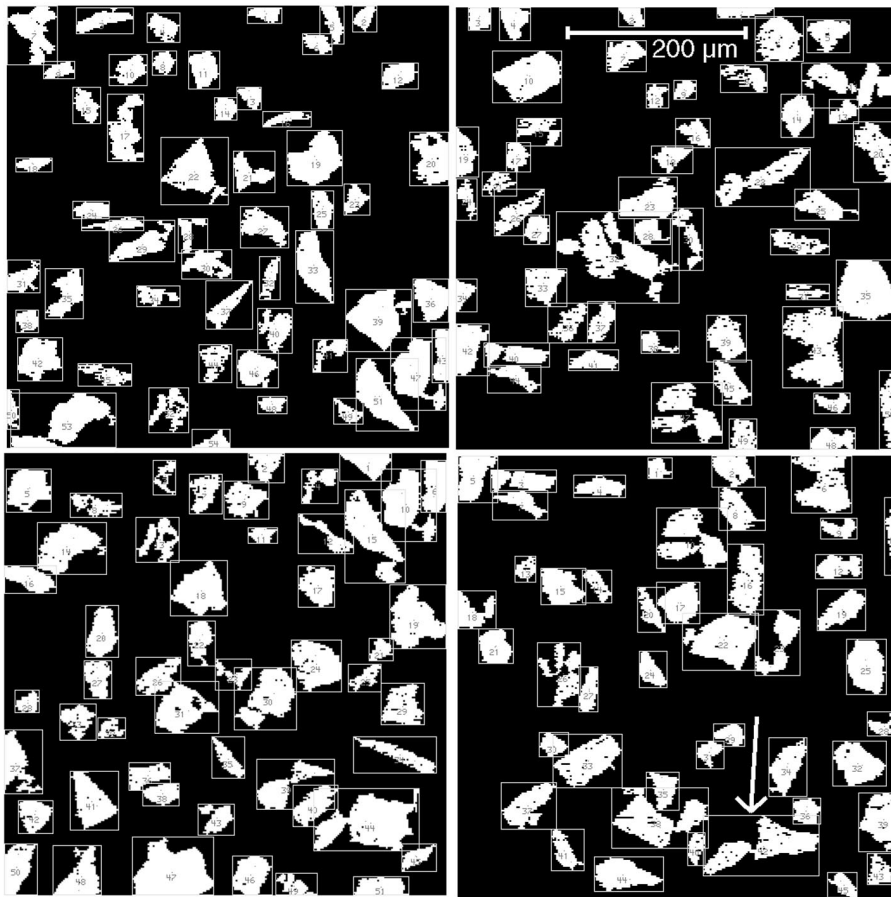
All four methods, ModAn calculation, XRD, feature image analysis, and X-ray mapping, portray reasonable estimates of the mineral content of the three reference materials. If we assume that XRD is the accepted method, then we can begin to compare results and test the validity of the other methods for determining mineralogy.

Results from the mathematical calculation ModAn are in general agreement with the XRD results for plagioclase, K-feldspar, and for quartz in two of the three samples. Amphibole content in STSD-4 and chlorite in TILL-1 tend to be higher than the XRD estimates. In LKSD-1, there appears to be less pyrite and slightly more calcite (Table 4). Given that the amount

**Table 6.** Quantitative mineralogical results of TILL-1 based on ModAn, XRD, and both SEM methods, feature image analysis and X-ray mapping. For feature image analysis the percentage is based on number of grains given in parenthesis. Note that for X-ray mapping, clinopyroxene includes amphibole.

Mineral	ModAn	XRD	Feature image analysis	X-ray mapping
	wt %	wt %	modal %	area %
Quartz	28	46	33 (66)	44
Plagioclase	30	29	32 (64)	33
K-feldspar	13	15	15 (30)	10
Orthopyroxene		?tr		
Clinopyroxene			2 (4)	5
Amphibole	9	6	12 (24)	
Tremolite				
Garnet				
Muscovite		tr		
Biotite				
Chlorite	20	4	2 (4)	
Epidote			2 (4)	3
Titanite			3 (5)	tr
Ilmenite			3 (5)	2
Rutile				tr
Fe-oxide		tr	<1 (1)	1
Pyrite				
Calcite				
Dolomite				
Apatite			<1 (1)	1
Total	100	100	100 (199)	99

tr = trace



**Figure 3.**

*Scanning electron microscope photomicrograph of STSD-4 showing how grains are processed using feature image analysis. The box outline defines discrete grains or features distinguished from the background. Each grain is numbered and the EDS data captured from the central part. Note in the lower right hand corner how two touching grains are captured as one larger grain (arrow).*

of total S in this material is not very high (1.67 wt %), the modal estimate for pyrite by ModAn is probably more accurate. This suggests that the reference intensity ratio values used in Jade™ may be in error, or standard minerals differ significantly from minerals in the samples under study. A limitation of using ModAn is having bulk chemical composition available as well as independent knowledge of sample mineralogy.

Both the feature image analysis and X-ray mapping techniques have a built-in verification system. Elements are pre-assigned to particular mineral phases, however, as the user examines the grains and their compositions, problems can be dealt with easily. Also, some minerals such as apatite and rutile have unique elemental signatures and therefore these trace minerals are readily detected.

The feature image analysis data are comparable to XRD results. Quartz content is similar or slightly lower for STSD-4 and TILL-1. Plagioclase and K-feldspar quantities compare well in all three. The amount of amphibole tends to be high for all three materials, and the sulphide and calcite content low for LKSD-1. Other minerals detected, including ilmenite, titanite, epidote, pyroxene, garnet, and apatite occur in trace amounts and are below the detection limit of XRD analysis.

The results from X-ray mapping are very similar to the feature image analysis results. In comparison to the XRD data, quartz and K-feldspar are very similar and plagioclase is

only slightly higher. Amphibole levels are also comparable. Again, the detection limit of XRD does not allow detection of titanite, ilmenite, rutile, apatite, epidote, and pyroxene which occur in trace quantities.

### ***Efficacy of methods***

Semiquantitative XRD analysis provided a reasonable estimate of the major mineral phases in the samples studied. If trace mineral information is required, then SEM methods must be utilized. The SEM methods described here are comparable from a mineralogical perspective; however, they vary greatly in the time required to carry out the analysis, the location where the analysis takes place, and the degree of user input to control the outcome. As an acceptable method, XRD can take between 30 and 60 minutes including sample preparation, analysis, and interpretation of the diffractograms. Time is increased if there are unknown minerals; however, the use of the software in semiquantitative analysis and fitting of phases can alleviate this potential problem. If chemical composition and mineralogy are known, ModAn is a fast method to obtain modal estimates of the minerals. Extra time is necessary to carry out the iterations in determining the best fit of the raw data.

In feature image analysis, all data capture is fully automated but data processing can be lengthy, especially when large amounts of data are collected. The current system

software is not Windows® compatible and considerable time was spent transferring data in ASCII format from the Oxford eXLII to a Windows®-based spreadsheet program. The data was plotted and the corresponding minerals were calculated and tabulated. Depending on the amount of data, up to one day per sample was spent calculating the final modal results using current instrumentation and software. Newer instruments and software would decrease the time required to carry out these same functions.

The X-ray mapping method was the most time-consuming technique presented here, however, it also provided mineralogical information not readily determined by the other methods including grain-edge effects, mineral phase relationships, and mineral alteration. Other than data acquisition, X-ray mapping was carried out remotely from the collection site thus releasing the instrument for other users. This also allowed for greater control of the mineralogical determination by the user through manipulation of threshold values, erosion and dilation limits, and the determination of cutoff values. Depending upon the degree of information required, complete analysis after data capture can vary from five hours to one day per sample.

## CONCLUSIONS

The methods described above illustrate several ways in which to determine, (semi-)quantitative mineralogy of unconsolidated materials. Each method provides valuable information that is reasonable and comparable; however, each method has limitations that must be considered such as: need of bulk composition and mineralogy data to run ModAn; detection limit of 2–3 weight per cent of a mineral for XRD and accurate determination of reference intensity ratios; automated X-ray beam positioning in feature image analysis; and extended processing time for X-ray mapping.

More stringent tests would be required to determine the accuracy and precision of each of these methods.

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