Geological Survey of Canada

CURRENT RESEARCH 2001-E9

Mineralogical investigations of Canadian till and lake- and stream-sediment reference materials: part 1. Standardized X-ray diffraction and scanning electron microscope methods

J.B. Percival, P. Hunt, and M. Wygergangs

Natural Resources Canada | Ressources naturelles Canada

Canada

©Her Majesty the Queen in Right of Canada, 2001
Catalogue No. M44-2001/E9E-IN
ISBN 0-662-30772-0

Available in Canada from the
Geological Survey of Canada Bookstore website at:
http://www.nrcan.gc.ca/gsc/bookstore (Toll-free: 1-888-252-4301)

A copy of this publication is also available for reference by depository libraries across Canada through access to the Depository Services Program's website at http://dsp-psd.pwgsc.gc.ca

Price subject to change without notice

All requests for permission to reproduce this work, in whole or in part, for purposes of commercial use, resale, or redistribution shall be addressed to: Earth Sciences Sector Information Division, Room 200, 601 Booth Street, Ottawa, Ontario K1A 0E8.

Mineralogical investigations of Canadian till and lake- and stream-sediment reference materials: part 1. Standardized X-ray diffraction and scanning electron microscope methods[1]

J.B. Percival*, *P. Hunt*, and *M. Wygergangs
Mineral Resources Division, Ottawa

[1] Contribution to the Metals in the Environment Program

Percival, J.B., Hunt, P., and Wygergangs, M., 2001: Mineralogical investigations of Canadian till and lake- and stream-sediment reference materials: part 1. Standardized XRD and SEM methods; Geological Survey of Canada, Current Research 2001-E9, 11 p.

Abstract

Reference materials are used in geochemical studies as quality control in chemical analyses, and in mineralogical analyses for identification of unknowns and modal proportions. In this Metals in the Environment (MITE) project, the mineralogy of twelve geochemical reference materials were evaluated through X-ray diffraction and scanning electron microscope analyses. The reference materials are derived from soil, till, and lake and stream sediments, and mineralogical analyses are based on the bulk sample and the clay-sized fraction. The effect of a pretreatment to remove X-ray amorphous organic matter from the clay-sized fraction prior to semiquantitative X-ray diffraction analyses was examined, and ways to assess the amount of this material in a sample were summarized through a literature review. In addition, the resolution of scanning electron microscope images of clay-sized materials using carbon and gold coatings were compared. A standardized procedure for mineralogical characterization of soil, till, and sediment materials is presented.

Résumé

Des matériaux de référence sont utilisés lors des études géochimiques afin de s'assurer de la qualité des analyses chimiques. On les utilise aussi dans le cadre des analyses minéralogiques afin d'identifier des matériaux inconnus et pour l'évaluation des proportions modales. Dans le cadre du projet des Métaux dans l'environnement (MEDE), on a évalué la composition minéralogique de douze matériaux de référence par diffraction X et microscopie électronique à balayage. Les matériaux de référence proviennent d'échantillons de sol, de till, de sédiments lacustres et de sédiments de ruisseau. Les analyses minéralogiques ont été effectuées sur des échantillons complets et sur la fraction granulométrique des argiles. On a examiné quelle était l'incidence de l'application d'un traitement préliminaire visant à retirer de la fraction granulométrique des argiles la matière organique amorphe sous rayons X avant d'exécuter les analyses semi-quantitatives par diffraction X . Les méthodes destinées à évaluer la quantité de ce matériau dans un échantillon sont brièvement exposées par le biais d'une analyse documentaire. On a également comparé les enduits de carbone aux enduits d'or dans la résolution des images de matériaux de la dimension des argiles obtenues par microscopie électronique à balayage. Enfin, une procédure normalisée est présentée pour effectuer la caractérisation minéralogique des échantillons de sol, de till et de sédiments.

INTRODUCTION

On-going studies within the Metals in the Environment (MITE) program of the Geological Survey of Canada are directed at distinguishing anthropogenic from natural sources of metals through detailed lake sediment and soil studies near point sources of metal emissions (e.g. Henderson et al., 1999) and in areas remote from industrial activity. The texture, bulk properties (e.g. density, moisture content, particle size distribution), and chemical characteristics of surficial materials are ultimately related to their mineralogy and the cumulative effects of depositional and postdepositional processes (e.g. compaction, diagenesis, and pedogenesis). Detailed mineralogical analyses can identify the mineral and nonmineral phases that comprise the sediment or soil and extent of weathering. Some of these minerals may be

authigenic and related to early diagenetic (or pedogenetic) processes, others may be highly altered to various clay minerals such as smectite, and others form distinctive morphologies due to their origin as atmospherically transported particulates (e.g. fly ash as spheroidal particles). Thus, mineralogy forms an important aspect of sediment and soil studies.

Geochemical analyses including sequential extraction of materials also forms a major component of some of the MITE projects (e.g. McMartin et al., 2000; Plouffe et al., in press). Generally, the lake and till reference materials have been used for geochemical quality controls at commercial analytical laboratories (I. Girard, pers. comm., 2001). These same reference materials are being tested by the mineralogy laboratory for comparison with sediment and soil and/or till samples collected in MITE projects. Understanding the mineralogy of these reference materials and unknown samples can assist in the selection of the most appropriate procedures to be used in sequential extraction experiments, and more importantly, the interpretation of the results.

As part of the MITE program, it was proposed to establish a routine method of sample preparation for both X-ray diffraction (XRD) and scanning electron microscope (SEM) analyses of MITE samples. The approach in this project was to use till (TILL-1 to TILL-4), lake sediment (LKSD-1 to LKSD-4), and stream sediment (STSD-1 to STSD-4) reference materials obtained from Canada Centre for Mineral and Energy Technology (CANMET). The objectives were to 1) conduct detailed bulk and clay-size mineralogical analysis using XRD and SEM analyses; 2) examine the effect of pretreatments to remove organic matter prior to qualitative and semiquantitative mineralogical analyses by XRD; 3) investigate methods to identify and quantify X-ray amorphous phases in multiphase samples through a literature search; and 4) compare the resolution of SEM imaging of clay-sized material using carbon and gold coatings. This paper summarizes the findings and presents a standardized procedure for XRD and SEM analyses of fine-grained, unconsolidated reference materials in the X-ray and Microbeam laboratories, respectively, of the Mineral Resources Division.

MATERIALS AND METHODS

Twelve reference materials were obtained from CANMET. These materials have been pulverized and homogenized such that they are suitable for quality control in geochemical analyses. For details concerning their preparation *see* Lynch (1990, 1996). The collection locations for each of the reference materials is summarized in **Table 1**. Note that some of the lake and stream materials may consist of composite samples (1 to 5) that were prepared by mixing unused portions of regional survey samples collected in the designated NTS areas (Lynch, 1990). The lake-sediment materials, 'LKSD' series, were prepared from a composite of lake sediments collected at diverse sites in the Canadian Shield. All samples were collected from the central part of the lake. Similarly, the stream-sediment samples are a mixture as shown in Table 1. The 'TILL' materials include two composite soil samples, TILL-1 and TILL-3, collected from B and C horizons at Joe Lake near Lanark, Ontario and the O'Brien mine near Cobalt, Ontario, respectively. Sample TILL-2 is till material collected near Scisson's Brook, New Brunswick and TILL-4 is a composite of till from Scisson's Brook and a site adjacent to a molybdenite occurrence near Hull, Quebec (Lynch, 1996).

Mineralogical analyses of reference materials are based on packed powder mounts of the bulk material and glass slide mounts of the clay-sized fraction. Water suspensions of the bulk materials were centrifuged in the Sedimentology laboratory to separate the clay-sized fraction (<2 μm), which was then freeze-dried. A split of the clay-sized material was treated with H_2O_2 to remove organic matter following the method of Jackson (1979). For XRD analyses, 40 mg samples were suspended in approximately 1 mL of distilled water, pipetted onto glass slides, and air-dried overnight to produce oriented mounts. X-ray patterns of the bulk packed powder and of the air-dried clay-sized samples were recorded on a Philips PW1710 automated powder diffractometer equipped with a graphite monochromator, Co Kα radiation set at 40 kV and 30 mA. Air-dried clay-sized samples were also X-rayed following saturation with

ethylene glycol and heating for two hours at 550°C. Digital data were captured and then processed using JADE™ (v3.1; Materials Data, Inc.), a PC-based program that enables manipulation of the X-ray pattern for optimization (e.g. correction for background, instrument error) in identification of mineral species. Semiquantitative analyses are based on comparison with a set of mineralogical standards using a predetermined reference intensity ratio (RIR).

Duplicate grain mounts of three samples were prepared by pipetting a dilute (<10–20 ppm) suspension of each onto polished carbon planchettes. One set was carbon-coated and the other gold-coated. All sets were examined with a Leica Cambridge Stereoscan S360 scanning electron microscope (SEM). The SEM is equipped with an Oxford/Link eXL-II energy-dispersion X-ray analyzer, Oxford/Link Pentafet Be window/light element detector, and an Oxford/Link Tetra backscattered electron detector. In order to take high-resolution images, the SEM was operated at an accelerating voltage of 20 kV, a beam current of 100 pA and a working distance of 14 mm or 25 mm. Scanning electron microscope images were digitally captured at 768 x 576 pixels at 256 levels of greyscale and stored for further processing.

RESULTS

Semiquantitative mineralogical analysis of bulk reference materials is reported in **Table 2**. Except for LKSD-1 and LKSD-4, all samples are mineralogically similar. They are dominated by quartz, plagioclase, and K-feldspar. Amphibole and chlorite occur in minor amounts and mica (illite) in minor to trace amounts. Trace amounts of smectite and hematite occur in some samples. Sample LKSD-1 contains minor calcite and pyrite and LKSD-4 is highly amorphous and so semiquantitative data is suspect.

Semiquantitative results for the clay-sized fraction are shown in **Table 3**. In the untreated samples (row marked by U), quartz content is lower (up to 50%) than in the bulk materials whereas chlorite and mica (illite) have generally increased. Six of the reference materials contain some amount of X-ray amorphous material, likely in the form of organic material and/or Fe-oxides. One sample, LKSD-4 is highly X-ray amorphous (Fig. 1); thus, no data were obtained. For the untreated sample LKSD-4, the uncorrected (by Jade™) X-ray pattern is shown in **Figure 1a** (only electronic spikes have been removed). The noisy background and amorphous broad peak or hump do not allow easy identification of X-ray peaks. Jade™ corrections such as polynomial curve filters and background corrections enhance individual X-ray peaks, although their intensity remains low, near background levels (**Fig. 1b**).

Traditionally, mineralogical analyses of soil materials using XRD, especially the clay-sized fraction, require a series of pretreatments to remove carbonate minerals, organic matter, and Fe-oxides (Day, 1965; Jackson, 1979), usually in that order. A variety of pretreatment methods are available (Jackson, 1979; Sheldrick, 1984): sodium acetate (NaOAC buffered at pH 5) for carbonate minerals; hydrogen peroxide (H_2O_2) for organic matter; dithionite-citrate-bicarbonate, hydroxylamine hydrochloride, or acid ammonium oxalate for Fe-oxides. These methods have been adapted for use in sequential extraction experiments to determine partitioning of elements among organic and inorganic components of a soil, sediment, and rock (e.g. Tessier et al., 1979; Chao, 1984; Percival et al., 1990), and have gained acceptance in exploration and environmental programs.

To reduce problems in semiquantitative XRD analysis of till and soil materials, organic material is removed by H_2O_2 pretreatment by the Sedimentology laboratory of the Terrain Sciences Division (TSD) following the method of Jackson (1979). To characterize the effects of the pretreatment, the clay-sized fractions of the reference materials were also subjected to H_2O_2 treatment. Results are given in Table 3 (row marked T). Highly amorphous samples show major changes in mineralogy. For example, in

STSD-2, quartz content increases from 21 weight per cent to 46 weight per cent and the chlorite and mica (illite) contents decrease. Sample LKSD-4 (T) now has a discernable X-ray pattern (Fig. 2). **Figure 2a** illustrates the uncorrected (except for electronic spike removal) X-ray pattern and **Figure 2b** the corrected (using Jade™) pattern. Note that the hump or broad background peak shown in **Figure 1a** has been greatly reduced in size facilitating the measurement of X-ray peak intensities. Materials that were only slightly amorphous also registered a change in their modal amounts. The proportions of clay minerals such as illite and chlorite appear reduced and other silicate minerals have increased. No doubt this is the result of lowering the background to the baseline under the quartz and/or feldspar peaks in the central part of the X-ray pattern.

Although the treatment with H_2O_2 has permitted the X-rays peaks to become unmasked or enhanced, potential problems may arise including destruction of sulphides and carbonate minerals. Note that in sample LKSD-1 (Table 3), the calcite is nearly absent from the sample following treatment and only a trace amount of pyrite remains.

Methods used to determine the amount of amorphous material by XRD analysis were examined through a literature survey. Amorphous or microcrystalline material causes scattering of X-rays. Quantitative estimates of amorphous material can be calculated based on the difference between the mass absorption coefficient for the bulk sample and the sum of the mass absorption coefficients of each crystalline component present (Bader et al., 1970; Rex et al., 1971). Bader et al. (1970) applied smoothing functions and background corrections to their X-ray patterns to improve the peak intensities, but noted that random noise still occurred which made peak identification and absolute quantitative analysis difficult. The background corrections done within Jade™ probably match their approach; however, as shown in **Figures 1b** and **2b**, the broad peak due to organic material in the sample is not affected. More recently, Cyr et al. (1998) compared several methods to quantify amorphous material content of polymers. Cyr

et al. (1998) indicated that, in order to quantify the amorphous content, the mass adsorption coefficient of the amorphous material must be known. In one of their methods, they obtained quantitative results by normalizing the intensity of the broad peak relative to the total intensity of the X-ray pattern; however, Cyr et al. (1998) noted that this method worked best if the amorphous material was of the same composition as the crystalline material. A similar approach such as determining the percentage of area under the broad peak relative to the total area of all peaks may enable estimation of the amount of amorphous material present prior to its removal. Discussions with MDI Inc. (Q. Johnson, pers. comm., 2000) indicate that it is possible to improve the background correction by first stripping the amorphous broad peak using a reference pattern; however, attempts to find a suitable standard failed.

To complete the mineralogical analyses of fine-grained materials and determine the trace mineral components not detectable by XRD (i.e. <2–3 wt %), the SEM is required. As well as the identity of trace minerals through EDS analysis, the SEM can provide information on grain size and shape, and identify contaminants from sample processing (e.g. Ni-Cr from stainless steel). Secondary electron imaging is useful for looking at the textural and surface features of grains (**Fig. 3**, **4**, left-hand side) whereas backscatter imaging shows the difference in mean atomic number (Fig. 3, 4, right-hand side). With fine-grained material, especially in the clay (<2 μm) to fine clay-sized fraction (<0.2 μm), it is difficult to get useful images at high magnification (i.e. 5000x or more). At the Microbeam laboratory (MRD), carbon-coating of samples is routine. For enhancement of image resolution, especially in secondary electron mode, gold-coating is superior. Note that qualitative EDS analysis of minerals is possible with either coating. Examples of images taken from a selection of the samples are shown in Figures 3 and 4.

Figure 3 shows photomicrographs of carbon-coated LKSD-2, STSD-1, and TILL-3 in secondary electron and backscattered mode. Images were taken at 5000x magnification at a working distance of 14 mm for secondary electron images, and 25 mm for backscattered images. Note that the edges in secondary

electron mode tend to be fuzzy and the third dimension is not readily visible. In Figure 4, similar secondary electron and backscattered images of gold-coated grain mounts are shown. Magnification and working distance are the same as in **Figure 3**. Note the details of the grains and the edges are sharp in secondary electron mode relative to the carbon-coated specimens, even for grains less than 1 μm. High resolution is needed to be able to detect subtle grain coatings; physical alteration features produced by impact, crushing, and abrasion; and chemical alteration or weathering features such as etch pits and alteration zones.

RECOMMENDATIONS

As discussed above, unconsolidated materials such as soil, till, and waterlain sediment samples can be problematic for XRD analysis, especially those containing large amounts of X-ray amorphous material. Pretreatment of samples to remove carbonate minerals, organic matter, and Fe-oxides may be useful in some studies to unmask or enhance the X-ray peaks of crystalline material. It is important to decide what information is required and whether or not data on bulk samples or clay-sized mineralogy are essential to fulfill study objectives.

In carrying out a mineralogical study, a representative suite of samples should be selected for analysis. For fine-grained materials, bulk samples should be analyzed as well as the clay-sized fraction, without pretreatments. If there are no problems associated with excess amorphous material, then semiquantitative analysis can be completed. If excessive amorphous material is present such as in LKSD-4, a pretreatment is necessary. This does, however, add to sample preparation time and may affect the sample mineralogy through destruction of sulphide and carbonate minerals. For determination of trace minerals not detectable by XRD, SEM analysis is recommended. To enhance resolution, especially in clay to fine clay specimens, the preferable method is to gold-coat specimens rather than the traditional carbon-coating.

ACKNOWLEDGMENTS

This MITE project benefited from the laboratory assistance of M. Sarfi (Carleton University), discussions with R. Knight (TSD), and encouragement from R. Garrett (MRD). We are especially grateful to J. Stirling and R. Klassen for critical reviews.

REFERENCES

Bader, R.G., Gerard, R.D., Benson, W.E., Bolli, H.M., Hay, W.W., Rothwell, W.T., Jr., Ruef, M.H., Riedel, W.R., and Sayles, F.L.
1970: Appendix III - Shore-based laboratory procedures; *in* Bader, R.G., et al., Initial Reports of the Deep Sea Drilling Project, Volume IV, U.S. Government Printing Office, Washington, D.C., p. 745–753.

Chao, T.T.
1984: Use of partial dissolution techniques in geochemical exploration; Journal of Geochemical Exploration, v. 20, p. 101–135.

Cyr, M., Husson, B., and Carles-Gibergues, A.
1998: Détermination, par diffraction des rayons X, de la teneur en phase amorphe de certain matériaux minéraux; Journal de Physique IV, France, v. 8, p. 5–23.

Day, P.R.
1965: Particle fractionation and particle size analysis; *in* Methods of Soil Analysis. Part I, (ed.) C.A. Black; American Society of Agronomy Inc., Madison, Wisconsin, p. 545–567.

Henderson, P.J., Knight, R., and McMartin, I.
1999: Heavy-metal concentrations in soils surrounding Canadian base-metal smelters: a comparative study; *in* Geological Survey of Canada, Current Research 1999-D, p. 17–26.

Jackson, M.L.
1979: Soil Chemical Analysis- Advanced Course; 2nd edition, 11th printing; published by the author, Madison, Wisconsin, 895 p.

Lynch, J.
1990: Provisional elemental values for eight new geochemical lake sediment and stream sediment reference materials LKSD-1, LKSD-2, LKSD-3, LKSD-4, STSD-1, STSD-2, STSD-3 and STSD-4; Geostandards Newsletter, v. 14, p. 153–167.
1996: Provisional elemental values for four new geochemical soil and till reference materials, TILL-1, TILL-2, TILL-3 and TILL-4; Geostandards Newsletter, v. 20, p. 277–287.

McMartin, I., Hall, G.E.M., Kerswill, J., Sangster, A., Douma, S., and Vaive, J.
2000: Mercury cycling in perennially frozen soils of arctic Canada, Kaminak lake area, Nunuvut; *in* Proceedings of 25th International Conference on Heavy Metals in the Environment; University of Michigan, School of Public Health, Ann Arbor, Michigan, August 2000, 4 p. (CD-ROM).

Percival, J.B., Torrance, J.K., and Bell, K.
1990: On the development of a sequential extraction procedure with application to leachability problems; *in* Acid Mine Drainage, Designing for Closure, (ed.) J.W. Gadsby, J.A. Malick, and S.J. Day; Bitech Publishers Ltd., Vancouver, British Columbia, p. 51–62.

Plouffe, A., Hall, G.E.M., and Pelchat, P.
in press: Leaching of loosely bound elements during wet grain size separation with sodium hexametaphosphate: implications for selective extraction analysis; Geochemistry: Exploration, Environment, Analysis.

Rex, R.W., Eklund, W.A., and Jamieson, I.M.
1971: X-ray mineralogy studies – leg 6; *in* Initial Reports of the Deep Sea Drilling Project, Volume VI; A.G. Fisher et al., U.S. Government Printing Office, Washington, D.C., p. 753–760.

Sheldrick, B.H. (ed.)
1984: Analytical Methods Manual 1984; Land Resource Research Institute, Contribution 8430, Agriculture Canada, Ottawa.

Tessier, A., Campbell, P.G.C., and Bisson, M.
1979: Sequential extraction procedure for speciation of particulate trace metals; Analytical Chemistry, v. 51, p. 844–851.

Geological Survey of Canada Projects 890043MC, 680023ZC

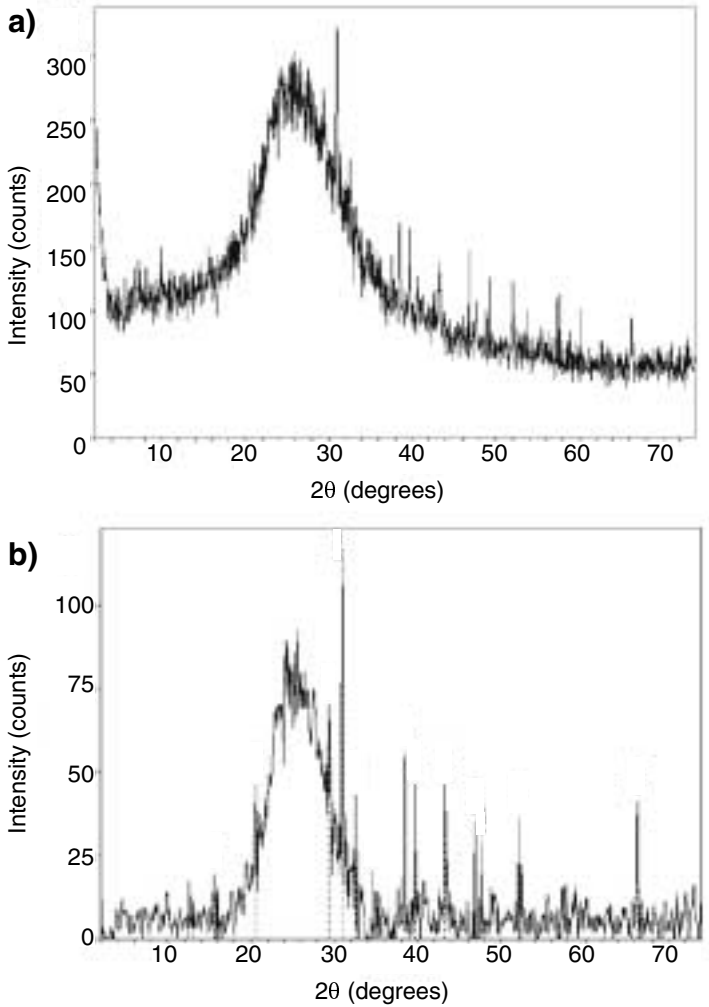

Figure 1. a) Unprocessed XRD pattern of clay-size, untreated LKSD-4 sample showing its highly amorphous nature; **b**) XRD pattern of same material after processing by Jade™. Note the slight reduction in the size of the hump and the enhancement of mineral X-ray peaks along the hump and throughout the diffractogram.

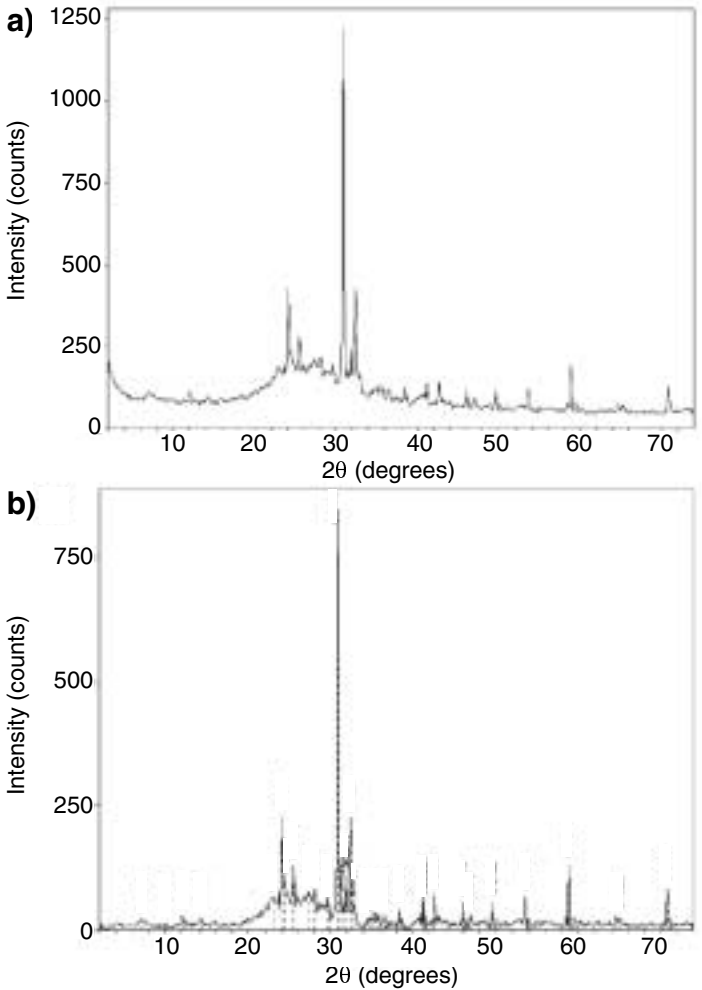

Figure 2. a) Unprocessed XRD pattern of clay-size, treated (with H_2O_2) LKSD-4 sample. The amorphous hump is considerably smaller than in Figure 1a; **b**) XRD pattern of same material after processing by Jade™. Semiquantitative analysis is now possible.

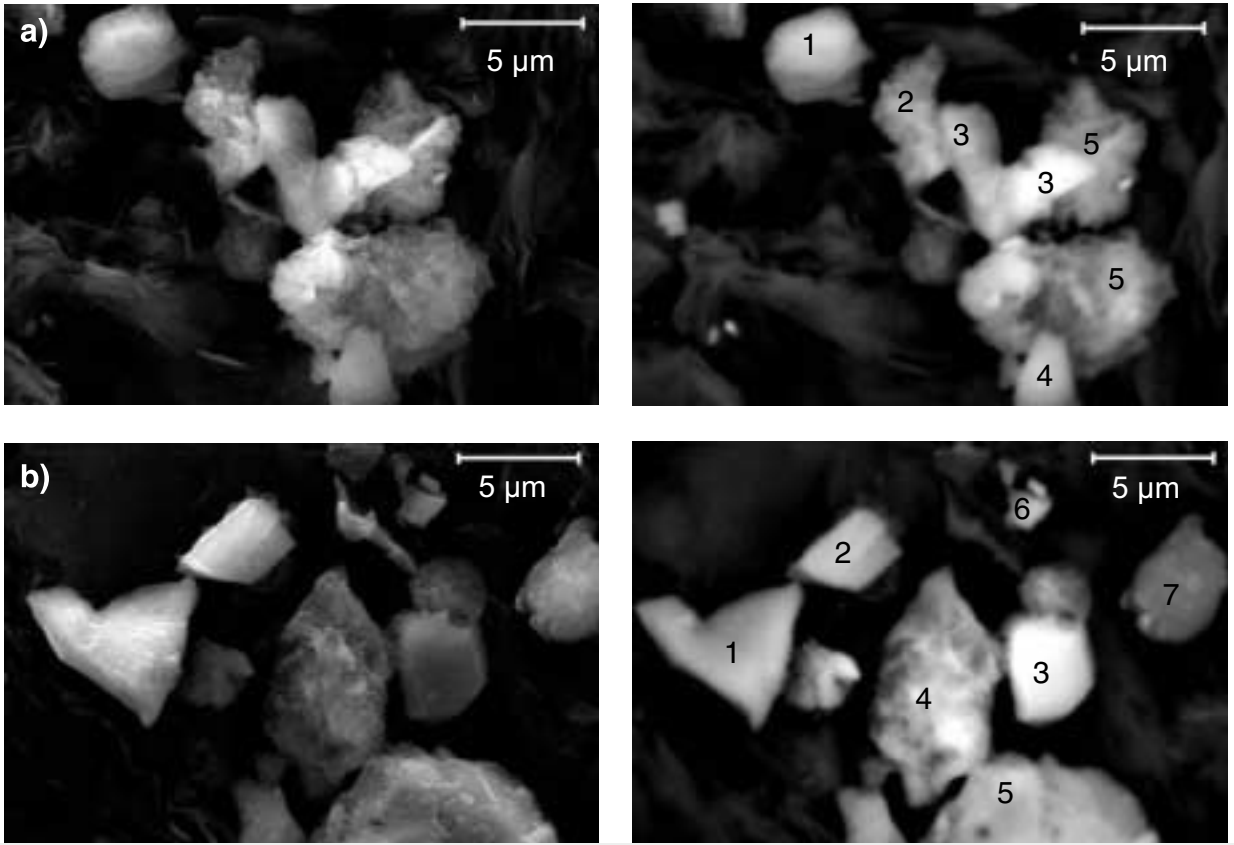

Figure 3. SEM photomicrographs of reference materials with carbon-coated grains; secondary electron (SE) image on left side and backscattered image on right side. Elements detected by X-ray analysis for each grain listed in order of abundance. **a**) LKSD-2 (1 = Si, O, Al, Na (albite); 2 = Si, O, Al, Fe; 3 = O, Si, Al, Mg, Fe; 4 = Si, O (quartz); 5 = Si, O, Al, Fe, (minor K, Ca)); **b**) STSD-1 (1 = Si, O (quartz); 2 = Si, O, Al, Na (albite); 3 = Si, O, Mg, Al, Cr, Fe; 4 = Mn, O, Fe; 5 = Si, O, Al, Na, Ca (plagioclase); 6 = Si, O, Al, K (K-feldspar); 7 = Ca, O, C (calcite)).

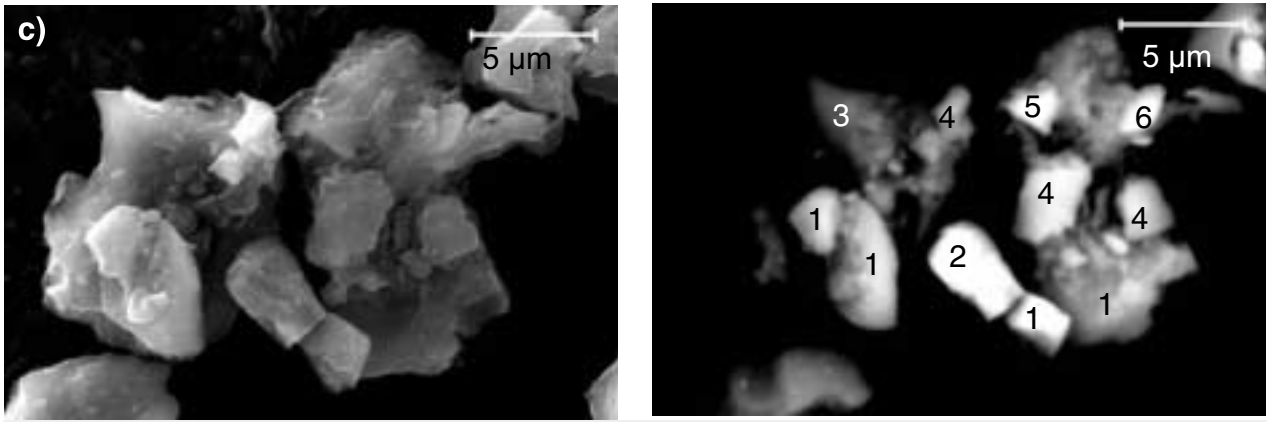

Figure 3. c) TILL-3 (1 = O, Si, Al, Mg, Fe (chlorite); 2 = Si, Ca, Ti (titanite); 3 = Si, O (quartz); 4 = Si, O, Al, Mg, K, Fe (biotite); 5 = Si, O, Al, Ca, Fe, Mg; 6 = Si, O, Al, Mg, K, Ca, Fe).

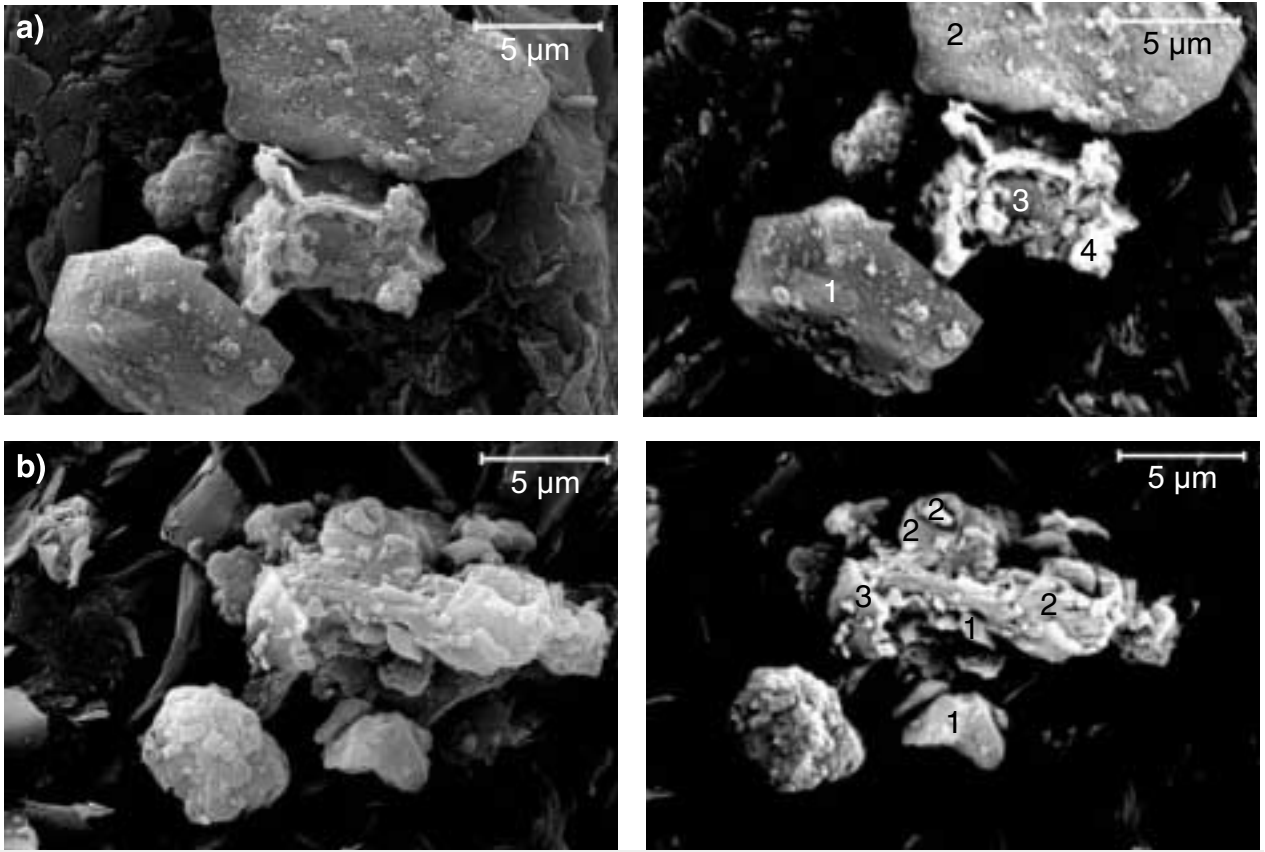

Figure 4. SEM photomicrographs of reference materials with gold-coated grains; secondary electron image on left side and backscattered image on right side. Elements detected by X-ray analysis for each grain listed in order of abundance. **a**) LKSD-2 (1 = Si, O (quartz); 2 = Si, O, Mg, Al, Fe; 3 = Si, Al, O, Na (albite); 4 = Si, Al, Fe); **b**) STSD-1 (1 = Si, Al, O, Na, Ca (plagioclase); 2 = Ca, O, C (calcite); 3 = Si, O, Mg, Al, Ca, Fe; 4 = O, Si, Al, Ca, Fe).

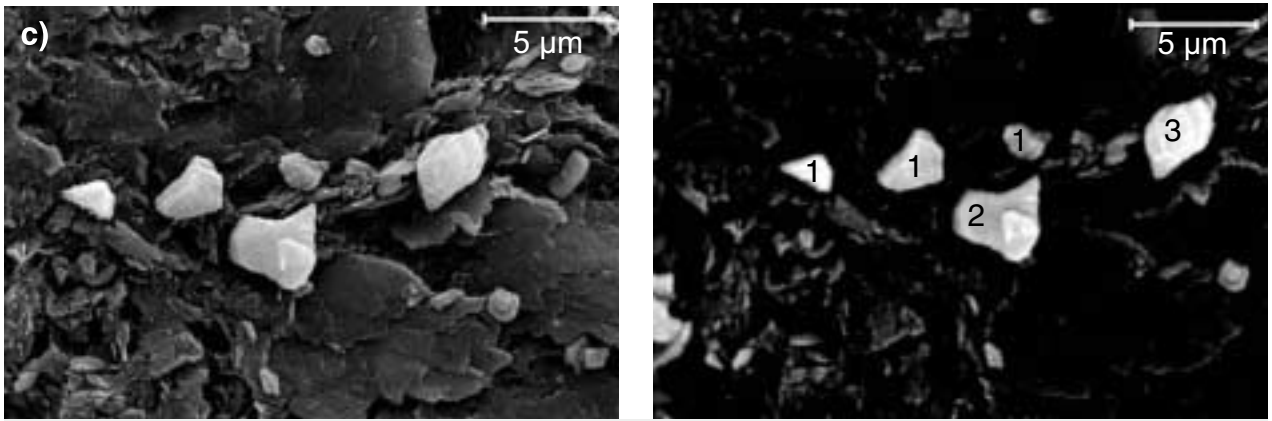

Figure 4. **c**) TILL-3 (1 = Na, Al, Si, Ca, O (plagioclase); 2 = Si, O (quartz); 3 = Si, O, Al, K (K-feldspar)).

Table 1. Sample collection locations (*after* Lynch, 1990, p. 154; Lynch, 1996, Table A, p. 278).

Sample no.	NTS designation	Location
LKSD-1	31F 31M	Joe Lake Brady Lake
LKSD-2	31F 86K, 86L	Calabogie Lake Composite sample 1
LKSD-3	31F 64L, 64M 31M, 31N, 32C, 32D, 41P, 42A	Calabogie Lake Composite sample 2 Composite sample 3
LKSD-4	31C 74H 74H	Big Gull Lake Key Lake Sea Horse Lake
STSD-1	31F	Lavant Creek
STSD-2	104P 93A, 93B	Hirok Stream Composite sample 4
STSD-3	104P 31F 93A, 93B	Hirok Stream Lavant Creek Composite sample 4
STSD-4	31F 93A, 93B	Composite sample 5 Composite sample 4
TILL-1	31F	Joe Lake
TILL-2	21C	Scisson's Brook (5 km west of brook)
TILL-3	31M	O'Brien mine, Cobalt
TILL-4	21C 31C	Scisson's Brook Hull

Table 2. Semiquantitative mineralogy of bulk powdered reference materials using XRD.

Mineral	LKSD				STSD				TILL			
	-1	-2	-3†	-4*	-1	-2*	-3†	-4†	-1†	-2	-3	-4
Quartz	26	50	49	59	52	30	51	45	46	55	53	46
Plagioclase	27	26	28	32	25	25	19	30	29	25	24	29
K-feldspar	10	15	14	tr	10	24	16	13	15	12	14	15
Amphibole	4	5	5	9	6	4	7	5	6	5	4	6
Pyroxene									?tr			
Chlorite	2	4	4	tr	7	12	6	4	4	3	5	4
Mica (illite)		tr	tr			5	1	tr	tr	tr	tr	tr
Smectite						tr		tr	tr			
Hematite				?tr	tr			3	tr			
Pyrite	12											
Calcite	18											

† = slightly amorphous; * = highly amorphous; tr = trace

Table 3. Semiquantitative mineralogy of untreated (U) and H_2O_2-treated (T) clay-sized reference materials using XRD.

Mineral	LKSD				STSD				TILL			
	-1	-2	-3†	-4*	-1	-2*	-3†	-4†	-1†	-2	-3	-4
Quartz U	5	26	24		32	21	43	28	22	26	37	23
Quartz T	***25***	***45***	***31***	***38***	***29***	***46***	***24***	***40***	***31***	***26***	***41***	***43***
Plagioclase U	7	23	26		24	23	21	28	24	25	28	29
Plagioclase T	***58***	***27***	***39***	***29***	***39***	***20***	***35***	***38***	***38***	***38***	***34***	***34***
K-feldspar U		25	22		10	26	20	17	17	19	20	24
K-feldspar T	***7***	***14***	***16***	***22***	***22***	***19***	***25***	***11***	***22***	***26***	***19***	***19***
Amphibole U		tr	14		15	3		9	15		tr	2
Amphibole T	***6***	***3***	***4***	***5***	***4***	***4***	***3***	***3***	***6***		***3***	***2***
Chlorite U		9	7		9	15	8	8	7	11	10	4
Chlorite T	***1***	***5***	***5***	***4***	***5***	***7***	***6***	***3***	***3***	***5***	***3***	***2***
Mica (illite) U		17	7		tr	12	8	10	4	19	5	8
Mica (illite) T		***6***	***5***	***2***	***tr***	***4***	***5***	***tr***	***tr***	***5***		
Smectite U						m	tr	tr		tr	tr	tr
Smectite T						***tr***	***tr***	***tr***	***tr***			
Hematite U			tr		6							tr
Hematite T												
Pyrite U	17											
Pyrite T	***tr***											
Calcite U	70				4						tr	
Calcite T	***3***											
Dolomite U												
Dolomite T					***1***				***tr***			

*† = slightly amorphous; * = highly amorphous; tr = trace; m = minor*