

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*

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The collection and preparation of four lake and four stream sediment reference materials are described. Provisional values related to both total concentrations and concentrations derived from partial extraction procedures are presented for major, minor and trace element constituents. As large amounts of samples (160-200 kg) have been prepared, they should be of interest to soil analysts.

The need for geochemical reference samples has been recognized for the past thirty years and many such samples have been prepared and characterized. While numerous rocks, ores and concentrates have been certified for many elements, there are relatively few reference samples representing secondary materials. A survey by Abbey (1) indicates that there are 15 stream sediments, 5 lake sediments, 12 soils, 3 marine sediments, 1 pond sediment and 1 river sediment out of 167 reference samples of geological origin. These totals include the 8 samples which are to be described in this report. Flanagan (2) indicates, in his historical account of reference materials, that there is a similar number of soil and sediment reference samples.

When the collection and preparation of these 8 samples were being planned, the following guidelines were used.

1. The lake sediment samples should be centre lake bottom and collected in various locations within the Canadian Shield. Logistics permitting, the stream sediment

samples should represent various geochemical environments in Canada.

2. The preparation of these should simulate, as closely as possible, the type of preparation used on routine samples.

3. Efforts would be made to incorporate a concentration gradient for a substantial number of elements within each sample type. For example, the provisional values for arsenic in LKSD-2, -4, -3 and -1 are 11, 16, 27 and 40 ppm, respectively and the provisional values for lithium in STSD-1, -4, -3 and -2 are 11, 14, 28 and 65 ppm, respectively.

4. The use or incorporation of reference samples highly anomalous in one or more elements was to be avoided.

5. Along with characterization for "total" values, the samples also were to be characterized for values which would relate to a specific type of partial extraction. The term "partial extraction" is used to denote a decomposition wherein the sample is not totally dissolved prior to analysis, usually by atomic absorption spectrometry or inductively coupled plasma emission spectrometry. A partial extraction dissolves very little of the silicate components in the sample. While each year many hundreds of thousands of geochemical and environmental samples are analyzed for a variety of elements using partial extractions, there have been only a few attempts to certify reference materials relative to specific partial decompositions; most of the data used for certification are "total". For the GXR samples described by Allcott and Lakin (3) there are data which relate to partial extractions. These data are contained in a subsequent report by Allcott and Lakin (4). In

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this report, the data were sorted according to element and extractions used; however, no values were assigned. Using these data from (4), Gladney (5) calculated values for a number of elements related to the extractions used. The large number of decompositions reported resulted in a dilution of the data for any single decomposition; for example, 16 different extractions were reported for Mn. Krumgalz and Fainshtein (6) describe the partial decomposition of four certified reference sediment samples using concentrated HNO₃ in a pressurized vessel of 140°C for 3 hours. Their values for Zn, Cu, Pb and Cd agree quite well with published "total" values while the values for Fe are 10% to 20% low. Flegal (7) recognized the need for environmentally-related reference samples to be certified for partial extractions. Knechtel and Fraser (8) report the use of some partial extractions for the analysis of a sludge ash derived from a municipal incinerator. They reported low results for Al, As, Cr, K, Na and Zn using an aqua regia extraction. Tessier et al. (9) describe a speciation study of the marine mud, MAG-1, using a series of sequential leaches in which Co, Cu, Ni, Pb, Zn, Fe and Mn are determined in exchangeable, carbonate, Fe-Mn oxide, organic and residual fractions. Xie and Yan (10) have compiled data from 41 laboratories within China for 8 drainage sediment reference samples. Recommended values for 50 trace and minor elements have been calculated. Their data sets for some elements contain values derived by partial extractions. For the purpose of calculation, these appear to have been mixed with "total" values; only a single recommended value was assigned for each element. While past efforts to characterize reference samples for elements related to specific partial extractions have been rather sporadic, it is felt that exploration geochemists and environmental scientists do have a genuine need for this type of reference sample data.

SAMPLE COLLECTION LOCATIONS

Material collected at the following locations was used to prepare the various reference samples. The National Topographical System (NTS) for identifying maps in Canada is used.

Lake Sediment Locations

| Sample Number | 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 |

Composite samples 1, 2, 3 and 4 were produced by mixing the unused portions of regional survey samples collected in the corresponding NTS sheets. Composite sample 5 was collected originally to provide material for an "in-house" reference sample.

Stream Sediment Locations

| Sample Number | NTS Designation | Location |
|---------------|-------------------------|--|
| 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 |

COLLECTION AND PREPARATION

Lake Sediment Collection

An Ekman dredge was used to collect material from Joe Lake and Calabogie Lake which were sampled through the ice in mid-winter. The same type of sampler was used from an aircraft pontoon in midsummer for the Key Lake and Seahorse Lake samples. A different type of sampler was built for use in Big Gull Lake. This consisted of a 25L capacity pail with weights attached externally along one side. A nylon rope, 1 cm x 30 m, was attached to the bail of the sampler. In practice, two people, an helmsman and a collector worked together; the collector lowered the sampler into the water and the boat was moved ahead slowly until there was tension on the nylon rope. The speed of the

boat was increased slowly until the pail was full which was indicated by increased tension on the rope. The weights attached along one side of the pail facilitated a horizontal orientation during the early filling. The loaded sampler then was raised to the surface by hand and poured into another 25L shipping pail lined with a polyethylene bag which was tied when filled and a lid was attached for shipping. The components of composite samples 1, 2 and 3 were collected using a centre lake bottom sampler which has been described by Hornbrook and Garrett (11). Brady Lake was sampled near the shore using a shovel. Only a small quantity of this material was collected.

Stream Sediment Collection

Shovels were used to collect the material at Lavant Creek and Hirok. The components of composite samples 4 and 5 were collected by hand.

Lake Sediment Preparation

Centre lake bottom sediment material is inherently very fine grained. Hence, all of the sample is used without a preliminary sieving to remove oversize material. Ferromanganese nodules which can be 1 cm or more in diameter are not removed since their presence in the sediment is the result of a local chemical reaction and influences the interpretation of the subsequent analyses. After drying, the whole sample was passed twice through a jaw crusher; this process reduced all pieces of the material to less than 1 cm. The sample then was ball-milled and sieved through a 200 mesh screen (74 μm). The oversize material was ball-milled a second time and sieved through the same screen. The oversize from the second sieving was discarded. The sieved material was then combined into a single batch and tumbled in a conical blender for eight hours.

When the mixing was terminated, the contents of the blender were subsampled immediately; a total of 48 samples, approximately 20 g each, was removed from four quadrants in each of three levels. The analyses of these sub-samples were subsequently used for homogeneity testing. The remainder of the material was bottled in 100 g lots. All bottles were numbered in the order in which they were filled. The number of bottles prepared for LKSD-1, LKSD-2, LKSD-3 and LKSD-4 were respectively 1608, 1608; 1600 and 1822.

Stream Sediment Preparation

Unlike lake sediments, various size fractions are used for the analysis of routine stream sediment samples. While

it is not unique, the -80 mesh (180 μm) fraction is one of the more commonly used. This fraction was selected for the stream sediment reference samples. During the drying period, a garden rake was used to remove rocks, twigs and leaves from the samples. When dry, each sample was sieved and only the -80 mesh fraction was retained. This fraction then was ball-milled and processed in the same manner as the lake sediment reference samples. The number of 100 g bottles prepared for STSD-1, STSD-2, STSD-3 and STSD-4 were respectively 1800, 1595, 1798 and 1968.

Homogeneity Testing

After collection, each of the 48 sub-samples removed from the blender was divided in two to produce a total of 96 splits. These were analyzed for Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, V, Mo, As, Cd and U. A neutron activation - delayed neutron counting method, described by Boulanger et al. (12) was used by Atomic Energy of Canada Ltd. to determine U; the remaining elements were dissolved using a hot nitric acid-hydrochloric acid partial extraction. An atomic absorption spectrometric method involving hydride evolution, Aslin (13), was used for the determination of arsenic. All other elements were determined by conventional atomic absorption spectrometry using a nitrous oxide-acetylene flame for Mo and V and an air-acetylene flame for the remaining elements.

After bottling, a second set of homogeneity tests was performed. All of the numbered bottles of each sediment sample were arranged in ascending numerical order and returned to shelf cases, each of which contained 24 bottles. The whole set of bottles for a given sediment sample was divided into 8 or 9 blocks of approximately 200 samples each; the number of blocks, 8 or 9 cases of 24 bottles each, was a function of the number of bottles for each sediment sample. For this homogeneity test, each of the 8 or 9 blocks was sampled in the following manner. From each block, 2 cases were selected. From one case, a single bottle was selected and a sub-sample was withdrawn for analysis. From the remaining case, two bottles were selected. From one of these two bottles a single sub-sample was withdrawn for analysis. From the remaining bottle of this pair, two sub-samples were withdrawn for analysis. In summary, each block generated 4 sub-samples and in turn the 8 or 9 blocks of each reference sample generated 32 or 36 sub-samples. All of the sub-samples from the four lake sediment reference materials were combined into a single suite and subsequently analyzed. The sub-samples from the four stream sediment reference samples were selected and analyzed in the same manner. All case and bottle

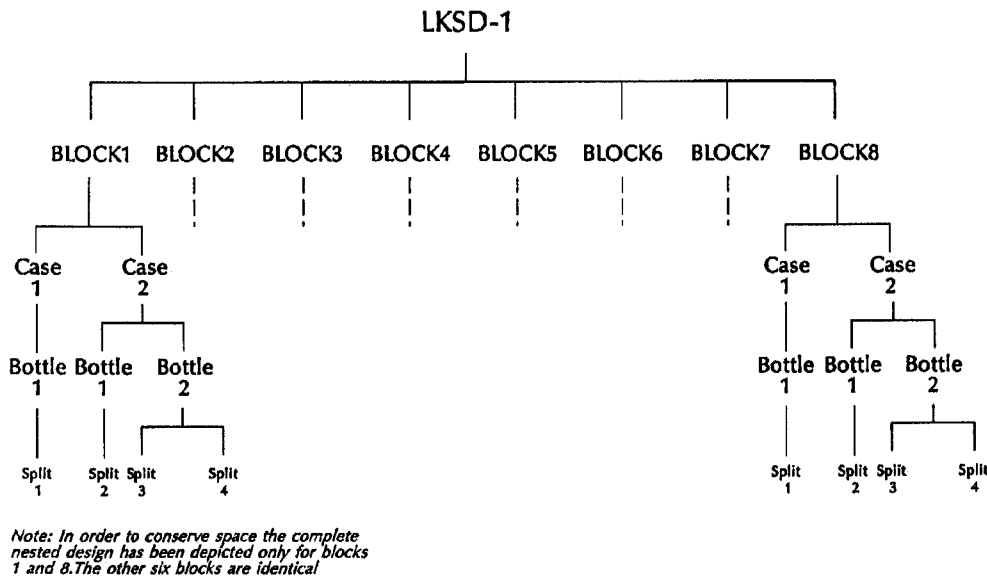


Figure 1. Block-case-bottle nested design for LKSD-1 homogeneity test

selections were done on the basis of computer generated random numbers. A schematic diagram of the nested design is contained in Figure 1. In this diagram, the term split is used to denote the sub-samples described above.

The elements determined and methods employed for this second set of homogeneity tests were the same as those used for the blender tests. In the blender tests, the sources of variation studied were levels, quadrants, levels X quadrants, samples in quadrants, analyses of samples, levels X samples and levels X analyses. In the block-case-bottle tests, analysis of variance between blocks/reference sample, cases/block, bottles/case and determinations/bottles was done. These two sets of homogeneity tests did not yield any significant evidence of inhomogeneity for the elements studied in any of the eight reference samples.

CHARACTERIZATION OF THE REFERENCE MATERIALS

When the 8 samples were prepared and bottled, requests were sent to 105 laboratories, soliciting analyses. Two bottles of each of the 8 reference materials were sent to those who had indicated a willingness to participate. Eventually, 35 participants produced data which were highly variable in volume. It was obvious that there were insufficient data to calculate certified values for any of the constituents. Hopefully the dissemination of provisional values based on available data may serve as a catalyst and many new analyses will be performed.

The production of provisional values did not justify a rigorous statistical treatment of the data. This will be done at a later date in a subsequent compilation(s).

For this initial compilation, all of the values for a given element related to a particular extraction were treated as a single population. Values for a given element related to extractions containing hydrofluoric acid were combined with values obtained from instrumental methods (INAA, XRF etc.) and were classified as "total". A two step trimming method involving means and standard deviations was used to remove outliers. The first step tended to remove extreme outliers; the second step produced a tighter data set. In the first step, all values outside the mean plus or minus two standard deviations were discarded and a new mean was calculated. The second step was a repetition of the first. The third mean produced at the end of these two trimming steps was used as the provisional value.

Results

The provisional values for the various constituents in the eight sediment samples are grouped as follows:

- Table 1. Major and minor elements expressed as oxides of the elements
- Table 2. Summation of major and minor elements expressed as oxides
- Table 3. "Total" elements
- Table 4. Elements derived from the analysis of concentrated nitric acid-concentrated hydrochloric acid extractions

Table 5. Elements derived from the analysis of dilute nitric acid - dilute hydrochloric acid extractions

In these tables,

N = number of laboratories after outliers have been removed

n = number of determinations after outliers have been removed

\bar{x} = mean

σ = standard deviation

Qualified = number of values reported below the detection limit. If more than 50% of the values from a laboratory were below the detection limit for a given element in a particular

Table 1. Major and minor elements expressed as oxides

SiO₂ (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 43 | 40.1 | 0.3 | 0 | 5 |
| LKSD-2 | 5 | 35 | 58.9 | 0.6 | 0 | 3 |
| LKSD-3 | 5 | 37 | 58.5 | 0.6 | 0 | 2 |
| LKSD-4 | 5 | 35 | 41.6 | 0.6 | 0 | 3 |
| STSD-1 | 5 | 34 | 42.5 | 0.5 | 0 | 3 |
| STSD-2 | 4 | 34 | 53.7 | 0.3 | 0 | 5 |
| STSD-3 | 5 | 35 | 48.6 | 0.5 | 0 | 3 |
| STSD-4 | 5 | 35 | 58.9 | 0.5 | 0 | 3 |

CaO (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 47 | 10.8 | 0.6 | 0 | 1 |
| LKSD-2 | 6 | 38 | 2.2 | 0.2 | 0 | 0 |
| LKSD-3 | 6 | 39 | 2.3 | 0.2 | 0 | 0 |
| LKSD-4 | 6 | 38 | 1.8 | 0.2 | 0 | 0 |
| STSD-1 | 6 | 37 | 3.6 | 0.3 | 0 | 0 |
| STSD-2 | 6 | 39 | 4.0 | 0.4 | 0 | 0 |
| STSD-3 | 6 | 38 | 3.3 | 0.2 | 0 | 0 |
| STSD-4 | 6 | 38 | 4.0 | 0.3 | 0 | 0 |

TiO₂ (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 44 | 0.53 | 0.02 | 0 | 4 |
| LKSD-2 | 5 | 34 | 0.56 | 0.04 | 0 | 4 |
| LKSD-3 | 6 | 35 | 0.52 | 0.02 | 0 | 4 |
| LKSD-4 | 5 | 36 | 0.36 | 0.02 | 0 | 2 |
| STSD-1 | 6 | 37 | 0.75 | 0.07 | 0 | 0 |
| STSD-2 | 5 | 35 | 0.79 | 0.03 | 0 | 4 |
| STSD-3 | 3 | 38 | 0.72 | 0.08 | 0 | 0 |
| STSD-4 | 5 | 35 | 0.76 | 0.05 | 0 | 3 |

Al₂O₃ (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 47 | 7.8 | 0.2 | 0 | 1 |
| LKSD-2 | 5 | 36 | 12.3 | 0.4 | 0 | 2 |
| LKSD-3 | 6 | 39 | 12.5 | 0.4 | 0 | 0 |
| LKSD-4 | 6 | 38 | 5.9 | 0.4 | 0 | 0 |
| STSD-1 | 6 | 35 | 9.0 | 0.3 | 0 | 2 |
| STSD-2 | 5 | 38 | 16.1 | 0.4 | 0 | 1 |
| STSD-3 | 5 | 36 | 10.9 | 0.2 | 0 | 2 |
| STSD-4 | 5 | 36 | 12.1 | 0.1 | 0 | 2 |

Na₂O (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 44 | 2.00 | 0.04 | 0 | 4 |
| LKSD-2 | 6 | 37 | 1.93 | 0.06 | 0 | 1 |
| LKSD-3 | 6 | 39 | 2.32 | 0.09 | 0 | 0 |
| LKSD-4 | 5 | 34 | 0.73 | 0.02 | 0 | 4 |
| STSD-1 | 5 | 33 | 1.75 | 0.04 | 0 | 4 |
| STSD-2 | 5 | 34 | 1.72 | 0.04 | 0 | 5 |
| STSD-3 | 5 | 34 | 1.53 | 0.05 | 0 | 4 |
| STSD-4 | 5 | 37 | 2.70 | 0.10 | 0 | 1 |

P₂O₅ (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 35 | 0.18 | 0.01 | 0 | 3 |
| LKSD-2 | 5 | 28 | 0.28 | 0.03 | 0 | 0 |
| LKSD-3 | 5 | 25 | 0.25 | 0.01 | 0 | 4 |
| LKSD-4 | 4 | 24 | 0.33 | 0.03 | 0 | 4 |
| STSD-1 | 5 | 27 | 0.38 | 0.02 | 0 | 0 |
| STSD-2 | 5 | 28 | 0.32 | 0.02 | 0 | 1 |
| STSD-3 | 5 | 28 | 0.36 | 0.01 | 0 | 0 |
| STSD-4 | 4 | 25 | 0.22 | 0.01 | 0 | 3 |

Fe₂O₃(T) (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 48 | 4.11 | 0.13 | 0 | 0 |
| LKSD-2 | 6 | 38 | 6.24 | 0.29 | 0 | 0 |
| LKSD-3 | 6 | 38 | 5.74 | 0.12 | 0 | 0 |
| LKSD-4 | 5 | 35 | 4.09 | 0.06 | 0 | 3 |
| STSD-1 | 6 | 36 | 6.48 | 0.13 | 0 | 1 |
| STSD-2 | 6 | 37 | 7.51 | 0.17 | 0 | 2 |
| STSD-3 | 6 | 38 | 6.17 | 0.18 | 0 | 0 |
| STSD-4 | 6 | 38 | 5.70 | 0.27 | 0 | 0 |

K₂O (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 43 | 1.14 | 0.04 | 0 | 5 |
| LKSD-2 | 6 | 38 | 2.64 | 0.10 | 0 | 0 |
| LKSD-3 | 6 | 39 | 2.22 | 0.09 | 0 | 0 |
| LKSD-4 | 6 | 38 | 0.82 | 0.06 | 0 | 0 |
| STSD-1 | 6 | 37 | 1.25 | 0.07 | 0 | 0 |
| STSD-2 | 5 | 38 | 2.12 | 0.08 | 0 | 1 |
| STSD-3 | 5 | 37 | 1.80 | 0.07 | 0 | 1 |
| STSD-4 | 4 | 35 | 1.80 | 0.03 | 0 | 3 |

LOI (1000°C) (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 34 | 29.9 | 0.4 | 0 | 2 |
| LKSD-2 | 5 | 34 | 13.6 | 0.2 | 0 | 2 |
| LKSD-3 | 5 | 32 | 13.4 | 0.1 | 0 | 4 |
| LKSD-4 | 3 | 30 | 43.6 | 0.1 | 0 | 6 |
| STSD-1 | 4 | 31 | 31.6 | 0.1 | 0 | 5 |
| STSD-2 | 4 | 31 | 10.3 | 0.2 | 0 | 5 |
| STSD-3 | 3 | 30 | 23.6 | 0.2 | 0 | 6 |
| STSD-4 | 4 | 31 | 11.6 | 0.1 | 0 | 5 |

MgO (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 48 | 1.73 | 0.11 | 0 | 0 |
| LKSD-2 | 6 | 38 | 1.67 | 0.14 | 0 | 0 |
| LKSD-3 | 6 | 39 | 1.99 | 0.10 | 0 | 0 |
| LKSD-4 | 6 | 38 | 0.93 | 0.08 | 0 | 0 |
| STSD-1 | 6 | 37 | 2.21 | 0.11 | 0 | 0 |
| STSD-2 | 6 | 39 | 3.11 | 0.16 | 0 | 0 |
| STSD-3 | 6 | 38 | 2.20 | 0.10 | 0 | 0 |
| STSD-4 | 6 | 38 | 2.13 | 0.09 | 0 | 0 |

MnO (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 39 | 0.09 | 0.00 | 0 | 9 |
| LKSD-2 | 5 | 34 | 0.26 | 0.01 | 0 | 4 |
| LKSD-3 | 6 | 39 | 0.18 | 0.01 | 0 | 0 |
| LKSD-4 | 4 | 29 | 0.06 | 0.00 | 0 | 9 |
| STSD-1 | 6 | 37 | 0.50 | 0.04 | 0 | 0 |
| STSD-2 | 4 | 33 | 0.14 | 0.01 | 0 | 6 |
| STSD-3 | 6 | 38 | 0.34 | 0.03 | 0 | 0 |
| STSD-4 | 5 | 34 | 0.19 | 0.01 | 0 | 4 |

sample, all of the values for that element in that sample were deleted and did not appear in either of the last two columns. If the qualified values were not discarded they were set arbitrarily to one half of the detection limit.

Outliers = values which were deleted by the two step trimming process.

For most of the elements, there were no restrictions placed on the initial selection of data. However, the sources of data for major and minor elements (as oxides) shown in Table 1 were restricted to those laboratories which determined these elements as a group. When major element data were acquired as part of a trace element

Table 2. Summation of major and minor elements expressed as oxides (%)

| | LKSD 1 | LKSD 2 | LKSD 3 | LKSD 4 | STSD 1 | STSD 2 | STSD 3 | STSD 4 |
|--------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| SiO ₂ | 40.1 | 58.9 | 58.5 | 41.6 | 42.5 | 53.7 | 48.6 | 58.9 |
| Al ₂ O ₃ | 7.8 | 12.3 | 12.5 | 5.9 | 9.0 | 16.1 | 10.9 | 12.1 |
| Fe ₂ O ₃ | 4.1 | 6.2 | 5.7 | 4.1 | 6.5 | 7.5 | 6.2 | 5.7 |
| MgO | 1.7 | 1.7 | 2.0 | 0.9 | 2.2 | 3.1 | 2.2 | 2.1 |
| CaO | 10.8 | 2.2 | 2.3 | 1.8 | 3.8 | 4.0 | 3.3 | 4.0 |
| Na ₂ O | 2.0 | 1.9 | 2.3 | 0.7 | 1.8 | 1.7 | 1.5 | 2.7 |
| K ₂ O | 1.1 | 2.6 | 2.2 | 0.8 | 1.2 | 2.1 | 1.8 | 1.6 |
| MnO | 0.1 | 0.3 | 0.2 | 0.1 | 0.5 | 0.1 | 0.3 | 0.2 |
| TiO ₂ | 0.5 | 0.6 | 0.5 | 0.4 | 0.8 | 0.8 | 0.7 | 0.8 |
| P ₂ O ₅ | 0.2 | 0.3 | 0.2 | 0.3 | 0.4 | 0.3 | 0.4 | 0.2 |
| LOI(1000°) | 29.9 | 13.6 | 13.4 | 43.6 | 31.6 | 10.3 | 23.6 | 11.6 |
| SO ₄ * | 1.6 | - | - | - | - | - | - | - |
| Sum. | 99.9 | 100.6 | 99.8 | 100.2 | 100.1 | 99.7 | 99.5 | 99.9 |

*One laboratory determined SO₄ in LKSD-1 only.

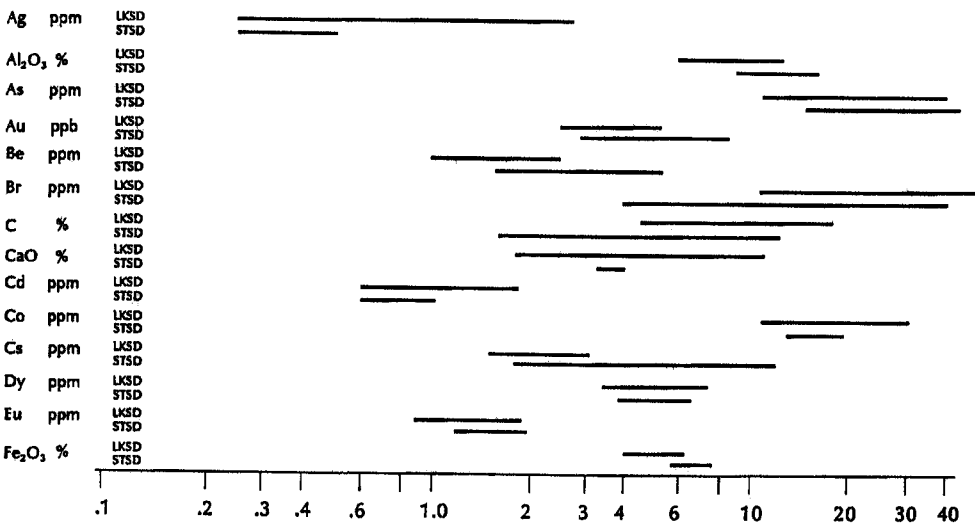


Figure 2 (1). Concentration ranges for LKSD and STSD samples

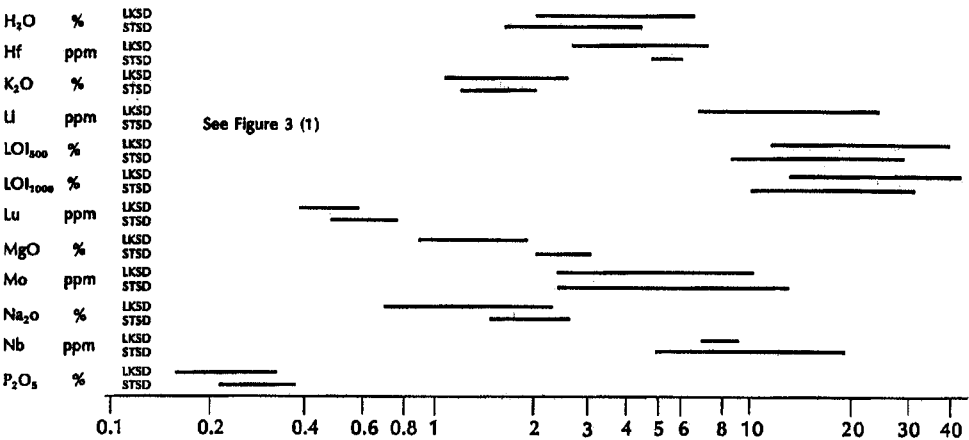


Figure 2 (2). Concentration ranges for LKSD and STSD samples

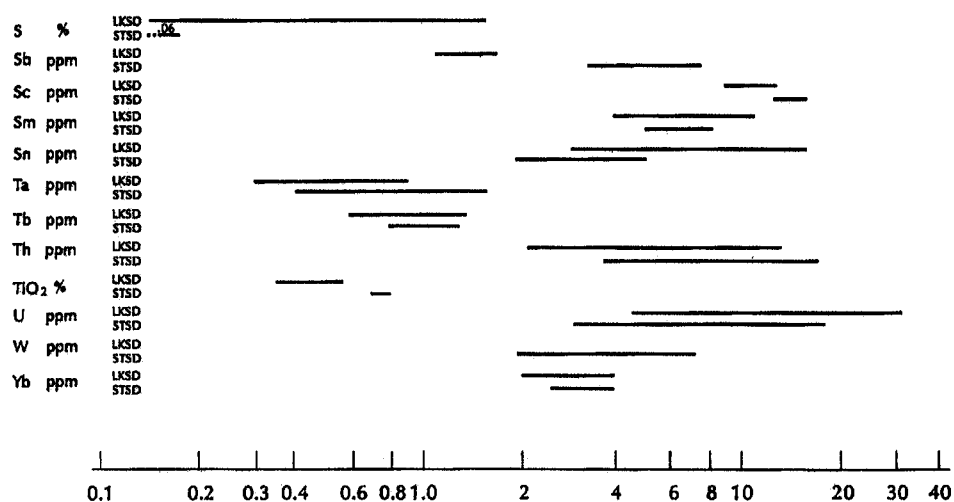


Figure 2 (3). Concentration ranges for LKSD and STSD samples

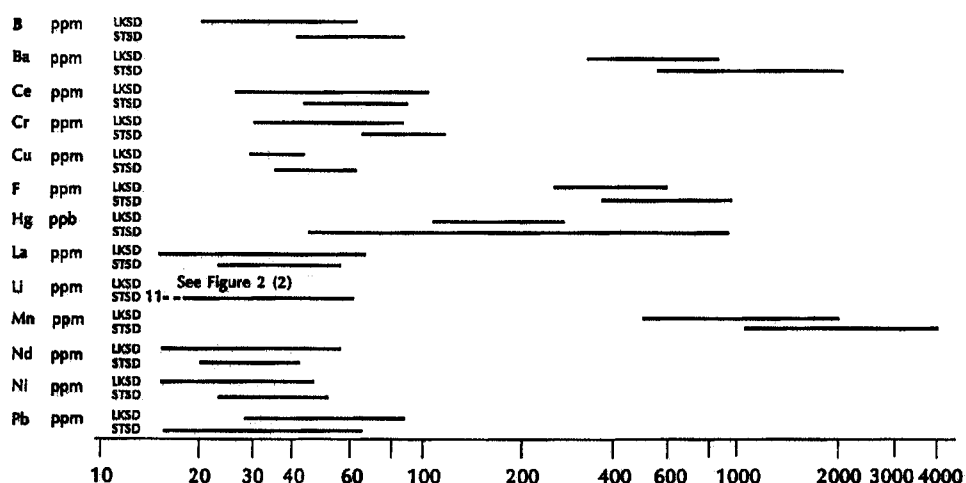


Figure 3 (1). Concentration ranges for LKSD and STSD samples

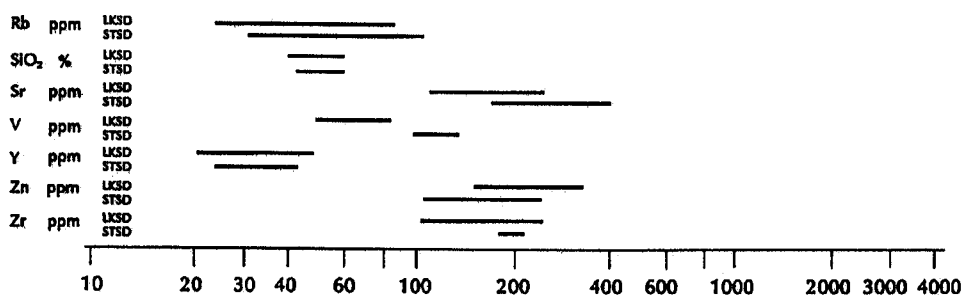


Figure 3 (2). Concentration ranges for LKSD and STSD samples

Table 3. "Total" elements

Ag (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 3 | 16 | 0.6 | 0.05 | 0 | 0 |
| LKSD-2 | 2 | 14 | 0.8 | 0.06 | 0 | 2 |
| LKSD-3 | 2 | 14 | 2.7 | 0.11 | 0 | 2 |
| LKSD-4 | 3 | 16 | <0.5 | - | 12 | - |
| STSD-1 | 3 | 16 | <0.5 | - | 12 | - |
| STSD-2 | 3 | 15 | 0.5 | 0.08 | 1 | 0 |
| STSD-3 | 3 | 16 | <0.5 | - | 12 | - |
| STSD-4 | 2 | 14 | <0.5 | - | 10 | - |

Be (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 23 | 1.1 | 0.1 | 0 | 4 |
| LKSD-2 | 4 | 25 | 2.5 | 0.6 | 0 | 2 |
| LKSD-3 | 3 | 22 | 1.9 | 0.2 | 0 | 5 |
| LKSD-4 | 4 | 21 | 1.0 | 0.03 | 0 | 4 |
| STSD-1 | 5 | 26 | 1.6 | 0.6 | 1 | 1 |
| STSD-2 | 5 | 27 | 5.2 | 0.7 | 0 | 0 |
| STSD-3 | 4 | 23 | 2.6 | 0.3 | 0 | 4 |
| STSD-4 | 5 | 27 | 1.7 | 0.3 | 0 | 0 |

Cr (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 13 | 72 | 31 | 3 | 0 | 10 |
| LKSD-2 | 14 | 80 | 57 | 8 | 0 | 14 |
| LKSD-3 | 13 | 89 | 87 | 8 | 0 | 5 |
| LKSD-4 | 12 | 66 | 33 | 6 | 0 | 16 |
| STSD-1 | 15 | 116 | 67 | 9 | 0 | 12 |
| STSD-2 | 16 | 112 | 116 | 13 | 0 | 6 |
| STSD-3 | 15 | 113 | 80 | 10 | 0 | 7 |
| STSD-4 | 16 | 116 | 93 | 14 | 0 | 7 |

As (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 51 | 40 | 2 | 0 | 5 |
| LKSD-2 | 7 | 54 | 11 | 1 | 0 | 2 |
| LKSD-3 | 7 | 54 | 27 | 2 | 0 | 2 |
| LKSD-4 | 7 | 53 | 16 | 1 | 0 | 3 |
| STSD-1 | 8 | 86 | 23 | 2 | 0 | 4 |
| STSD-2 | 8 | 76 | 42 | 3 | 0 | 6 |
| STSD-3 | 8 | 78 | 28 | 2 | 0 | 4 |
| STSD-4 | 8 | 84 | 15 | 1 | 0 | 5 |

Br (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 35 | 11 | 1 | 0 | 4 |
| LKSD-2 | 5 | 39 | 18 | 2 | 0 | 5 |
| LKSD-3 | 5 | 42 | 16 | 1 | 0 | 5 |
| LKSD-4 | 5 | 45 | 49 | 6 | 0 | 2 |
| STSD-1 | 7 | 68 | 40 | 3 | 0 | 7 |
| STSD-2 | 7 | 58 | 4 | 1 | 0 | 8 |
| STSD-3 | 7 | 53 | 24 | 3 | 0 | 3 |
| STSD-4 | 7 | 60 | 13 | 1 | 0 | 4 |

Cs (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 43 | 1.5 | 1.2 | 3 | 4 |
| LKSD-2 | 9 | 60 | 3.0 | 0.6 | 0 | 6 |
| LKSD-3 | 9 | 60 | 2.3 | 0.3 | 0 | 9 |
| LKSD-4 | 9 | 61 | 1.7 | 0.6 | 0 | 8 |
| STSD-1 | 9 | 83 | 1.8 | 0.3 | 0 | 14 |
| STSD-2 | 11 | 95 | 12 | 1.4 | 0 | 3 |
| STSD-3 | 9 | 68 | 5.2 | 0.8 | 0 | 10 |
| STSD-4 | 9 | 75 | 1.9 | 0.6 | 0 | 10 |

Au (ppb)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 54 | 5 | 2 | 2 | 2 |
| LKSD-2 | 8 | 70 | 3 | 2 | 12 | 1 |
| LKSD-3 | 8 | 72 | 3 | 2 | 12 | 2 |
| LKSD-4 | 6 | 53 | 2 | 2 | 4 | 1 |
| STSD-1 | 11 | 98 | 8 | 4 | 3 | 8 |
| STSD-2 | 8 | 71 | 3 | 2 | 7 | 2 |
| STSD-3 | 10 | 78 | 7 | 4 | 2 | 5 |
| STSD-4 | 9 | 75 | 4 | 2 | 7 | 5 |

C (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 35 | 12.3 | 0.5 | 0 | 1 |
| LKSD-2 | 3 | 32 | 4.5 | 0.3 | 0 | 5 |
| LKSD-3 | 3 | 30 | 4.5 | 0.3 | 0 | 4 |
| LKSD-4 | 4 | 33 | 17.7 | 0.8 | 0 | 3 |
| STSD-1 | 3 | 32 | 12.3 | 0.4 | 0 | 4 |
| STSD-2 | 4 | 32 | 1.6 | 0.1 | 0 | 4 |
| STSD-3 | 4 | 34 | 8.4 | 0.4 | 0 | 2 |
| STSD-4 | 4 | 36 | 4.1 | 0.3 | 0 | 0 |

Cu (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 12 | 57 | 44 | 5 | 0 | 5 |
| LKSD-2 | 11 | 55 | 37 | 4 | 0 | 7 |
| LKSD-3 | 13 | 55 | 35 | 3 | 0 | 11 |
| LKSD-4 | 14 | 57 | 81 | 4 | 0 | 5 |
| STSD-1 | 12 | 55 | 36 | 4 | 0 | 7 |
| STSD-2 | 12 | 53 | 47 | 5 | 0 | 7 |
| STSD-3 | 14 | 59 | 39 | 4 | 0 | 5 |
| STSD-4 | 11 | 53 | 65 | 6 | 0 | 7 |

B (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 3 | 22 | 49 | 4 | 0 | 2 |
| LKSD-2 | 3 | 19 | 65 | 2 | 0 | 5 |
| LKSD-3 | 2 | 20 | 25 | 1 | 0 | 4 |
| LKSD-4 | 2 | 20 | 22 | 2 | 0 | 4 |
| STSD-1 | 3 | 24 | 89 | 9 | 0 | 0 |
| STSD-2 | 2 | 20 | 42 | 4 | 0 | 4 |
| STSD-3 | 3 | 22 | 82 | 4 | 0 | 2 |
| STSD-4 | 2 | 20 | 46 | 4 | 0 | 4 |

Ce (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 44 | 27 | 2 | 0 | 3 |
| LKSD-2 | 6 | 52 | 108 | 12 | 0 | 0 |
| LKSD-3 | 6 | 50 | 90 | 7 | 0 | 5 |
| LKSD-4 | 6 | 49 | 48 | 6 | 0 | 6 |
| STSD-1 | 8 | 78 | 51 | 6 | 0 | 5 |
| STSD-2 | 8 | 72 | 93 | 10 | 0 | 3 |
| STSD-3 | 8 | 62 | 63 | 8 | 0 | 2 |
| STSD-4 | 8 | 66 | 44 | 3 | 0 | 5 |

Dy (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 29 | 3.4 | 0.4 | 0 | 3 |
| LKSD-2 | 4 | 32 | 7.3 | 0.7 | 0 | 0 |
| LKSD-3 | 4 | 31 | 4.9 | 0.6 | 0 | 1 |
| LKSD-4 | 4 | 28 | 3.7 | 0.2 | 0 | 4 |
| STSD-1 | 4 | 27 | 5.6 | 0.9 | 0 | 5 |
| STSD-2 | 4 | 31 | 6.5 | 0.6 | 0 | 1 |
| STSD-3 | 4 | 29 | 5.4 | 0.6 | 0 | 3 |
| STSD-4 | 4 | 29 | 3.8 | 0.5 | 1 | 3 |

Ba (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 15 | 100 | 430 | 40 | 0 | 10 |
| LKSD-2 | 17 | 108 | 780 | 75 | 0 | 7 |
| LKSD-3 | 16 | 104 | 680 | 55 | 0 | 14 |
| LKSD-4 | 18 | 108 | 330 | 55 | 0 | 10 |
| STSD-1 | 17 | 128 | 630 | 51 | 0 | 17 |
| STSD-2 | 17 | 123 | 540 | 43 | 0 | 13 |
| STSD-3 | 19 | 116 | 1490 | 120 | 0 | 11 |
| STSD-4 | 18 | 123 | 2000 | 222 | 0 | 9 |

Co (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 9 | 67 | 11 | 1 | 0 | 9 |
| LKSD-2 | 11 | 64 | 17 | 1 | 0 | 12 |
| LKSD-3 | 11 | 66 | 30 | 2 | 0 | 10 |
| LKSD-4 | 11 | 68 | 11 | 1 | 0 | 6 |
| STSD-1 | 10 | 69 | 17 | 1 | 0 | 7 |
| STSD-2 | 9 | 64 | 19 | 2 | 0 | 10 |
| STSD-3 | 10 | 64 | 16 | 1 | 0 | 12 |
| STSD-4 | 9 | 65 | 13 | 1 | 0 | 7 |

Eu (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 51 | 0.9 | 0.2 | 0 | 5 |
| LKSD-2 | 7 | 54 | 1.9 | 0.2 | 0 | 8 |
| LKSD-3 | 6 | 52 | 1.5 | 0.3 | 0 | 3 |
| LKSD-4 | 7 | 55 | 1.1 | 0.3 | 3 | 10 |
| STSD-1 | 9 | 81 | 1.6 | 0.4 | 0 | 12 |
| STSD-2 | 9 | 73 | 2.0 | 0.4 | 0 | 10 |
| STSD-3 | 8 | 64 | 1.3 | 0.5 | 12 | 0 |
| STSD-4 | 8 | 70 | 1.2 | 0.5 | 10 | 1 |

Table 3 (Cont'd.). "Total" elements

| F (ppm) | | | | | | | |
|---------------|---|----|-----------|----------|-----------|----------|--|
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 9 | 52 | 300 | 60 | 0 | 0 | |
| LKSD-2 | 9 | 53 | 590 | 80 | 0 | 0 | |
| LKSD-3 | 9 | 53 | 490 | 60 | 0 | 0 | |
| LKSD-4 | 9 | 44 | 260 | 40 | 5 | 9 | |
| STSD-1 | 9 | 47 | 950 | 100 | 0 | 2 | |
| STSD-2 | 8 | 49 | 940 | 120 | 0 | 4 | |
| STSD-3 | 9 | 53 | 850 | 180 | 0 | 0 | |
| STSD-4 | 9 | 47 | 380 | 50 | 0 | 6 | |

| Li (ppm) | | | | | | | |
|---------------|---|----|-----------|----------|-----------|----------|--|
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 5 | 41 | 7 | 2 | 0 | 3 | |
| LKSD-2 | 5 | 40 | 20 | 2 | 0 | 4 | |
| LKSD-3 | 5 | 39 | 25 | 2 | 0 | 5 | |
| LKSD-4 | 5 | 41 | 12 | 2 | 0 | 1 | |
| STSD-1 | 5 | 38 | 11 | 1 | 0 | 6 | |
| STSD-2 | 5 | 44 | 65 | 8 | 0 | 0 | |
| STSD-3 | 5 | 39 | 28 | 2 | 0 | 5 | |
| STSD-4 | 5 | 38 | 14 | 2 | 0 | 6 | |

| Nb (ppm) | | | | | | | |
|---------------|---|----|-----------|----------|-----------|----------|--|
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 3 | 22 | 7 | 8 | 5 | 0 | |
| LKSD-2 | 4 | 26 | 8 | 1 | 0 | 6 | |
| LKSD-3 | 4 | 25 | 8 | 1 | 1 | 7 | |
| LKSD-4 | 3 | 22 | 9 | 7 | 1 | 0 | |
| STSD-1 | 4 | 27 | 5 | 3 | 0 | 5 | |
| STSD-2 | 4 | 23 | 20 | 3 | 0 | 9 | |
| STSD-3 | 4 | 29 | 12 | 4 | 0 | 3 | |
| STSD-4 | 5 | 32 | 9 | 5 | 1 | 1 | |

| Fe (%) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 19 | 132 | 2.8 | 0.1 | 0 | 19 | |
| LKSD-2 | 20 | 131 | 4.3 | 0.2 | 0 | 15 | |
| LKSD-3 | 21 | 132 | 4.0 | 0.2 | 0 | 19 | |
| LKSD-4 | 22 | 133 | 2.8 | 0.2 | 0 | 17 | |
| STSD-1 | 24 | 158 | 4.7 | 0.5 | 0 | 18 | |
| STSD-2 | 22 | 142 | 5.2 | 0.3 | 0 | 25 | |
| STSD-3 | 24 | 149 | 4.4 | 0.4 | 0 | 10 | |
| STSD-4 | 23 | 145 | 4.1 | 0.4 | 0 | 13 | |
| LOI (500°) % | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 6 | 24 | 23.5 | 0.5 | 0 | 4 | |
| LKSD-2 | 6 | 27 | 12.3 | 0.4 | 0 | 2 | |
| LKSD-3 | 6 | 25 | 11.8 | 0.6 | 0 | 1 | |
| LKSD-4 | 6 | 26 | 40.8 | 0.7 | 0 | 3 | |
| STSD-1 | 6 | 28 | 29.7 | 0.8 | 0 | 0 | |
| STSD-2 | 6 | 26 | 8.7 | 0.6 | 0 | 3 | |
| STSD-3 | 6 | 24 | 21.6 | 0.4 | 0 | 5 | |
| STSD-4 | 6 | 26 | 10.2 | 0.5 | 0 | 3 | |
| Nd (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 4 | 24 | 16 | 1.7 | 0 | 2 | |
| LKSD-2 | 4 | 23 | 58 | 4.6 | 0 | 3 | |
| LKSD-3 | 4 | 23 | 44 | 3.6 | 0 | 3 | |
| LKSD-4 | 4 | 25 | 25 | 2.4 | 0 | 1 | |
| STSD-1 | 4 | 24 | 28 | 4.2 | 0 | 2 | |
| STSD-2 | 4 | 24 | 43 | 4.4 | 0 | 2 | |
| STSD-3 | 3 | 22 | 39 | 3.5 | 0 | 4 | |
| STSD-4 | 3 | 21 | 21 | 1.7 | 0 | 5 | |
| H₂O (%) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 3 | 20 | 2.92 | 0.12 | 0 | 4 | |
| LKSD-2 | 3 | 24 | 2.23 | 0.26 | 0 | 0 | |
| LKSD-3 | 3 | 24 | 2.07 | 0.32 | 0 | 0 | |
| LKSD-4 | 2 | 20 | 6.55 | 0.16 | 0 | 4 | |
| STSD-1 | 2 | 20 | 4.46 | 0.14 | 0 | 4 | |
| STSD-2 | 2 | 20 | 2.43 | 0.09 | 0 | 4 | |
| STSD-3 | 3 | 21 | 3.47 | 0.32 | 0 | 3 | |
| STSD-4 | 2 | 20 | 1.73 | 0.06 | 0 | 4 | |
| Lu (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 3 | 17 | 0.4 | 0.1 | 0 | 0 | |
| LKSD-2 | 3 | 20 | 0.6 | 0.1 | 0 | 0 | |
| LKSD-3 | 3 | 25 | 0.4 | 0.1 | 0 | 0 | |
| LKSD-4 | 3 | 25 | 0.5 | 0.1 | 0 | 0 | |
| STSD-1 | 5 | 52 | 0.6 | 0.1 | 0 | 1 | |
| STSD-2 | 5 | 44 | 0.7 | 0.4 | 0 | 0 | |
| STSD-3 | 5 | 31 | 0.8 | 0.1 | 0 | 3 | |
| STSD-4 | 5 | 40 | 0.5 | 0.1 | 0 | 1 | |
| Ni (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 9 | 56 | 16 | 3 | 0 | 5 | |
| LKSD-2 | 11 | 75 | 26 | 4 | 5 | 10 | |
| LKSD-3 | 12 | 85 | 47 | 5 | 0 | 8 | |
| LKSD-4 | 14 | 84 | 31 | 5 | 3 | 5 | |
| STSD-1 | 13 | 99 | 24 | 5 | 7 | 18 | |
| STSD-2 | 13 | 98 | 53 | 6 | 0 | 8 | |
| STSD-3 | 13 | 81 | 30 | 6 | 5 | 9 | |
| STSD-4 | 13 | 94 | 30 | 5 | 3 | 10 | |
| Hf (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 8 | 53 | 3.6 | 0.5 | 0 | 8 | |
| LKSD-2 | 7 | 58 | 7.0 | 1.0 | 0 | 8 | |
| LKSD-3 | 7 | 63 | 4.8 | 0.7 | 0 | 6 | |
| LKSD-4 | 7 | 59 | 2.8 | 0.5 | 0 | 10 | |
| STSD-1 | 10 | 87 | 6.1 | 0.9 | 0 | 10 | |
| STSD-2 | 10 | 79 | 5.0 | 0.8 | 0 | 9 | |
| STSD-3 | 10 | 75 | 5.1 | 1.2 | 0 | 3 | |
| STSD-4 | 10 | 80 | 5.5 | 1.0 | 0 | 5 | |
| Mn (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 11 | 86 | 700 | 30 | 0 | 14 | |
| LKSD-2 | 12 | 76 | 2020 | 100 | 0 | 13 | |
| LKSD-3 | 12 | 79 | 1440 | 80 | 0 | 11 | |
| LKSD-4 | 13 | 82 | 500 | 30 | 0 | 8 | |
| STSD-1 | 13 | 80 | 3950 | 270 | 0 | 9 | |
| STSD-2 | 10 | 75 | 1060 | 80 | 0 | 14 | |
| STSD-3 | 12 | 82 | 2730 | 210 | 0 | 8 | |
| STSD-4 | 10 | 77 | 1520 | 90 | 0 | 9 | |
| Pb (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 10 | 47 | 82 | 5 | 0 | 3 | |
| LKSD-2 | 10 | 47 | 44 | 4 | 0 | 3 | |
| LKSD-3 | 10 | 48 | 29 | 3 | 0 | 4 | |
| LKSD-4 | 10 | 44 | 91 | 6 | 0 | 5 | |
| STSD-1 | 10 | 48 | 35 | 3 | 0 | 2 | |
| STSD-2 | 9 | 45 | 86 | 4 | 0 | 3 | |
| STSD-3 | 11 | 49 | 40 | 3 | 0 | 2 | |
| STSD-4 | 9 | 44 | 16 | 3 | 0 | 3 | |
| La (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 10 | 73 | 16 | 2 | 0 | 0 | |
| LKSD-2 | 9 | 72 | 68 | 6 | 0 | 6 | |
| LKSD-3 | 9 | 72 | 52 | 3 | 0 | 9 | |
| LKSD-4 | 10 | 76 | 28 | 2 | 0 | 5 | |
| STSD-1 | 12 | 104 | 30 | 3 | 0 | 5 | |
| STSD-2 | 12 | 98 | 59 | 6 | 0 | 2 | |
| STSD-3 | 12 | 84 | 39 | 3 | 0 | 6 | |
| STSD-4 | 12 | 97 | 24 | 3 | 0 | 0 | |
| Mo (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 12 | 68 | 10 | 2 | 0 | 7 | |
| LKSD-2 | 13 | 88 | <5 | - | 54 | - | |
| LKSD-3 | 13 | 81 | <5 | - | 58 | - | |
| LKSD-4 | 13 | 89 | <5 | - | 33 | - | |
| STSD-1 | 15 | 119 | <5 | - | 64 | - | |
| STSD-2 | 14 | 102 | 13 | 2 | 0 | 6 | |
| STSD-3 | 14 | 94 | 6 | 2 | 0 | 2 | |
| STSD-4 | 13 | 103 | <5 | - | 44 | - | |
| Rb (ppm) | | | | | | | |
| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers | |
| LKSD-1 | 11 | 73 | 24 | 7 | 0 | 6 | |
| LKSD-2 | 10 | 68 | 85 | 10 | 0 | 11 | |
| LKSD-3 | 11 | 73 | 78 | 10 | 0 | 6 | |
| LKSD-4 | 11 | 75 | 28 | 10 | 0 | 2 | |
| STSD-1 | 13 | 107 | 30 | 7 | 0 | 6 | |
| STSD-2 | 13 | 102 | 104 | 10 | 0 | 3 | |
| STSD-3 | 13 | 104 | 68 | 11 | 0 | 1 | |
| STSD-4 | 13 | 107 | 39 | 6 | 0 | 5 | |

Table 3 (Cont'd.). "Total" elements

S (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 34 | 1.57 | 0.13 | 0 | 4 |
| LKSD-2 | 5 | 42 | 0.14 | 0.04 | 0 | 0 |
| LKSD-3 | 5 | 42 | 0.14 | 0.03 | 0 | 0 |
| LKSD-4 | 4 | 34 | 0.99 | 0.09 | 0 | 4 |
| STSD-1 | 5 | 41 | 0.18 | 0.05 | 0 | 1 |
| STSD-2 | 5 | 40 | 0.06 | 0.01 | 0 | 2 |
| STSD-3 | 5 | 42 | 0.14 | 0.04 | 0 | 0 |
| STSD-4 | 5 | 42 | 0.09 | 0.03 | 0 | 0 |

Sb (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 46 | 1.2 | 0.1 | 0 | 6 |
| LKSD-2 | 6 | 45 | 1.1 | 0.1 | 0 | 7 |
| LKSD-3 | 6 | 47 | 1.3 | 0.1 | 0 | 5 |
| LKSD-4 | 5 | 48 | 1.7 | 0.1 | 0 | 4 |
| STSD-1 | 8 | 82 | 3.3 | 0.3 | 0 | 4 |
| STSD-2 | 8 | 76 | 4.8 | 0.4 | 0 | 2 |
| STSD-3 | 8 | 75 | 4.0 | 0.4 | 0 | 3 |
| STSD-4 | 8 | 83 | 7.3 | 0.7 | 0 | 1 |

Sc (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 10 | 63 | 9 | 2 | 0 | 2 |
| LKSD-2 | 9 | 65 | 13 | 2 | 0 | 5 |
| LKSD-3 | 9 | 64 | 13 | 2 | 0 | 9 |
| LKSD-4 | 10 | 70 | 7 | 1 | 0 | 3 |
| STSD-1 | 10 | 93 | 14 | 2 | 0 | 8 |
| STSD-2 | 11 | 84 | 16 | 2 | 0 | 8 |
| STSD-3 | 11 | 80 | 13 | 2 | 0 | 2 |
| STSD-4 | 11 | 83 | 14 | 2 | 0 | 7 |

Sm (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 42 | 4 | 0.5 | 0 | 5 |
| LKSD-2 | 6 | 46 | 11 | 1.1 | 0 | 6 |
| LKSD-3 | 6 | 50 | 8 | 0.6 | 0 | 5 |
| LKSD-4 | 6 | 48 | 5 | 0.9 | 0 | 7 |
| STSD-1 | 8 | 75 | 6 | 0.7 | 0 | 8 |
| STSD-2 | 8 | 66 | 8 | 0.8 | 0 | 8 |
| STSD-3 | 8 | 59 | 7 | 0.8 | 0 | 5 |
| STSD-4 | 8 | 65 | 5 | 0.5 | 0 | 6 |

Sn (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 3 | 24 | 16 | 4 | 0 | 0 |
| LKSD-2 | 3 | 22 | 5 | 2 | 0 | 2 |
| LKSD-3 | 3 | 21 | 3 | 2 | 0 | 3 |
| LKSD-4 | 3 | 19 | 5 | 1 | 0 | 5 |
| STSD-1 | 3 | 22 | 4 | 1 | 0 | 2 |
| STSD-2 | 3 | 20 | 5 | 1 | 0 | 4 |
| STSD-3 | 3 | 21 | 4 | 2 | 0 | 3 |
| STSD-4 | 3 | 22 | 2 | 1 | 1 | 2 |

Sr (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 39 | 250 | 53 | 0 | 0 |
| LKSD-2 | 6 | 38 | 220 | 41 | 0 | 1 |
| LKSD-3 | 6 | 38 | 240 | 42 | 0 | 1 |
| LKSD-4 | 7 | 37 | 110 | 38 | 0 | 0 |
| STSD-1 | 7 | 39 | 170 | 42 | 0 | 0 |
| STSD-2 | 6 | 37 | 400 | 65 | 0 | 1 |
| STSD-3 | 7 | 39 | 230 | 52 | 0 | 0 |
| STSD-4 | 5 | 36 | 350 | 60 | 0 | 1 |

Ta (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 2 | 19 | 0.3 | 0.03 | 0 | 2 |
| LKSD-2 | 4 | 41 | 0.8 | 0.08 | 0 | 5 |
| LKSD-3 | 4 | 47 | 0.7 | 0.10 | 1 | 2 |
| LKSD-4 | 2 | 25 | 0.4 | 0.04 | 0 | 4 |
| STSD-1 | 4 | 55 | 0.4 | 0.12 | 0 | 2 |
| STSD-2 | 7 | 70 | 1.6 | 0.20 | 0 | 8 |
| STSD-3 | 6 | 54 | 0.9 | 0.10 | 0 | 4 |
| STSD-4 | 6 | 65 | 0.6 | 0.16 | 4 | 0 |

Tb (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 37 | 0.6 | 0.2 | 5 | 0 |
| LKSD-2 | 5 | 38 | 1.4 | 0.2 | 0 | 4 |
| LKSD-3 | 5 | 40 | 1.0 | 0.1 | 0 | 5 |
| LKSD-4 | 4 | 41 | 1.2 | 0.7 | 2 | 0 |
| STSD-1 | 7 | 61 | 1.2 | 0.3 | 1 | 12 |
| STSD-2 | 7 | 62 | 1.3 | 0.2 | 0 | 2 |
| STSD-3 | 7 | 51 | 1.1 | 0.2 | 0 | 3 |
| STSD-4 | 7 | 57 | 0.8 | 0.2 | 1 | 4 |

Th (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 9 | 62 | 2.2 | 0.3 | 1 | 9 |
| LKSD-2 | 9 | 70 | 13.4 | 1.0 | 0 | 6 |
| LKSD-3 | 9 | 67 | 11.4 | 0.7 | 0 | 12 |
| LKSD-4 | 9 | 70 | 5.1 | 0.7 | 0 | 9 |
| STSD-1 | 11 | 100 | 3.7 | 0.5 | 0 | 7 |
| STSD-2 | 12 | 96 | 17.2 | 1.3 | 0 | 12 |
| STSD-3 | 10 | 75 | 8.5 | 0.7 | 0 | 11 |
| STSD-4 | 11 | 89 | 4.3 | 0.4 | 1 | 6 |

Ti (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 11 | 85 | 3010 | 260 | 0 | 9 |
| LKSD-2 | 12 | 78 | 3460 | 450 | 2 | 6 |
| LKSD-3 | 11 | 71 | 3330 | 330 | 0 | 4 |
| LKSD-4 | 13 | 84 | 2270 | 470 | 0 | 0 |
| STSD-1 | 9 | 65 | 4600 | 370 | 0 | 8 |
| STSD-2 | 12 | 76 | 4870 | 400 | 0 | 8 |
| STSD-3 | 11 | 75 | 4400 | 390 | 0 | 8 |
| STSD-4 | 10 | 73 | 4530 | 270 | 0 | 9 |

U (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 10 | 74 | 9.7 | 1.0 | 0 | 7 |
| LKSD-2 | 10 | 84 | 7.6 | 0.9 | 0 | 2 |
| LKSD-3 | 10 | 80 | 4.6 | 0.5 | 0 | 9 |
| LKSD-4 | 9 | 78 | 31.0 | 1.8 | 0 | 11 |
| STSD-1 | 12 | 104 | 8.0 | 0.6 | 0 | 13 |
| STSD-2 | 11 | 95 | 18.6 | 1.0 | 0 | 13 |
| STSD-3 | 12 | 90 | 10.5 | 0.9 | 0 | 8 |
| STSD-4 | 12 | 102 | 3.0 | 0.5 | 1 | 3 |

V (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 10 | 62 | 50 | 5 | 0 | 3 |
| LKSD-2 | 11 | 64 | 77 | 8 | 0 | 2 |
| LKSD-3 | 9 | 58 | 82 | 8 | 0 | 8 |
| LKSD-4 | 11 | 57 | 49 | 8 | 0 | 7 |
| STSD-1 | 10 | 58 | 98 | 15 | 1 | 4 |
| STSD-2 | 9 | 62 | 101 | 10 | 0 | 2 |
| STSD-3 | 10 | 63 | 134 | 18 | 0 | 2 |
| STSD-4 | 9 | 62 | 106 | 10 | 0 | 0 |

W (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 12 | 70 | <4 | - | 50 | - |
| LKSD-2 | 11 | 84 | <4 | - | 62 | - |
| LKSD-3 | 11 | 90 | <4 | - | 67 | - |
| LKSD-4 | 11 | 90 | <4 | - | 67 | - |
| STSD-1 | 15 | 118 | <4 | - | 94 | - |
| STSD-2 | 11 | 103 | 7 | 2 | 1 | 4 |
| STSD-3 | 9 | 68 | <4 | - | 14 | - |
| STSD-4 | 13 | 106 | <4 | - | 91 | - |

Y (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 23 | 19 | 9 | 0 | 3 |
| LKSD-2 | 3 | 22 | 44 | 7 | 0 | 4 |
| LKSD-3 | 4 | 24 | 30 | 10 | 0 | 2 |
| LKSD-4 | 4 | 26 | 23 | 10 | 0 | 0 |
| STSD-1 | 4 | 26 | 42 | 11 | 0 | 0 |
| STSD-2 | 3 | 22 | 37 | 6 | 0 | 4 |
| STSD-3 | 4 | 26 | 36 | 9 | 0 | 1 |
| STSD-4 | 4 | 25 | 24 | 8 | 0 | 1 |

Yb (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 46 | 2.0 | 0.3 | 1 | 7 |
| LKSD-2 | 8 | 54 | 4.0 | 0.5 | 0 | 8 |
| LKSD-3 | 7 | 54 | 2.7 | 0.4 | 0 | 7 |
| LKSD-4 | 7 | 47 | 2.0 | 0.2 | 0 | 4 |
| STSD-1 | 11 | 86 | 4.0 | 0.8 | 0 | 7 |
| STSD-2 | 10 | 76 | 3.7 | 0.6 | 1 | 8 |
| STSD-3 | 9 | 63 | 3.4 | 0.5 | 1 | 12 |
| STSD-4 | 9 | 70 | 2.6 | 0.6 | 0 | 3 |

Table 3 (Cont'd.). "Total" elements

Zn (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 12 | 75 | 331 | 22 | 0 | 3 |
| LKSD-2 | 13 | 73 | 209 | 18 | 0 | 5 |
| LKSD-3 | 13 | 71 | 152 | 14 | 2 | 7 |
| LKSD-4 | 12 | 73 | 184 | 19 | 0 | 3 |
| STSD-1 | 12 | 76 | 178 | 16 | 0 | 2 |
| STSD-2 | 13 | 73 | 246 | 21 | 0 | 3 |
| STSD-3 | 13 | 75 | 204 | 16 | 0 | 3 |
| STSD-4 | 10 | 59 | 107 | 12 | 0 | 5 |

Zr (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 36 | 134 | 12 | 0 | 1 |
| LKSD-2 | 6 | 37 | 254 | 33 | 0 | 0 |
| LKSD-3 | 5 | 35 | 178 | 16 | 0 | 2 |
| LKSD-4 | 5 | 36 | 105 | 17 | 0 | 1 |
| STSD-1 | 6 | 35 | 218 | 34 | 0 | 2 |
| STSD-2 | 5 | 33 | 185 | 9 | 0 | 4 |
| STSD-3 | 6 | 36 | 196 | 25 | 0 | 1 |
| STSD-4 | 5 | 36 | 190 | 16 | 0 | 1 |

Table 4. Partial extraction elements; concentrated HNO₃ - concentrated HCl

Ag (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 9 | 54 | 0.6 | 0.2 | 0 | 5 |
| LKSD-2 | 10 | 56 | 0.8 | 0.2 | 0 | 3 |
| LKSD-3 | 9 | 57 | 2.4 | 0.4 | 0 | 2 |
| LKSD-4 | 6 | 39 | 0.2 | 0.1 | 2 | 3 |
| STSD-1 | 11 | 68 | 0.3 | 0.1 | 0 | 2 |
| STSD-2 | 12 | 67 | 0.5 | 0.2 | 0 | 4 |
| STSD-3 | 10 | 63 | 0.4 | 0.1 | 0 | 4 |
| STSD-4 | 6 | 39 | 0.3 | 0.1 | 0 | 1 |

Co (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 11 | 50 | 9 | 1 | 0 | 12 |
| LKSD-2 | 7 | 48 | 17 | 1 | 0 | 14 |
| LKSD-3 | 9 | 50 | 30 | 2 | 0 | 11 |
| LKSD-4 | 8 | 51 | 11 | 1 | 0 | 11 |
| STSD-1 | 10 | 76 | 14 | 2 | 0 | 12 |
| STSD-2 | 9 | 70 | 17 | 1 | 0 | 16 |
| STSD-3 | 10 | 73 | 14 | 1 | 0 | 15 |
| STSD-4 | 6 | 66 | 11 | 1 | 0 | 18 |

Fe (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 8 | 43 | 1.8 | 0.3 | 0 | 2 |
| LKSD-2 | 8 | 45 | 3.5 | 0.3 | 0 | 0 |
| LKSD-3 | 8 | 43 | 3.5 | 0.3 | 0 | 2 |
| LKSD-4 | 8 | 45 | 2.7 | 0.3 | 0 | 0 |
| STSD-1 | 12 | 75 | 3.5 | 0.2 | 0 | 2 |
| STSD-2 | 12 | 74 | 4.1 | 0.4 | 0 | 1 |
| STSD-3 | 12 | 69 | 3.4 | 0.1 | 0 | 8 |
| STSD-4 | 10 | 71 | 2.6 | 0.3 | 0 | 2 |

As (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 11 | 48 | 30 | 6 | 0 | 4 |
| LKSD-2 | 11 | 51 | 9 | 3 | 0 | 1 |
| LKSD-3 | 11 | 50 | 23 | 6 | 0 | 2 |
| LKSD-4 | 11 | 51 | 12 | 3 | 0 | 0 |
| STSD-1 | 11 | 51 | 17 | 5 | 0 | 1 |
| STSD-2 | 11 | 50 | 32 | 8 | 0 | 0 |
| STSD-3 | 11 | 52 | 22 | 6 | 0 | 0 |
| STSD-4 | 9 | 46 | 11 | 3 | 0 | 2 |

Cr (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 47 | 12 | 2 | 0 | 3 |
| LKSD-2 | 7 | 49 | 29 | 3 | 0 | 3 |
| LKSD-3 | 7 | 50 | 51 | 5 | 0 | 2 |
| LKSD-4 | 7 | 46 | 21 | 2 | 0 | 6 |
| STSD-1 | 7 | 50 | 28 | 3 | 0 | 2 |
| STSD-2 | 8 | 51 | 50 | 9 | 0 | 0 |
| STSD-3 | 8 | 52 | 34 | 6 | 0 | 0 |
| STSD-4 | 7 | 50 | 30 | 6 | 0 | 0 |

Hg (ppb)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 7 | 40 | 110 | 15 | 0 | 6 |
| LKSD-2 | 7 | 42 | 160 | 19 | 0 | 4 |
| LKSD-3 | 7 | 45 | 290 | 36 | 0 | 1 |
| LKSD-4 | 5 | 39 | 190 | 17 | 0 | 7 |
| STSD-1 | 6 | 42 | 110 | 11 | 0 | 4 |
| STSD-2 | 7 | 44 | 46 | 10 | 0 | 2 |
| STSD-3 | 7 | 43 | 90 | 7 | 0 | 3 |
| STSD-4 | 5 | 32 | 930 | 76 | 0 | 4 |

Cd (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 13 | 79 | 1.2 | 0.3 | 0 | 9 |
| LKSD-2 | 12 | 80 | 0.8 | 0.2 | 1 | 8 |
| LKSD-3 | 11 | 75 | 0.6 | 0.3 | 2 | 3 |
| LKSD-4 | 12 | 76 | 1.9 | 0.5 | 0 | 2 |
| STSD-1 | 16 | 100 | 0.8 | 0.2 | 0 | 8 |
| STSD-2 | 14 | 97 | 0.8 | 0.3 | 0 | 11 |
| STSD-3 | 16 | 110 | 1.0 | 0.2 | 0 | 12 |
| STSD-4 | 10 | 90 | 0.6 | 0.3 | 2 | 0 |

Cu (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 14 | 82 | 44 | 5 | 0 | 0 |
| LKSD-2 | 14 | 75 | 36 | 3 | 0 | 8 |
| LKSD-3 | 14 | 77 | 34 | 3 | 0 | 6 |
| LKSD-4 | 14 | 79 | 30 | 3 | 0 | 4 |
| STSD-1 | 17 | 103 | 36 | 2 | 0 | 10 |
| STSD-2 | 17 | 106 | 43 | 3 | 0 | 5 |
| STSD-3 | 17 | 97 | 38 | 2 | 0 | 16 |
| STSD-4 | 15 | 105 | 66 | 5 | 0 | 4 |

Mn (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 9 | 54 | 460 | 60 | 0 | 1 |
| LKSD-2 | 9 | 55 | 1840 | 180 | 0 | 0 |
| LKSD-3 | 9 | 54 | 1220 | 230 | 0 | 1 |
| LKSD-4 | 9 | 54 | 430 | 30 | 0 | 1 |
| STSD-1 | 12 | 77 | 3740 | 430 | 0 | 0 |
| STSD-2 | 13 | 84 | 720 | 120 | 0 | 1 |
| STSD-3 | 12 | 69 | 2630 | 140 | 0 | 8 |
| STSD-4 | 11 | 83 | 1200 | 130 | 0 | 0 |

Table 4 (Cont'd.). Partial extraction elements; concentrated HNO₃ - concentrated HCl

Mo (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 15 | 92 | 12 | 2 | 0 | 1 |
| LKSD-2 | 9 | 68 | 2 | 0.7 | 1 | 2 |
| LKSD-3 | 11 | 80 | 2 | 0.9 | 0 | 2 |
| LKSD-4 | 12 | 83 | 2 | 0.6 | 2 | 6 |
| STSD-1 | 9 | 75 | 2 | 0.5 | 0 | 5 |
| STSD-2 | 14 | 87 | 13 | 2 | 0 | 4 |
| STSD-3 | 15 | 91 | 7 | 2 | 0 | 2 |
| STSD-4 | 8 | 73 | 2 | 0.6 | 0 | 3 |

Pb (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 14 | 79 | 84 | 10 | 0 | 4 |
| LKSD-2 | 14 | 83 | 40 | 7 | 0 | 0 |
| LKSD-3 | 14 | 78 | 26 | 5 | 0 | 5 |
| LKSD-4 | 13 | 75 | 93 | 8 | 0 | 8 |
| STSD-1 | 16 | 104 | 34 | 4 | 0 | 9 |
| STSD-2 | 17 | 109 | 66 | 7 | 0 | 2 |
| STSD-3 | 17 | 102 | 39 | 5 | 0 | 11 |
| STSD-4 | 15 | 106 | 13 | 4 | 0 | 3 |

V (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 27 | 27 | 3 | 0 | 4 |
| LKSD-2 | 8 | 30 | 48 | 10 | 0 | 1 |
| LKSD-3 | 8 | 31 | 55 | 13 | 0 | 0 |
| LKSD-4 | 8 | 31 | 32 | 10 | 0 | 0 |
| STSD-1 | 8 | 31 | 47 | 11 | 0 | 0 |
| STSD-2 | 8 | 29 | 58 | 14 | 0 | 0 |
| STSD-3 | 8 | 31 | 61 | 22 | 0 | 0 |
| STSD-4 | 6 | 27 | 51 | 19 | 0 | 0 |

Ni (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|----|-----------|----------|-----------|----------|
| LKSD-1 | 11 | 59 | 11 | 1 | 0 | 10 |
| LKSD-2 | 12 | 65 | 23 | 3 | 0 | 4 |
| LKSD-3 | 12 | 62 | 44 | 4 | 0 | 7 |
| LKSD-4 | 12 | 69 | 32 | 5 | 0 | 0 |
| STSD-1 | 15 | 92 | 18 | 3 | 0 | 7 |
| STSD-2 | 15 | 88 | 47 | 4 | 0 | 9 |
| STSD-3 | 14 | 89 | 25 | 3 | 0 | 10 |
| STSD-4 | 13 | 87 | 23 | 2 | 0 | 8 |

Sb (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 25 | 1.2 | 0.4 | 0 | 2 |
| LKSD-2 | 5 | 26 | 1.2 | 0.5 | 0 | 1 |
| LKSD-3 | 5 | 26 | 1.4 | 0.5 | 0 | 1 |
| LKSD-4 | 6 | 27 | 1.5 | 0.6 | 0 | 0 |
| STSD-1 | 5 | 26 | 2.0 | 1.0 | 0 | 1 |
| STSD-2 | 5 | 25 | 2.6 | 1.5 | 0 | 1 |
| STSD-3 | 5 | 26 | 2.4 | 1.2 | 0 | 1 |
| STSD-4 | 4 | 24 | 3.6 | 2.5 | 0 | 1 |

Zn (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|----|-----|-----------|----------|-----------|----------|
| LKSD-1 | 12 | 72 | 337 | 11 | 0 | 11 |
| LKSD-2 | 14 | 70 | 200 | 6 | 0 | 13 |
| LKSD-3 | 14 | 78 | 139 | 10 | 0 | 5 |
| LKSD-4 | 13 | 77 | 189 | 10 | 0 | 6 |
| STSD-1 | 16 | 104 | 165 | 8 | 0 | 9 |
| STSD-2 | 17 | 108 | 216 | 15 | 0 | 5 |
| STSD-3 | 17 | 105 | 192 | 11 | 0 | 8 |
| STSD-4 | 15 | 104 | 82 | 8 | 0 | 5 |

Table 5. Partial extraction elements; Dilute HNO₃ - Dilute HCl

Ag (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 26 | 0.6 | 0.2 | 0 | 0 |
| LKSD-2 | 5 | 24 | 0.8 | 0.1 | 0 | 2 |
| LKSD-3 | 5 | 25 | 2.8 | 0.3 | 0 | 1 |
| LKSD-4 | 3 | 14 | 0.2 | 0.1 | 0 | 0 |

Cu (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 43 | 44 | 2 | 0 | 1 |
| LKSD-2 | 6 | 43 | 36 | 2 | 0 | 1 |
| LKSD-3 | 6 | 44 | 34 | 2 | 0 | 0 |
| LKSD-4 | 5 | 42 | 31 | 2 | 0 | 2 |

Ni (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 44 | 12 | 2 | 0 | 0 |
| LKSD-2 | 6 | 44 | 23 | 3 | 0 | 0 |
| LKSD-3 | 6 | 42 | 46 | 4 | 0 | 2 |
| LKSD-4 | 6 | 44 | 31 | 4 | 0 | 0 |

Cd (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 42 | 1.2 | 0.1 | 0 | 2 |
| LKSD-2 | 6 | 44 | 0.6 | 0.2 | 0 | 0 |
| LKSD-3 | 5 | 34 | 0.4 | 0.2 | 0 | 0 |
| LKSD-4 | 6 | 42 | 1.9 | 0.2 | 0 | 2 |

Fe (%)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 4 | 40 | 1.8 | 0.1 | 0 | 4 |
| LKSD-2 | 6 | 43 | 3.7 | 0.5 | 0 | 1 |
| LKSD-3 | 6 | 44 | 3.6 | 0.5 | 0 | 0 |
| LKSD-4 | 6 | 44 | 2.6 | 0.3 | 0 | 0 |

Pb (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 43 | 83 | 7 | 0 | 1 |
| LKSD-2 | 6 | 43 | 34 | 4 | 0 | 1 |
| LKSD-3 | 5 | 41 | 21 | 3 | 0 | 3 |
| LKSD-4 | 6 | 43 | 91 | 6 | 0 | 1 |

Co (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 6 | 44 | 8 | 1 | 0 | 0 |
| LKSD-2 | 6 | 44 | 16 | 2 | 0 | 6 |
| LKSD-3 | 6 | 44 | 30 | 3 | 0 | 0 |
| LKSD-4 | 6 | 43 | 9 | 1 | 0 | 1 |

Mn (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 42 | 410 | 35 | 0 | 2 |
| LKSD-2 | 6 | 42 | 1840 | 65 | 0 | 2 |
| LKSD-3 | 5 | 41 | 1300 | 55 | 0 | 3 |
| LKSD-4 | 5 | 39 | 420 | 9 | 0 | 5 |

Zn (ppm)

| Sample Number | N | n | \bar{x} | σ | Qualified | Outliers |
|---------------|---|----|-----------|----------|-----------|----------|
| LKSD-1 | 5 | 42 | 335 | 18 | 0 | 2 |
| LKSD-2 | 5 | 41 | 205 | 10 | 0 | 3 |
| LKSD-3 | 4 | 40 | 151 | 5 | 0 | 4 |
| LKSD-4 | 6 | 43 | 195 | 16 | 0 | 1 |

package (e.g. Fe, Mn), they were excluded from the oxide compilation. If warranted, a second compilation, expressed as % element, involving the combined oxide and non-oxide data was made.

e.g. For % Fe₂O₃ in STSD-1, N = 6 and n = 36
For % Fe in STSD-1, N = 24 and n = 158

This restricted selection of major element data sources is a simplified version of the select laboratories method described by Abbey (1).

The minimum and maximum values for each "total" constituent in each of the two sample types are plotted in Figures 2 and 3. The straight line joining each pair of points represents the concentration range of the constituent in each sample type.

Examination of the data indicates that the inclusion of material with highly anomalous concentrations of any element has been avoided. The 5 tables contain "total" data for 44 constituents; there are 15 elements which have been obtained using a concentrated nitric acid-concentrated hydrochloric acid extraction and an additional 9 elements which have been determined only in LKSD-1, 2, 3 and 4 using a dilute nitric acid- hydrochloric acid extraction. Unfortunately there were very few data reported for the concentrated nitric acid-concentrated perchloric acid extraction. This is rather surprising since a number of laboratories have used this extraction in the past for the analysis of routine samples.

Table 6. Major and minor elements expressed as oxides (%) in TILL-1, TILL-2, TILL-3 and TILL-4

| | TILL-1 | TILL-2 | TILL-3 | TILL-4 |
|--------------------------------|--------|--------|--------|--------|
| SiO ₂ | 60.9 | 60.8 | 69.1 | 65.1 |
| Al ₂ O ₃ | 13.8 | 16.2 | 12.2 | 14.5 |
| Fe ₂ O ₃ | 6.6 | 5.1 | 3.7 | 5.3 |
| MgO | 2.1 | 1.8 | 1.7 | 1.2 |
| CaO | 2.8 | 1.3 | 2.7 | 1.3 |
| Na ₂ O | 2.6 | 2.1 | 2.6 | 2.4 |
| K ₂ O | 2.3 | 3.1 | 2.4 | 3.3 |
| MnO | 0.2 | 0.1 | 0.1 | 0.1 |
| TiO ₂ | 1.0 | 0.9 | 0.5 | 0.8 |
| P ₂ O ₅ | 0.2 | 0.2 | 0.1 | 0.2 |
| LOI(1000) | 7.3 | 8.2 | 4.6 | 5.7 |
| Sum | 99.8 | 99.8 | 99.7 | 99.9 |

CARE: The data in Tables 6, 7, and 8 are from single sources and should be considered for information only.

Some Notes on Sample Collection

When the collection of reference materials is in the planning stages, preliminary sampling of potentially suitable sites should be performed. In all cases a broad spectrum of elements should be determined. Multiple samples and analyses at the same site give a rough estimate of site homogeneity. For lake sediments, a good measure of the dry weight/wet weight ratio should be obtained in order to estimate the amount of wet material to be collected in order to produce a specific weight of dried sample. Allowances for preparation losses should be included in these calculations. For LKSD-1, there were 3480 kg of wet sediment collected which produced 205 kg of dried material, a yield of only 5.9%. This low yield had been determined on a preliminary survey and sufficient material was collected. When collecting stream sediment, soil or till samples for reference material preparation, allowances should be made for the oversize fraction if this is to be discarded. In general, the -80 mesh fraction represents approximately

Table 7. "Total" elements in TILL-1, TILL-2, TILL-3 and TILL-4

| Element | Method | TILL-1 | TILL-2 | TILL-3 | TILL-4 |
|---------|--------|--------|--------|--------|--------|
| As ppm | INAA | 17 | 24 | 83 | 107 |
| Au ppb | INAA | 17 | 3 | 9 | 5 |
| Ba ppm | INAA | 730 | 550 | 550 | 420 |
| Br ppm | INAA | 5 | 11 | 4 | 8 |
| Ce ppm | INAA | 83 | 112 | 46 | 91 |
| Co ppm | INAA | 18 | 13 | 16 | 8 |
| Cr ppm | INAA | 67 | 80 | 126 | 56 |
| Cs ppm | INAA | 1 | 12 | 2 | 13 |
| Cu ppm | ICP | 43 | 139 | 22 | 223 |
| Eu ppm | INAA | 2 | 1 | <1 | <1 |
| Hf ppm | INAA | 13 | 10 | 6 | 11 |
| La ppm | INAA | 29 | 46 | 21 | 45 |
| Li ppb | ICP | 14 | 42 | 21 | 27 |
| Mo ppm | INAA | 2 | 15 | 2 | 18 |
| Nb ppb | ICP | 12 | 20 | 9 | 14 |
| Ni ppm | ICP | 20 | 29 | 38 | 14 |
| Pb ppm | ICP | 21 | 30 | 27 | 50 |
| Sb ppm | INAA | 8 | 0.8 | 0.8 | 1.0 |
| Sc ppm | INAA | 15 | 13 | 11 | 12 |
| Sm ppm | INAA | 7 | 9 | 4 | 8 |
| Sr ppm | ICP | 239 | 124 | 258 | 97 |
| Ta ppm | INAA | 0.7 | 2 | 0.6 | 2 |
| Tb ppm | INAA | 1 | 1 | <0.5 | 1 |
| Th ppm | INAA | 6 | 18 | 5 | 18 |
| U ppm | INAA | 2 | 6 | 2 | 5 |
| W ppm | INAA | <1 | 6 | <1 | 245 |
| Y ppm | ICP | 37 | 41 | 15 | 34 |
| Yb ppm | INAA | 4 | 4 | <2 | 4 |
| Zn ppm | ICP | 91 | 121 | 52 | 66 |
| Zr ppm | ICP | 518 | 385 | 220 | 394 |

Table 8. Partial extraction elements for TILL-1, TILL-2, TILL-3 and TILL-4; Concentrated HNO₃- concentrated-HCl

| Element | Method | TILL-1 | TILL-2 | TILL-3 | TILL-4 |
|---------|--------|--------|--------|--------|--------|
| Ag ppm | AAS | 0.2 | <0.2 | 1.6 | <0.2 |
| Cd ppm | AAS | <0.2 | <0.2 | <0.2 | <0.2 |
| Hg ppb | AAS | 90. | 70. | 100. | 30. |

only 5-10% of the total sample weight. There are exceptions on both sides of this estimate.

Future Work

A third set of four potential reference materials has been prepared. This set consists of 2 soil samples and 2 till samples and are designated TILL-1, TILL-2, TILL-3, and TILL-4. In part these are intended as replacements for the CCRMP reference soil materials SOIL-1, SOIL-2, SOIL-3 and SOIL-4. Future work would consist of augmenting existing data for the eight sediment samples in order to certify these materials for as many elements as possible. In addition, if sufficient data can be acquired, the soil and till reference materials could be certified without the intermediate step of assigning provisional values, at least for the more commonly determined elements. Some preliminary data for these four samples are contained in Tables 6, 7 and 8. **Care should be exercised; these data are from single sources and should be considered for information only.**

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RESUME

L'échantillonnage et la préparation de quatre sédiments de lac et quatre sédiments de ruisseau sont décrits. Des valeurs provisoires sont présentées pour les éléments majeurs, mineurs et en traces à la fois pour

les concentrations totales et les concentrations obtenues par des extractions partielles. Les échantillons ont été préparés en quantité importante (160 à 200 kg) et ils devraient donc intéresser les analystes du sol.

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