## INTRODUCTION

A portable X-Ray Fluorescence spectrometer (pXRF) has been utilized in multiple projects to characterize the geochemistry of a suite of elements and provides results similar to fusion and 4-acid methods. The pXRF analyses can provide near-instantaneous elemental composition of sediments, with minimal sample preparation and at low cost. However, questions persist regarding data precision and accuracy.

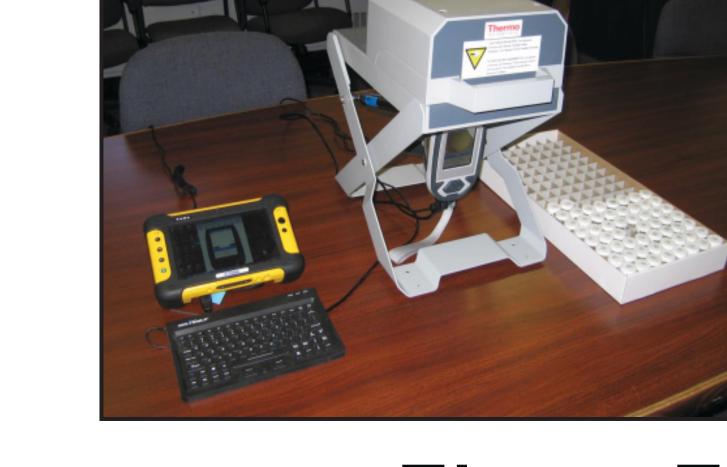
To provide a normalized sample grain-size, volume, and to minimize nugget effects in glacially-derived sediments, samples are dried and sieved to < 0.063 mm (silt + clay) prior to analysis. To ensure quality control, a number of Certified Reference Materials (CRM) and Standard Reference Materials (SRM) are analyzed with each project, and comparisons made with previously published results. For further quality control, a sub-suite of sediment samples are analyzed by ICP-MS/ES after lithium borate fusion and multi-acid digestions.

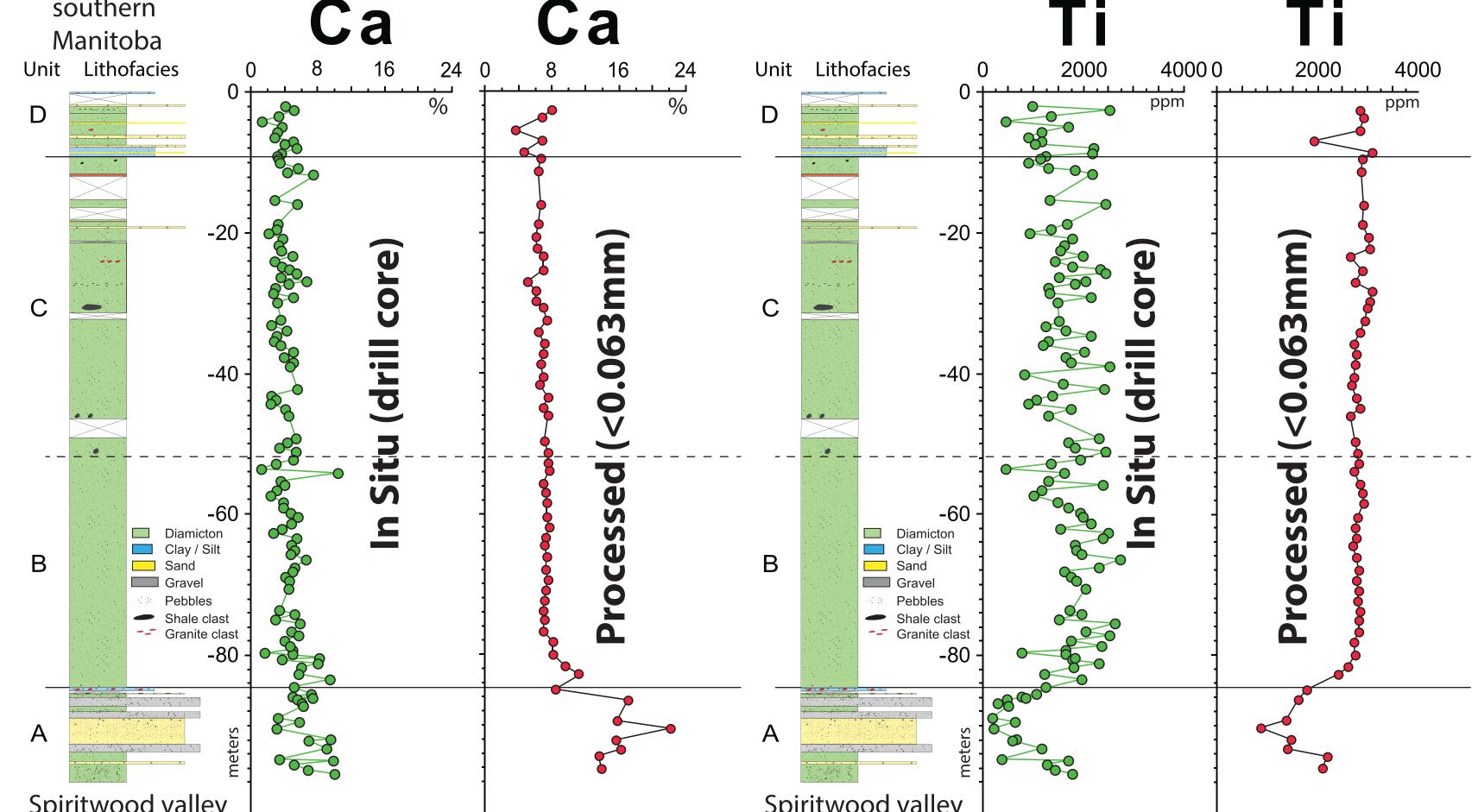
To date, this research supports the application of pXRF for the characterization of major and trace elements in glacial-derived sediments. We have found that pXRF provides reliable data for 14 elements, and can be used as a screening tool to select subsets of samples for traditional laboratory analytical methods. While routine collection of geochemical data by laboratory methods can be beyond the scope and budget of many programs, pXRF analyses can be used as an alternative analytical

# **Does the size fraction matter?**

Major grain size variation In Situ (drill core) vs. Processed (<0.063 mm)

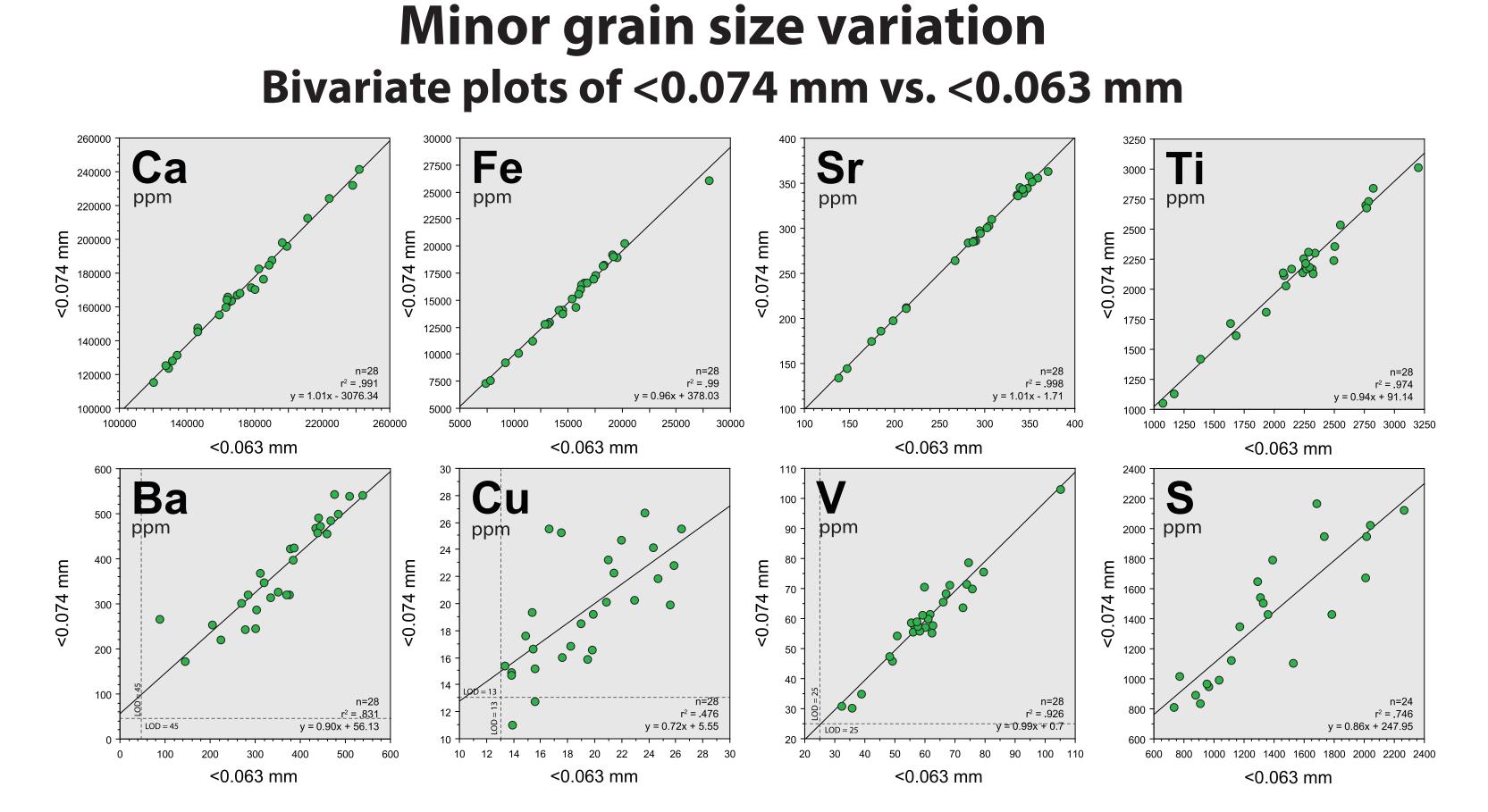


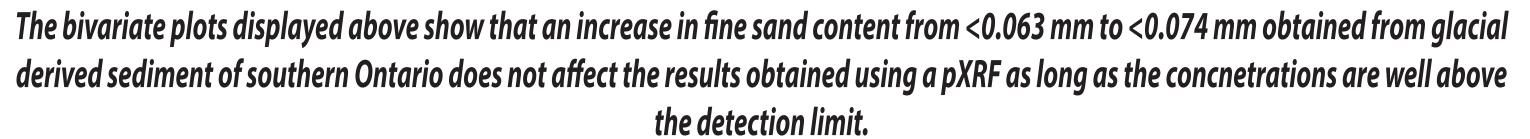




samples in this mud and pebble rich diamicton indicates that the field application of pXRF on unsieved samples will likely result in highly variable analytical results. Not only will pebbles under the surface influence analysis, but sand size particles will have significant effects on the analysis. For this reason pXRF spectrometry will not provide accurate results when pebbles and variable grain sizes are present in the sample being analysed.

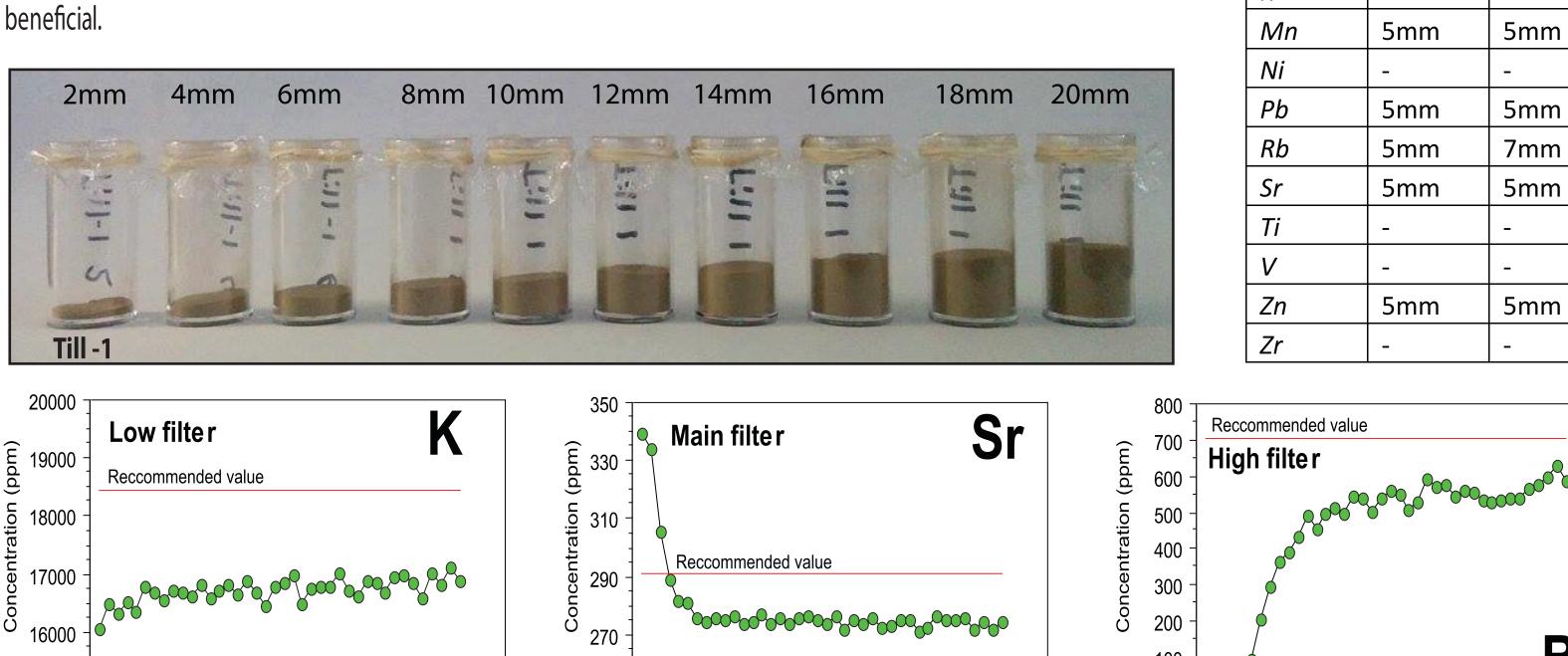
Removal of size fractions >0.063 mm provide quality data that assist in the interpretation of both visual core logging and downhole aeophysical methods.

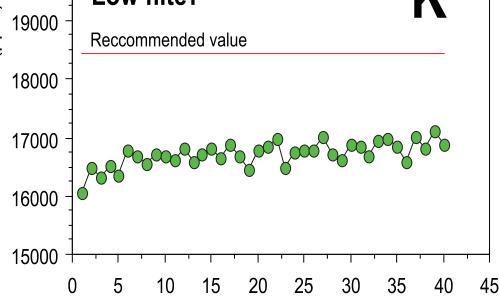




pXRF protocol for successful data acquisition relies on the assumption that the sample being analysed has an "infinite thickness". Infinite thickness corresponds to the thickness of a sample where the analyzer returns a result that will not change if the sample was thicker. Samples of less than infinite thickness will in many instances return results that are not precise.

The recommended depth of a sediment sample sieved to < 0.063 mm to obtain a consistent (precise) concentration for elements being tested in Soil mode is listed in Table 1. Blank depths indicate that the returned result was not impacted by the thickness of the sample; however for most elements post data collection to correct for poor accuracy would be

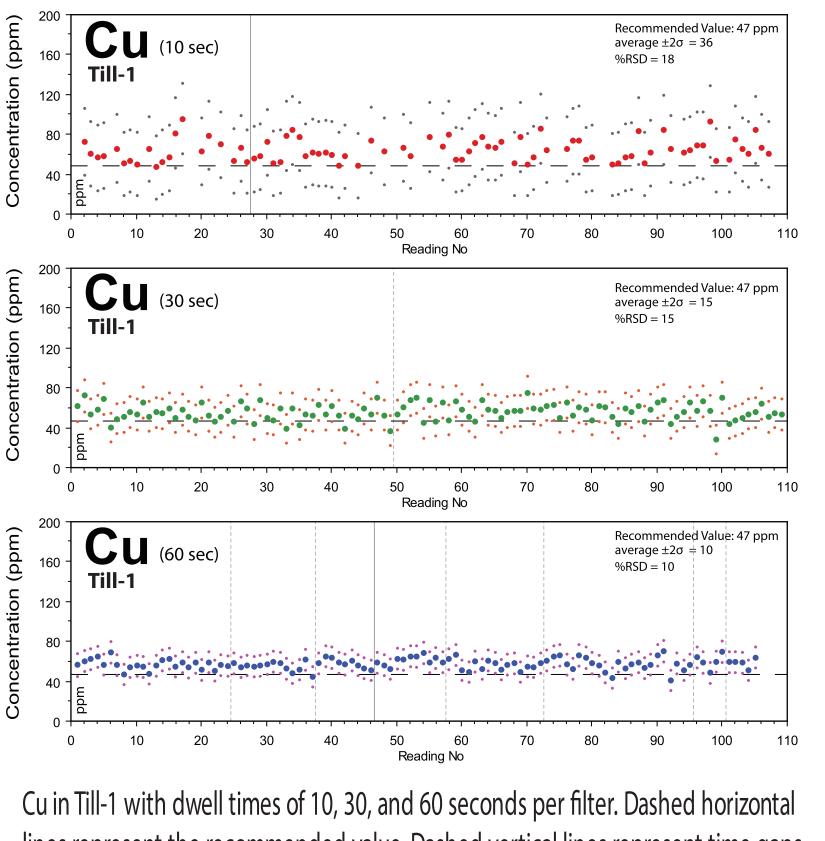




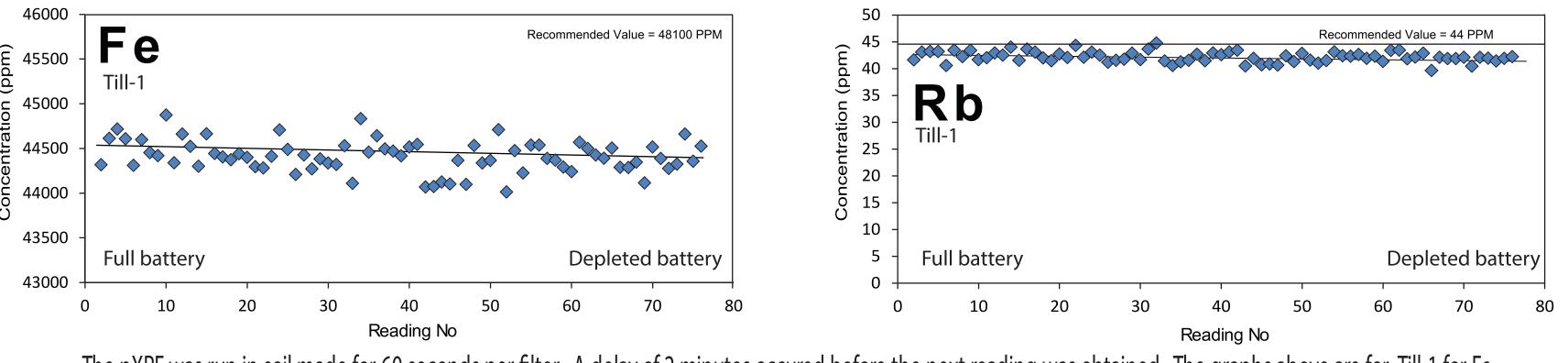
hickness of sample (mm) ain fairly consistent with increasing sample thickness include Ca. Cr. K. Ti and V. Elements concentration decreases with increasing thickness until infinite thickness is achieved (generally >6mm), include As, Cu n, and Zr. Of this group Mn has the lowest X-ray intensity and is determined using the Ka1 6.10keV line while Zr has the highest X-ray intensity and is determined using the Ka1 15.98 keV line. Ba was the only element detected where concentrations continue to increase until 20 -25mm of sample thickness is achieved. Barium is detected using the High filter and the Kα1 line of 32.70 keV.

Our results indicate that thicker samples provide a higher degree of compaction (increasing density) at the sample surface interface with the X-ray beam, allowing for more X-ray beam sediment interaction which provides more consistent results.

)ata collection below a "minimum" dwell time for an element results in a reduct of precision, whereas collection of data above this "minimum" dwell time should increase precision. For studies incorporating hundreds or thousands of analyses effective procedure in which analytical precision is not compromised. For any element present at low concentration levels, increasing the dwell time results in greater number of counts and should improve analytical precision.



lines represent the recommended value. Dashed vertical lines represent time gaps in analyses when the pXRF was shut down for <1 hour. Solid vertical lines represent a break in analyses > 24 hours. Large blue dots represent the data point while the smaller red dots represent  $\pm 2\sigma$ .



The pXRF was run in soil mode for 60 seconds per filter. A delay of 2 minutes occured before the next reading was obtained. The graphs above are for Till-1 for Fe and Rb until the battery was drained and the pXRF shut off on its own. These anaylses were carried out using both Till-1 and Till-4.

Department of Earth and Environmental Science, University of Ottawa, FSS Hall, 120 University Room 1505, Ottawa, Ontario Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario





## **QUALITY CONTROL OF pXRF SPECTROMETRY**

## A.R.R. Landon-Browne<sup>1</sup>, R.D. Knight<sup>2</sup>, B.A. Kjarsgaard<sup>2</sup>, and H.A.J. Russell<sup>2</sup>

## How much sample do I need?

## What dwell time should I use?

e graphs below display variable dwell times for Pb and Ca concentration in soil mode for CRM NIST 610. Open circles reprsent the mean value of ~100 analyses. Red and green dots represent  $\pm 2\sigma$ . The recommended value is represented by horizontal line. For Pb, all dwell times return highly accurate data however there is potential for highly variable precision for dwell time less than 30 seconds. For Ca, accuracy is not affected by dwell time, whereas precision increases with dwell time. Precision is slightly improved for dwell times beyond 30 to 40 seconds. The anomalous results at a dwell time of 80 seconds may be caused by silicon drift detector saturation, due to high count rates and increased dead time.

Table 1

5mm

5mm

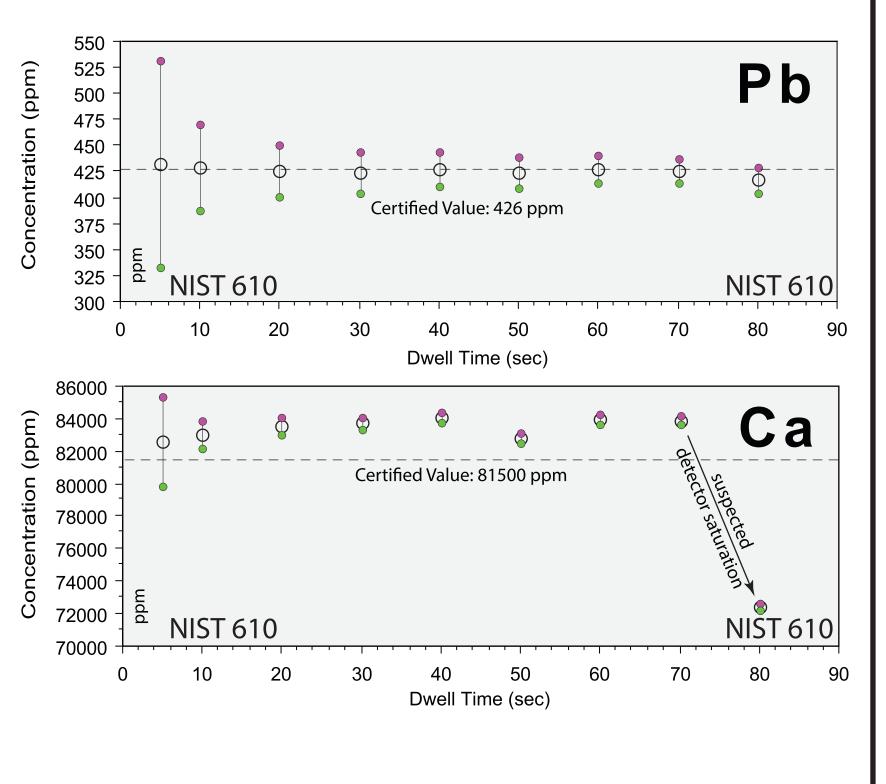
Till -1 Till -3

\_\_\_\_\_5mm

5mm

3mm 4mm

For many studies the optimal analytical dwell time ranges from 30 – 40 seconds.

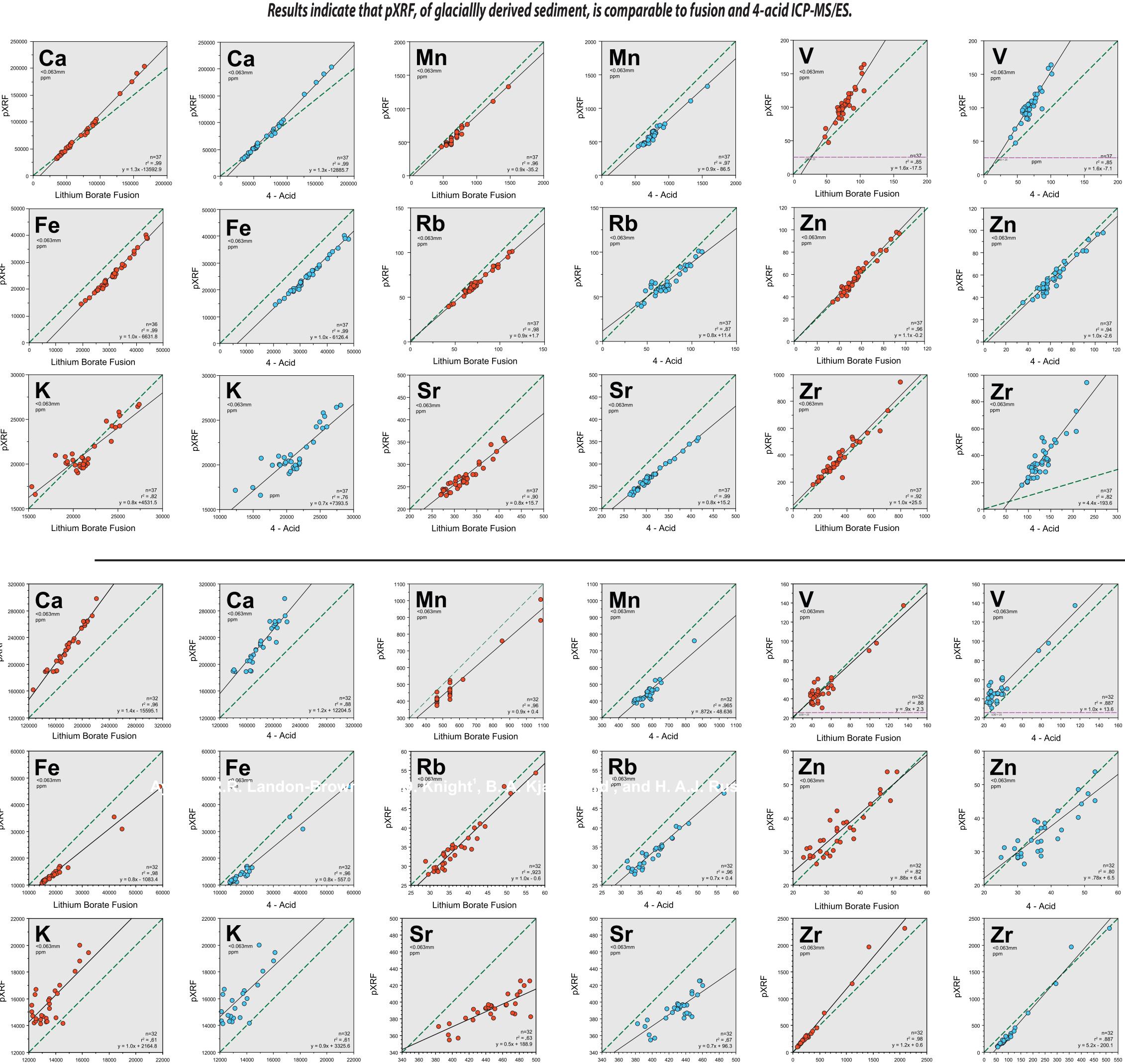


## **Does battery life affect the returned result?**

For elements that normally display a high degree of presicion, battery charge has no effect on the quality of the data.



The bivariate plots below display data aquired by pXRF compared with data obtained by lithium borate fusion (orange dots) and 4-acid (blue dots) digestions with ICP ES/MS analysis for sediments obtained from 2 boreholes located in southern Ontario and processed to < 0.063 mm. The green dashed line represents the 1:1 relationship. The black line represents a linear regression determined by the least squares approach.



## pXRF spectrometry the good, the not so good, the ugly

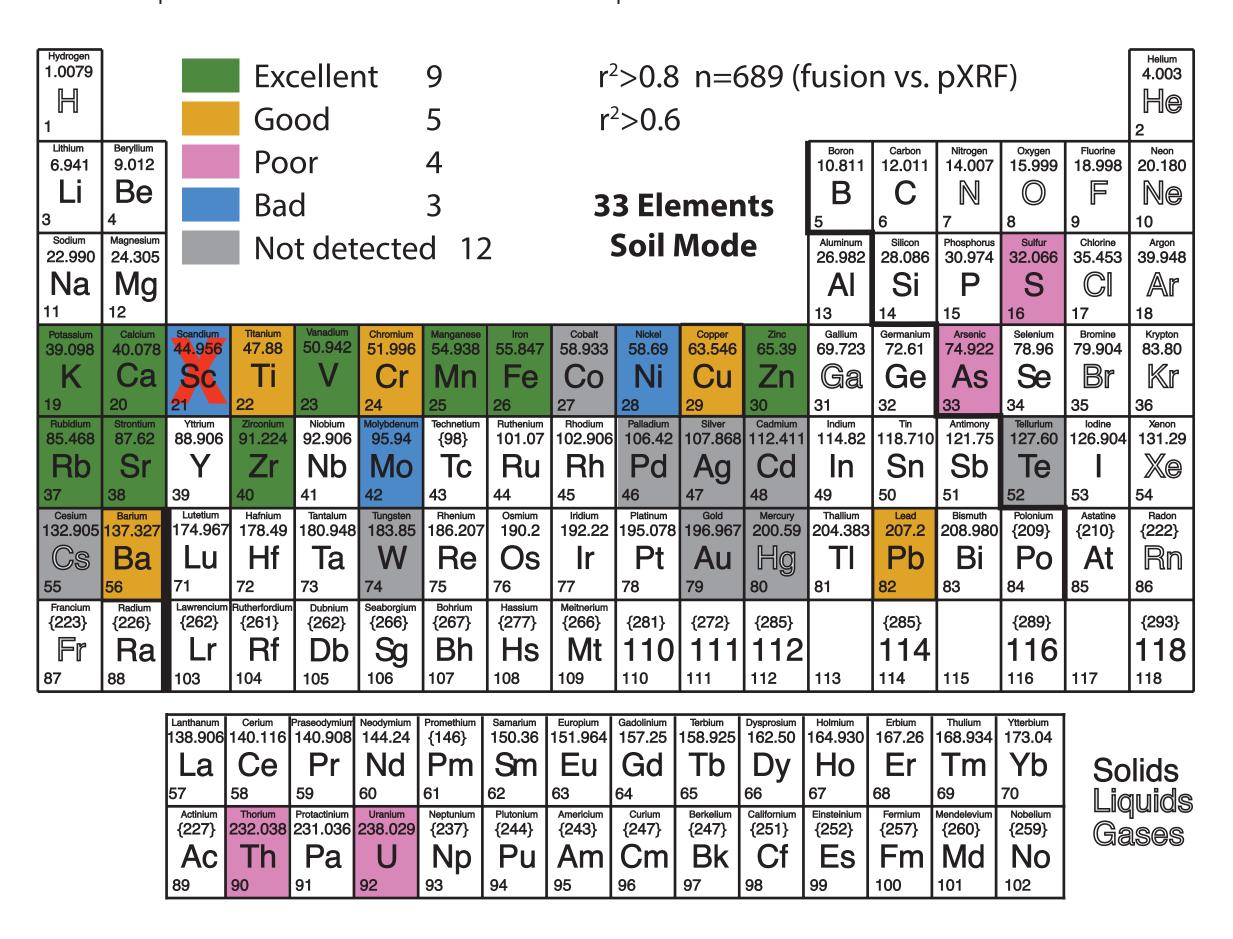
Lithium Borate Fusior

4 - Acid

4 - Acid

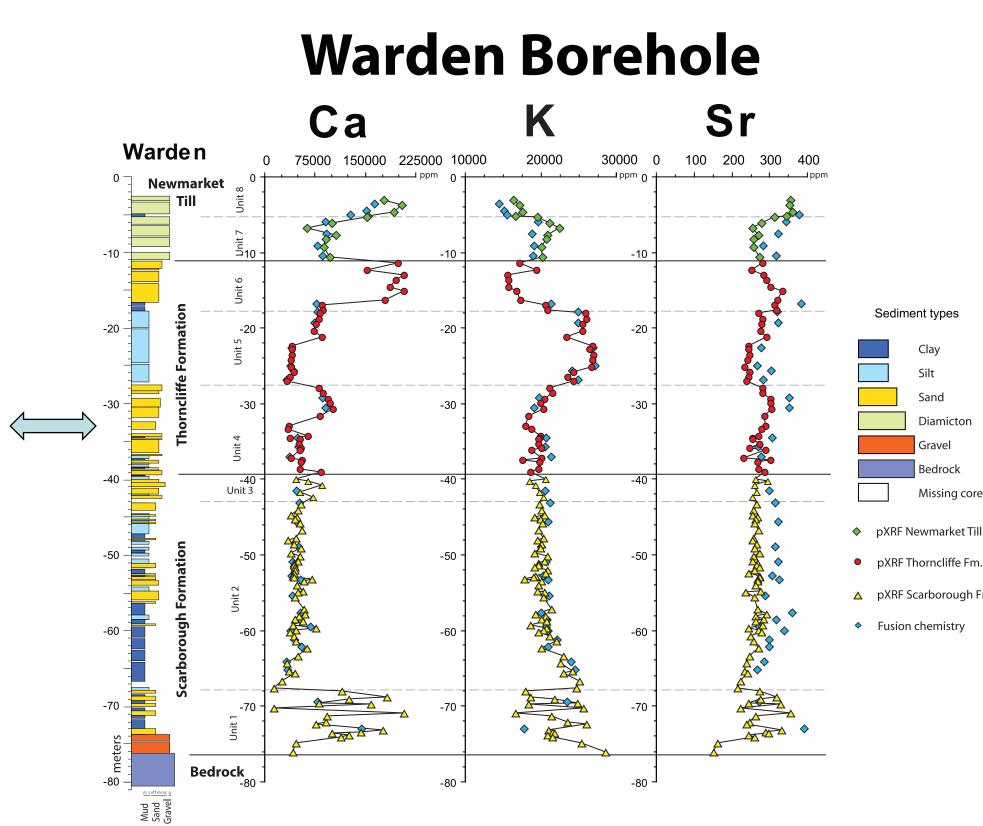
Lithium Borate Fusion

Comparing the analyses of 689 samples of sediments sieved to <0.063 mm with a pXRF and lithium borate fusion digestion and ICP ES/MS analysis we conclude that 9 elements return excellent results, 5 elements return good results, and 4 elements return poor results. Elements that are not detected (12) may be the result of samples not containing that element in sufficient concentration to be above the detection limit. This may also hold true for Ni and Mo, while Sc has an overlap with Ca and should not be identified with the pXRF.

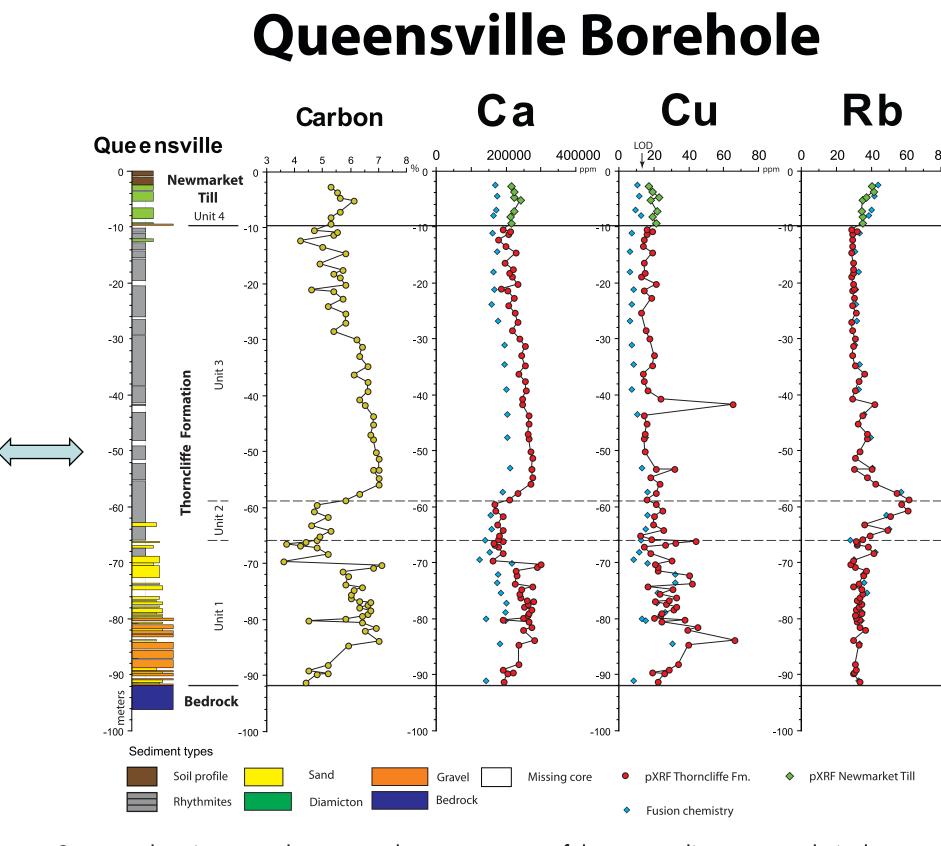


## pXRF vs Fusion and 4-acid methods

For groundwater studies, the collection of sediment geochemistry data is often beyond the scope, and budget of many programs, and is generally not included as a part of routine data collection. Portable X-ray fluorescent spectrometry has proven to be a successful tool to characterize the chemostratigraphy of glacially derived sediments, as well as improving the interpretation of downhole geophysics, micropaleontology results, and pore water geochemistry. Data collected from this method has now become a routine part of borehole studies within the Groundwater Geoscience Program at the Geological Survey of Canada.



The variation in concentration of some elements (e.g. Ca, Fe, Rb, V) between the Thorncliffe Formation and the overlying Newmarket Till indicate that the silt and clay size fraction of the upper Thorncliffe Formation was not incorporated into the matrix of the Newmarket Till.



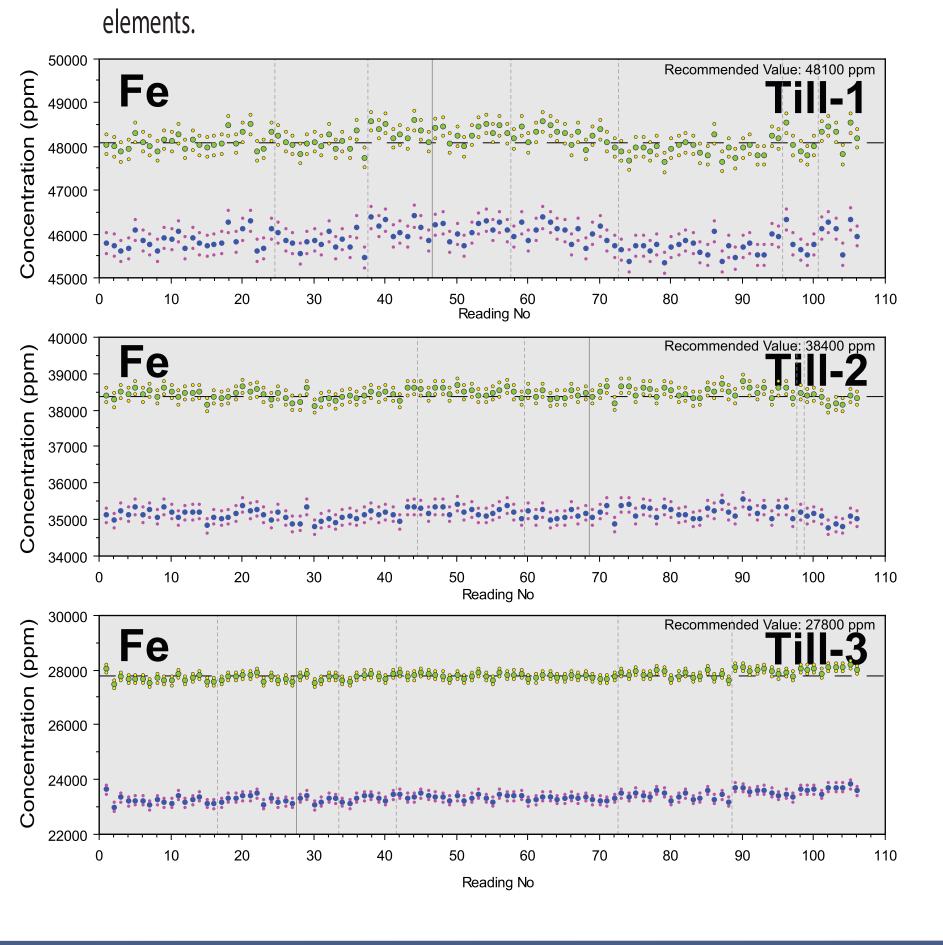
Core geochemistry trends suggest that provenance of the core sediment was relatively consistent and depositional processes did not partition sediment to impart a highly variable geochemical signal between stratigraphic units. For Ca the concentrations obtained by pXRF spectrometry mimic the % carbon content for all units.

## **Data correction for accuracy**

4 - Acid

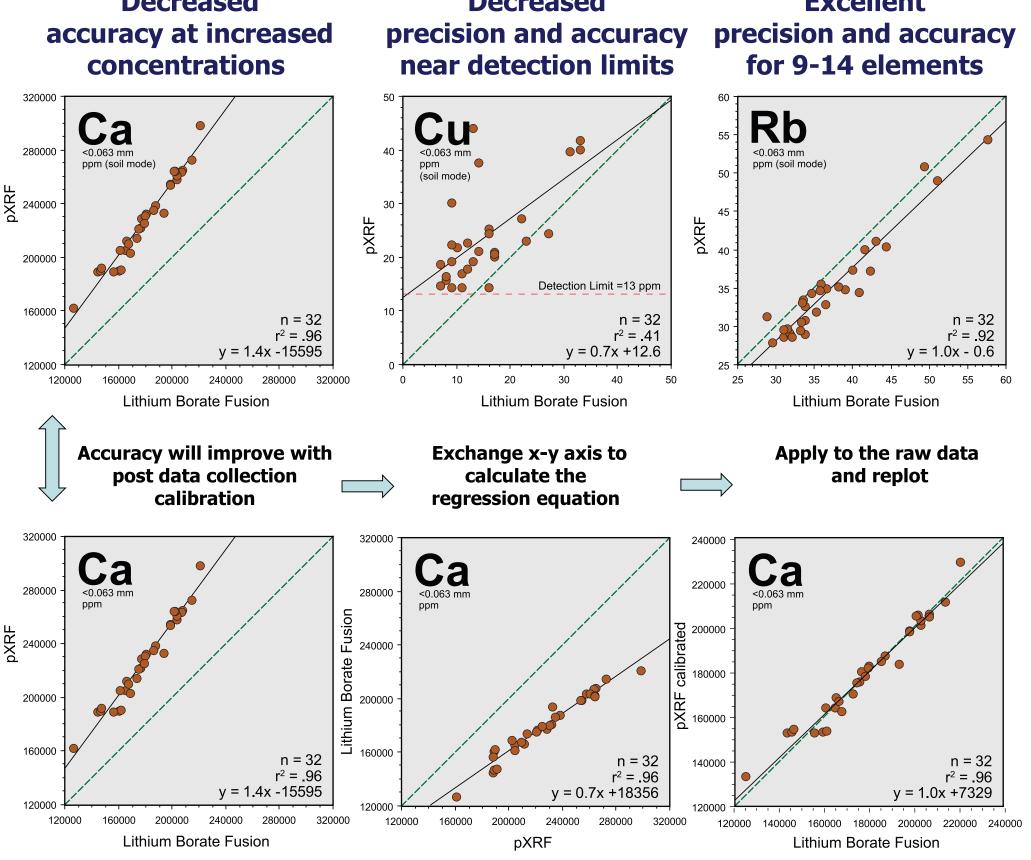
\_ithium Borate Fusior

Data correction or calibrations are typically carried out: 1) pre-collection, by entering a calibration slope and intercept into the pXRF spectrometer or; 2) post-collection, by correcting data based on analyses of standards. For the diagrams below the original raw data point for Fe in Till-1,-2, and -3 is represented by blue dots while the smaller red dots represent  $\pm 2\sigma$ . After post analysis correction based on a regression line obtained from CRM's the same data points are plotted as green and yellow dots. In general, calibration is not necessary for all



collection calibration. Cu is close to the detection limit and thus displays poor precision and accuracy. Elements that contain sufficient concentrations to be determined by soil mode gennerally do not need correction. The graphs below display how correction of the Ca data produces both precise and accurate results. Excellent

Calcium data collected from the Oueensville borehole would improve in accuracy by post



Publications in this series have not been edited; they are released as submitted by the author.

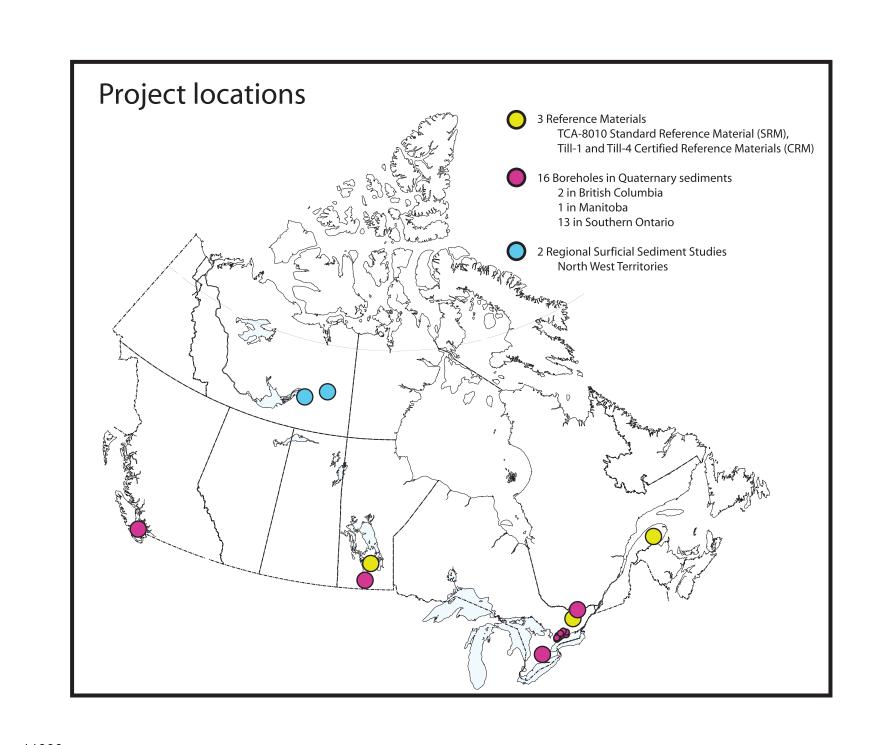
This publication is available for free download through GEOSCAN (http://geoscan.nrcan.gc.ca/).

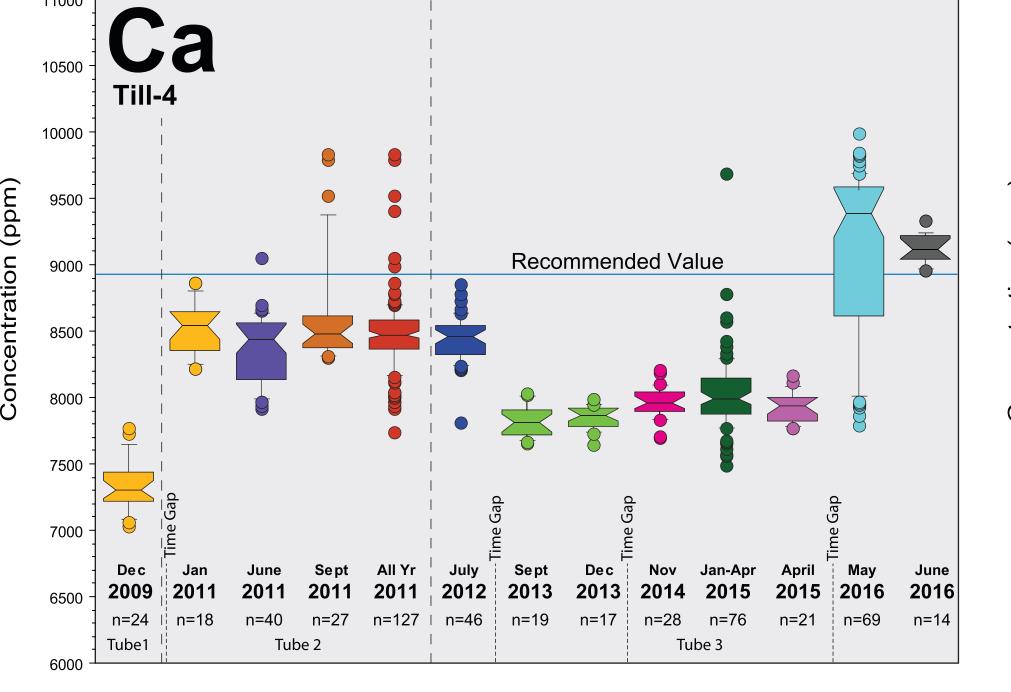
For information regarding reproduction rights, contact Natural Resources Canada at nrcan.copyrightdroitdauteur.rncan@canada.ca.

doi:10.4095/299726

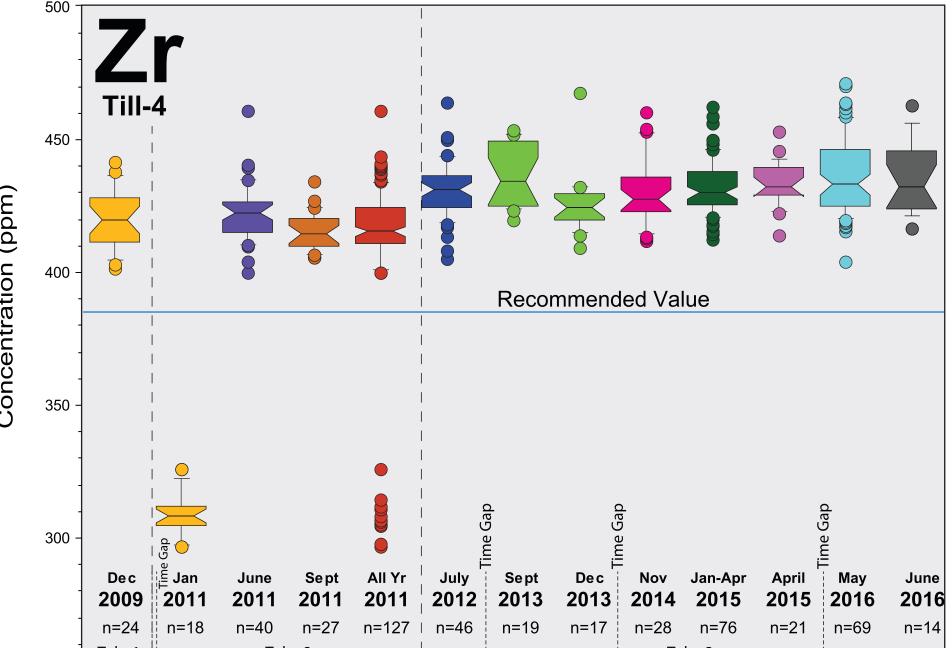
© Her Majesty the Queen in Right of Canada, as represented by the Minister of Natural Resources, 2017

### pXRF spectrometer drift: variable projects and analytical time gaps

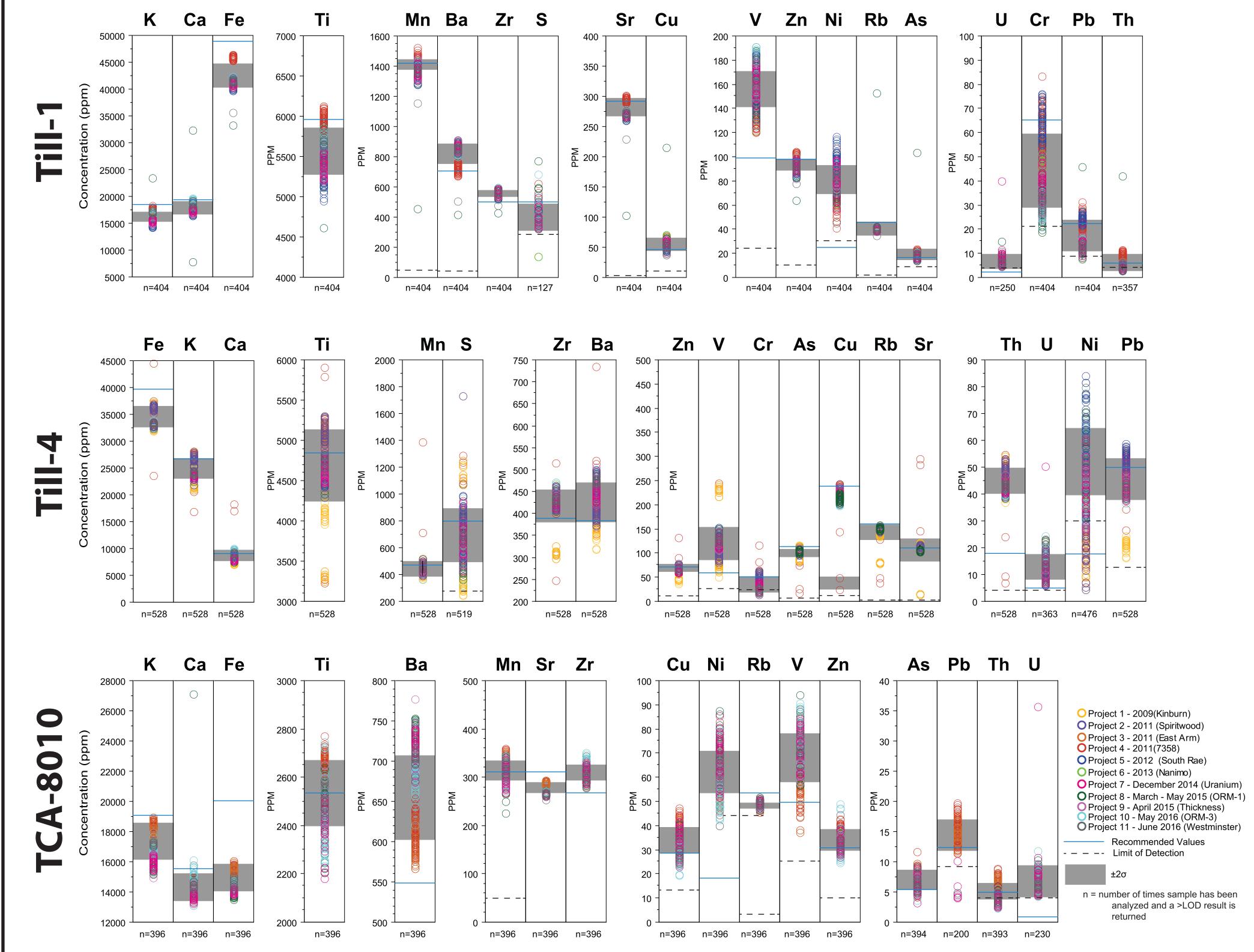




From 2009 to 2016 approximately 7000 analyses have been carried out on CRM/SRM as part of eleven different projects. For each analytical session a Teflon blank, silica blank, and a suit of standards are analyzed at the start and finish of each session, and after every ten samples. The box and whisker diagrams plotted below display the variation in Ca and Zr values obtained from Till-4. Data for individual projects is represented by a box and whisker diagram. The two mustard coloured box and whisker plots on the left side of the diagram are the same samples measured by the same instrument but with a different X-ray tube. The large variation in the light blue box and whisker plot for Ca may be the result of several operators for the pXRF during a particular project.



### pXRF spectrometer drift within and between projects



Elemental data collected from Till-1, Till-2, and TCA 8010 over eleven projects. Elements are group together using a common y-axis value. The solid horizontal blue line represents the recommended value, the dashed horizontal black line represents the limit of detection. Grey boxes represent ± 20. Variation in returned results between projects can vary substantially however variation within each project is, for many elements acceptable. Notice that occasionally there are outliers that most likely represent erroneous data.

Presented at Geological Society of America Annual Meeting and Exposition, Denver 2016 Date presented: September 2016

Recommended citation Landon-Browne, A.R.R., Knight, R.D., Kjarsgaard, B.A., and Russell, H.A.J., 2017. Quality control of pXRF spectrometry; Geological Survey of Canada, Scientific Presentation 53, 1 poster. doi:10.4095/299726

Although there is drift from project to project, for most elements there is very little drift within a project - demonstrating that samples from a given project should be analysed in as short a time frame as possible

