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Improving lithological discrimination in exploration drill-cores using portable X-ray fluorescence measurements: (1) testing three Olympus Innov-X analysers on unprepared cores

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ABSTRACT

Portable X-ray fluorescence (pXRF) analysers are increasingly popular tools for geoscientific applications, including mineral exploration. One promising application, illustrated in the companion paper, is to obtain high-spatial resolution down-hole geochemical profiles using pXRF on unprepared exploration drill-cores. However, the precision and accuracy of pXRF analysers on such samples is not well studied. We have tested three Olympus Innov-X analysers, both on a sediment standard and *in-situ* on unmineralized rock cores from volcanic and intrusive, mafic to felsic lithologies. We conclude that pXRF is quite precise for a number of elements, but not very accurate using factory calibrations. For example, the 1 σ precision of one Delta Premium analyser tested on a basaltic core, in mining plus mode, with a 60 s integration time, is better than 5% for Al, Ca, Fe, K, Mn, S, Si, Ti, Zn and Zr. The same analyser, tested on a range of volcanic and intrusive core samples, yielded the following average systematic errors: Al -23%, Ca -4%, Fe +1%, K -9%, Mg -17%, Mn -15%, P +218%, Si +4%, Ti -23%, Cu +220%, Zn +151%, Zr +17%. These systematic errors can largely be removed by the application of correction factors, which are unique to each analyser and each project. Without such corrections, the three analysers tested, including two 'identical' Delta Premium models, yield different results on the same sample. Another important finding is that within 20-cm long core samples, the effect of mineralogical heterogeneity on *in-situ* pXRF data is much larger than that of the instrument precision. Finally, with the Delta analysers, both the 'mining plus' and the 'soil' modes are needed to determine as

many elements as possible with the best data quality possible.

KEYWORDS: XRF, portable, handheld, accuracy, precision, cores

INTRODUCTION

Diamond drilling typically constitutes a major part of costs in advanced mineral exploration programs. This generates thousands of meters of rock cores during major exploration campaigns. Many exploration companies send unmineralized core samples to geochemical laboratories for whole rock analyses, in order to quantify hydrothermal alteration and improve lithological discrimination. The results of traditional laboratory geochemical analysis are normally accurate, precise, and if enough money is spent, complete in terms of the range of elements obtained. For example, one could combine wavelength-dispersive X-ray fluorescence (wdXRF) for major elements and some trace elements, with fusion ICP-MS for most trace elements. However, these destructive approaches typically have a low spatial resolution (10s of meters between samples) due to relatively high costs per sample, meaning that rapid down-hole geochemical variations will not be captured. Laboratory geochemistry also suffers from a long time between the decision to sample and the delivery of the results to the user (weeks or months).

An emerging complementary method is the use of portable X-ray fluorescence (pXRF) devices. The smallest of these are known as handheld analysers; they can detect and determine about 25 elements in approximately one minute. Spatial resolution (distance

between measurement spots) can be down to centimeters if needed. Understandably this technological advance has led to significant interest by mineral exploration companies, geological surveys and universities interested by exploration. The most popular use of pXRF analysers in mineral exploration seems to be the direct estimation of the sought-after elements, in soils or mineralized rocks (e.g. Glanzman & Closs 2007; Peter *et al.* 2009; Fajber & Simandl 2011). The analysis of non-mineralized rock samples to study hydrothermal alteration, better discriminate between lithologies, or screen samples for U-Pb dating are developing applications (e.g. Morris 2009; Gazley *et al.* 2011).

Commercial and academic geochemistry laboratories have long-established protocols for quality assurance and quality control, and the performance of laboratory instruments is generally well known (detection limits, precision, accuracy). In contrast, users of pXRF instruments may be unsure of how to evaluate the quality of their data; this is especially problematic when using pXRF analysers on unprepared (uncrushed) rocks, because no suitable standards are available for such samples.

In this paper, we evaluate the performance of three pXRF analysers, including two identical ones, on a sediment standard and on unprepared cores of unmineralized volcanic and intrusive rocks. We focus on quantifying precision and accuracy for each analyser, and on how systematic errors can be corrected. We also show that the variation in pXRF measurements due to mineralogical heterogeneity in volcanic and intrusive units is much larger than the instrumental random error for many elements. The companion paper (Ross *et al.* this volume) illustrates the usefulness of down-hole pXRF profiles for improving lithological discrimination in the Zn-Cu Matagami mining camp of Canada.

Portable XRF technology works relatively well on materials such as soils, volcanic glasses, ceramics or alloys because they are fine-grained or non-crystalline, and relatively homogeneous (Potts & West 2008; Nazaroff *et al.* 2010; Forster *et al.* 2011; Goodale *et al.* 2012). Using pXRF on rocks without sample preparation is more difficult because of mineralogical heterogeneity, grain-size influences and matrix effects (Potts *et al.* 1997; Ge 2008). The problem of mineralogical variation within the sample is critical, given that secondary X-rays originate from no more than a few mm in the sample (for heavy elements) and a few tens of μm for light elements, including Fe or Ti (Potts *et al.* 1997; Jones *et al.* 2005; Analytical Methods Committee 2008). Therefore, in general, it is recommended to perform several measurements on the same geological unit, especially if the rock is coarse-grained, and average them to improve precision and

accuracy (Potts *et al.* 1997; Forster *et al.* 2011). If one is to work on unprepared rocks, then slabs or cores are the best samples because these have a smooth surface and are free of weathering (cf. Potts *et al.* 2006).

METHODS

Instruments

INRS (Institut national de la recherche scientifique) owns identical Delta Premium analysers from Olympus Innov-X of Woburn, Massachusetts, which we will call 'Delta-A' and 'Delta-B'. They are programmed for the same list of elements. We also had an older Alpha model, from the same manufacturer, on loan over the period 2010-2011. When working on rock cores, our analysers are attached to laboratory stands placed on a table, and one of the Deltas can optionally be integrated into a multi-sensor core logger (Ross *et al.* 2011a, 2011b, 2012, submitted). Thus the instruments are not actually 'handheld' in this work.

The Deltas, when used in the analysis of geological materials, can operate in two distinct modes: 'soil' and 'mining plus'. The former is based on Compton normalization whereas the latter is based on 'fundamental parameters' (Jenkins 1999; Innov-X Systems Inc. 2010). Only the 'mining plus' mode measures the light elements Al, Mg and Si, so in practice this mode will be chosen by users requiring major element data. The soil mode is mostly suitable for trace elements, in principle. The user has no direct control on the internal (factory) instrument calibration, but corrections can be made to the reported concentrations to improve accuracy, as is discussed below. We have tested the Delta analysers in the two modes. Each mode has several beams, i.e. different tube conditions for specific lists of elements: two beams for "mining plus" and three for the soil mode.

By comparison with the newer Deltas Premiums, the Alpha model has a less advanced detector (silicon PIN vs. silicon drift), higher detection limits and lower precision for many elements, and does not detect Mg, Al and Si (and a number of other elements). All our tests with the Alpha analyser were carried out in soil mode, which has only one beam.

Alpha analyser

With the Alpha model we performed beam time, precision and accuracy tests on a sediment standard and on a core of basaltic lava from the Zn-Cu Matagami mining camp, Canada.

Beam time, precision and accuracy on a sediment standard Standard Reference Material (SRM) 2702, 'Inorganics in Marine Sediment' from the US National Institute of Standards and Technology (NIST) (Zeisler 2004) was supplied with the Alpha analyser (in a sample cup covered by thin film). We performed tests

on this material to assess the performance of the analyser on rock powders, soils or fine-grained sediments, the advantage being that a certified composition was available. The obvious disadvantage is that the composition of this material is not representative of, say, unmineralized Matagami rocks: for example, Zn is somewhat high at 485 ppm. The following integration (measurement) times, in seconds, were investigated: 10, 15, 20, 25, 30, 40, 50, 70, 90 and 120; ten repetitions were made for each integration time.

Beam time and precision on a basaltic core A precision test was performed by using the Alpha on a piece of NQ core from Matagami drill-hole BRC-08-72, at 45.94 m down-hole depth. This is a sample of relatively unaltered-looking, fine-grained, weakly amygdaloidal basalt. An area was delimited on the core surface with masking tape to ensure all pXRF measurements were taken on the same spot; the instrument did not move at all between measurements. Thirty measurements were taken in soil mode for each of the following integration times: 10 s, 20 s, 30 s, 45 s, 60 s, 90 s, and 120 s.

Accuracy on a basaltic core The accuracy of pXRF analysers on unprepared rock cores is not directly measurable in the absence of suitable standards. However we can compare traditional laboratory geochemistry with pXRF data, ideally on the very same samples. We used a cruder approach with the Alpha analyser, to get a rough approximation of accuracy without obtaining new laboratory analyses (a much better approach was used for the Deltas as explained below). A core interval several tens of meters long, which was relatively homogeneous in aspect (at dm-m scales), and in which several conventional geochemical analyses were already available, was chosen. Specifically we selected six core boxes (#1, #2, #4, #7, #8 and #11) from a basalt in drill-hole BRC-08-72, for which the composition was known. An average composition was calculated based on five of the seven laboratory analyses (the two excluded analyses turned out to be from dikes or had elevated Zr). This was our reference composition to which pXRF measurements could be compared.

We then performed pXRF measurements every 20-30 cm in soil mode with a 45 s integration time in these six core boxes, yielding 112 analyses. Eight extreme points were excluded based on comparatively much lower Fe and Ti values, suggesting they were measured in other lithologies (e.g. fine-grained dikes).

Delta analysers in the ‘mining plus’ mode

We tested the precision and accuracy of the Delta analysers in the ‘mining plus’ mode on both a sediment standard and several rock cores.

Precision and accuracy on a sediment standard SRM 2702 was tested with the two Delta analysers in the ‘mining plus’ mode. We only tested one integration time (60 s, i.e. 30 s per beam) and made 10 repetitions per analyser. The chosen time is the optimal measurement period on rocks, based on tests reported below.

Beam time and precision on rock cores The same piece of basaltic core from BRC-08-72 at 45.94 m used to test the Alpha was utilized again for a test with the Delta-A device. Investigated integration times were 10 s, 20 s, 30 s, 40 s, 50 s, 60 s, 80 s, 100 s, and 120 s; 31 consecutive measurements were made for each integration time, without moving the analyser. Each beam was used for half of the integration time. For the Delta-B device we only tested the presumed optimal 60 s measurement time on the basalt (31 consecutive measurements, 30 s per beam).

However with the Delta-B we also carried out a full beam time and precision test on an altered rhyolite, because precisions depend on elemental concentrations. The test was done with the same parameters as the Delta-A test on the basalt. This rhyolite sample is from BRC-08-72, from 610.5 to 610.7 m (the test was done on a single spot but the exact depth was not recorded).

Accuracy on rock cores and corrections The approach chosen to evaluate the accuracy of the Deltas was to compare traditional laboratory geochemistry on c. 20 cm-long pieces of non-porous core with numerous pXRF measurements performed on the very same samples. We chose seven representative NQ core samples from Matagami drill-hole BRC-08-72: basalt (box 4), andesite (box 65), gabbro (box 97), quartz gabbro (box 107), Bracemac Rhyolite (box 121), altered Watson Rhyolite (box 135), and less altered Watson Rhyolite (box 146), to cover the range of typical compositions for the Bracemac-McLeod area of the Matagami mining camp (see the companion paper for Matagami geology). We did not include massive sulfide samples for this test because of the extreme heterogeneity of such samples at mm-cm scales. For each analyser and each sample, 30 to 51 pXRF measurements were made to cover the whole core surface, depending on sample size. For each sample, the analyser was moved slightly down-core from left to right between each measurement until the end of the sample was reached; the core was then rotated by about 60° and another “line” of measurements started; the procedure repeated until the whole core surface was

covered. This means that for each analyser, slightly different measurement points were used on the same sample. But the averages should nevertheless have been the same had the analysers been calibrated in the same manner, because the effects of pXRF random errors and mineralogical variations are cancelled out by the averaging (Potts *et al.* 1997), except where disseminated sulfides are present. The averages for each sample can also be directly compared to laboratory geochemistry.

Subsequently to acquiring the pXRF data, the entire samples were crushed. Following pulverization of a representative fraction in a mild steel 'shutter box' (code RX2), laboratory analysis was performed by Activation Laboratories in Ancaster, Ontario, using wdXRF on glass disks for major oxides (code 4C) and pressed powder pellets for trace elements (code 4C1). We also analysed sulfur with a LECO instrument at INRS.

Delta analysers in soil mode

We tested the precision and accuracy of the Delta analysers in soil mode on SRM 2702. We only tested one integration time (90 s total, i.e. 30 s per beam), and made ten repetitions per analyser.

RESULTS

Alpha analyser

Beam time, precision and accuracy on a sediment standard The relative standard deviation (RSD) was calculated for each series of ten repetitions on SMR 2702 as an indication of 1σ precision. The RSDs are plotted as a function of measurement time on figure 1. The unsmooth aspect of the curves is thought to be due mostly to the low number of repetitions. As expected, the RSDs decrease substantially as measurement time is increased. For many elements, such as Zr, measuring longer than 60 s only leads to minor or no improvements in precision. For others elements, such as Zn, the RSDs continue to decrease when the measurement time is increased to the maximum of 120 s.

Therefore Table 1 summarizes the results at 120 s. This table compares the certified and reference values supplied by NIST, on the left, to the results of our test with the Alpha analyser, on the right. Cr and Cu have RSDs of 10-15%; As and Ba have RSDs between 5 and 10%; finally RSDs of 1-5% were obtained for Fe, Mn, Pb, Rb, Sr, Ti, Zn, and Zr. Other elements programmed in the analyser had higher RSDs or were not detected.

Accuracy of the pXRF data is assessed by comparing the average concentration for each element with the certified (or reference) values, for a 120 s measurement time. The difference, expressed in percentage form, is an indication of the systematic error

of the method on this SRM and appears in the right-most column of Table 1. Taking the absolute values of these differences, we get over 25% for As, Ba and Ti; between 10-25% for Cr, Cu, Mn and Zn; and better than 10% for Fe, Pb, Rb, and Sr. Unfortunately, no certified or reference value was available for Zr. It appears that for many elements, although good precision can be achieved with the Alpha analyser on this SRM, accuracy can be a problem: for example, 1σ precision is about 3% for Ti but the average concentration measured on the standard is off by 17%.

Beam time and precision on a basaltic core For the basalt sample, RSDs were calculated for each series of 30 measurements. They are plotted as a function of integration time on figure 2. The following could be quantified with a RSD better than 8% at 60 s or longer: Fe, Mn, Sr, Ti, Zn and Zr (Fig. 2). Beyond 60 s, there is not much gain in precision for these elements. In contrast, precision continues to improve for As, Ba, Cu and Pb.

Accuracy on a basaltic core Table 2 lists the five conventional geochemical analyses used to establish the reference composition of the basalt interval. Averaging these samples to get a reference composition assumes that they all belong to the same geochemical unit, and that the rock is homogenous when sampled in 10-25 cm-long core pieces. Such an assumption is reasonable for several elements, such as Fe, Ti, or Zr, given the low standard deviations and the stability of Ti and Zr concentrations with depth (Table 2). Other elements such as Mn, Sr and Zn however are weakly to strongly variable with depth, probably due to some hydrothermal alteration of the lavas, metamorphism and, for Mn, analytical uncertainty.

Table 3 contains descriptive statistics for the 104 valid pXRF measurements spread over the basalt interval. The average value for each element represents the best estimation of the basalt's composition from uncorrected pXRF measurements; these averages are further discussed below. The RSDs of these data are much larger than that of laboratory measurements in the same geological unit, except for Sr (Tables 2, 3), reflecting both the lower instrument precision and the much smaller amount of rock characterized by pXRF. A comparison of the RSDs of the pXRF data in the basalt interval with the estimated 1σ precision of the device in the same lithology (Table 3, two last rows) reveals that depending on the element, 60-90% of the variation in pXRF measurements within this lithology is apparently due to small-scale (mm-cm) variability of the cores (see also Fig. 3). This illustrates the need for averaging several pXRF measurements from the same lithology to reduce this important mineralogical heterogeneity effect.

Comparing the average values in Tables 2 and 3 for each element allows calculation of a pXRF systematic error, which is 11% for Zr, 20% for Mn, 32% for Fe, 34% for Ti and 63% for Zn (absolute values of the difference between the averages). (Strontium is too variable even at large scale (dm-m) to use in this comparison.) These rather large systematic errors can be removed from the pXRF data to improve their accuracy, by applying the following multiplication factors: Fe 0.758, Mn 1.246, Ti 0.748, Zn 0.612, and Zr 1.119, where a correction factor larger than one indicates that the Alpha analyser underestimates the element. This assumes that the intercept is zero. Correction factors are valid if a significant part of the measurement error is systematic, as suggested by Nazaroff *et al.* (2010). Figure 3 illustrates the Alpha data before and after the application of these factors. We stress again that we only used a single lithology to calculate these corrections factors, and that we did not use the ideal method of testing several pieces of core by pXRF and traditional geochemistry, so the factors must be used with great caution (and are analyser-specific).

Delta analysers in the ‘mining plus’ mode

Precision and accuracy on a sediment standard Table 4 summarizes the results of the tests performed with the two Deltas on SRM 2702. The RSDs are 3% or less for all the major elements (except Mg which is not detected) and are 5% or less with both analysers for Pb, Zn and Zr (Table 4). So in general the 1σ precision of Delta analysers in ‘mining plus’ mode on SRM 2702 is excellent for major elements and variable for trace elements.

However, the accuracy of the analysers, using the factory calibrations, is not satisfactory in general. For major elements the best performance is for Fe (4-5% systematic errors); other elements have systematic errors greater than 10% and ranging up to >200% (Table 4). For trace elements there is good agreement (errors less than 10%) between the pXRF averages and the certified concentrations for Cr and Zn. Also the Delta-A performs well on As and the Delta-B on Pb. Other elements have larger systematic errors, ranging up to disastrous for Ag (the sediment contains less than 1 ppm Ag but the Delta-A yields an average of 171 ppm). The very large systematic errors are probably due to interferences or bad calibrations; the instruments perform better on many trace elements in soil mode (see below).

We tried applying the corrections factors developed empirically for the Matagami rocks (see below) to the pXRF averages obtained on SRM 2702; this could only be done for Al, Fe, Mn and Ti (Si and Zr are not known for this SRM). For the Delta-A this greatly lowered the systematic errors for Mn and Ti,

bringing them down to +1% and -8%, respectively. For Al though, the systematic error was still -46%, and for Fe, the error actually increased slightly. With the Delta-B, applying the Matagami correction factors lowered the systematic errors for Mn and Ti to +4% and -3%, respectively, another major improvement. In contrast, for the elements Al and Fe, the errors became somewhat worse. This would seem to indicate that the information learned on analysing sediments with pXRF analysers is not directly applicable to analysing rocks, and vice versa.

It is also interesting to compare the Delta analysers to one another on SRM 2702. There are rather large differences in the uncorrected averages for many major elements, indicating that our two “identical” analysers have been calibrated differently at the factory. One extreme example is that the Delta-A underestimates potassium by 15% whereas the Delta-B overestimates it by 219% (Table 4).

Beam time and precision on rock cores The test with the Delta-A on the basalt revealed that 60 s measurements (30 s per beam) were optimal for most elements in the “mining plus” mode (Fig. 4). The following elements had RSDs of less than 5% at 60 s: Al, Ca, K, Fe, Mn, S, Si, Ti, Zn and Zr. For these elements there is no gain in precision to be obtained beyond 60 s. However precision incases at longer measurement times for elements such as Cu, P, and V.

The test with the Delta-B on the basalt at 60s integration time yielded RSDs of less than 5% for the following elements: Al, Ca, Fe, Mn, S, Si, Ti, Zn and Zr. Potassium was below the LOD with the Delta-B, although it was easily measured with the Delta-A.

The rhyolite test with the Delta-B showed again that 60 s measurements are optimal for most elements (full results available upon request). The following elements had RSDs of less than 5% at 60 s: Al, K, Fe, Mn, Si, Ti, and Zr. Calcium and sulfur were below the LOD. An element-by-element comparison of the RSDs for the basalt versus those for the altered rhyolite, at 60 s, shows that the sample containing the higher concentration yields the lower RSD (better 1σ precision). However, the effects are relatively modest, except for Mg, where reducing the concentration from 3.0% (in the altered rhyolite) to 1.9% (in the basalt) increases the RSD from 7% to 16%.

Comparison of the three analysers on the same sample Table 5 compares the average concentrations and RSDs obtained on the same basaltic core sample (BRC-08-72 at 45.94 m) for the three analysers tested. Recall that the area to be analysed was delimited with masking tape and that 30 to 31 measurements are averaged per analyser. Looking first at the RSDs, these are markedly lower for the Deltas analysers relative to the Alpha for

all elements, so instrumental precision was clearly improved by technological evolution over a few years. The more worrying information is contained in the average elemental concentrations. Although the two Deltas agree perfectly on Si in this particular sample, the differences are important for all other elements. For example, an average concentration range of 13 to 19% was obtained for iron and a range of 130 to 198 ppm was obtained for zirconium. Because we have used our two Deltas on the same research project in Matagami, it is especially important that their behavior be understood and that their data be corrected or at least leveled.

Accuracy on rock cores and corrections Results of pXRF measurements on the seven Matagami core samples are summarized in Tables 6 and 7 and illustrated for the Delta-A device only in Figures 5a to 5d (vertical axes). Analytical results from traditional geochemistry on the same samples are reported in Table 8 and illustrated in Figures 5a to 5d (horizontal axes). The mean normalized differences between pXRF averages and laboratory geochemistry are as follows for the Delta-A analyser: Al₂O₃: -23%, CaO: -4%, Fe₂O₃^T: +1%, K₂O: -9%, MgO: -17%, MnO: -15%, P₂O₅: +218%, SiO₂: +4%, TiO₂: -23%, Cu: +220%, Zn: +151%, Zr: +17%. For the Delta-B analyser, the average differences are Al₂O₃: +3%, CaO: +11%, Fe₂O₃^T: +9%, K₂O: +188%, MgO: -38%, MnO: +27%, P₂O₅: +50%, SiO₂: +30%, TiO₂: -18%, Cu: +210%, Zn: +118%, Zr: +19%. These numbers give indications of the average accuracy of the Delta analysers over a broad range of geochemical compositions. In general, the accuracies are poor, as was expected.

Comparing Tables 6 and 7 also shows that the two identical pXRF analysers do not produce comparable uncorrected average values on these samples. The differences are quite surprising: for example, the basalt, which contains 50.2% SiO₂ according to wdXRF, has averages of 54.8% SiO₂ with the Delta-A and 67.6% SiO₂ with the Delta-B. If we were to trust these numbers blindly, this sample would be classified as an andesite or even a rhyodacite/dacite based on its uncorrected pXRF silica contents on the Winchester and Floyd (1977) diagram. This further highlights the need for corrections to be made to the pXRF data.

For this purpose, two linear regressions were calculated on plots such as those of Figures 5a-5d for each element and each analyser. The first regression was forced through the origin, whereas the other was not. In cases where the determination coefficient was much better without forcing the line through the origin, the pXRF data are judged to be questionable. For the following elements, the seven samples appeared on the plots and the regression through the origin was good:

Al, Fe, Mn, Si, Ti and Zr; correction factors (Table 9) can be calculated for these elements (based on the reverse of the slopes), as applied in Figures 5e and 5f. A range of problems prevented calculation of corrections factors for other elements¹.

Causes of pXRF data scatter Figure 6 shows the uncorrected pXRF data collected with the Delta-B analyser in 'mining plus' mode for two of the 20 cm-long core samples, a basalt (top) and an altered rhyolite (bottom). The position of the analyser was changed for each measurement in order to cover the whole core surface. There is a significant amount of scatter on these plots. Comparing the standard deviation of these data to the 1 σ precision obtained on the very same samples demonstrates that most of the scatter is due to small-scale mineralogical variations. The error bars for precision are much smaller than those showing the standard deviation from the accuracy test for most elements. For example, the basalt contains an average of 189 ppm Zr (uncorrected), with a standard deviation of 30 ppm from the 51 measurements spread over the whole sample surface. But the 1 σ precision is just 5 ppm. For difficult to measure elements, such as Mg, the 1 σ precision is more comparable to the standard deviation from the accuracy test in the basalt.

Delta analysers in soil mode

Precision and accuracy on a sediment standard Table 10 contains the results of the tests on SRM 2702 with the Delta analysers in soil mode. For both analysers, RSDs are very low for major elements except for P and S. Accuracy is better than in 'mining plus' mode for K, Mn, S, and Ti, suggesting that although these are major (or minor) elements, it may be a good idea to use the soil mode to measure them.

The RSDs for trace elements in soil mode range from 1% to 23%. RSDs of 5% or less are obtained for 10-12 elements depending on the analyser. The systematic error is 10% or less for As, Co, Cu, Pb, Rb, Sr and Zn with both analysers. Although the Delta-A measures Nb perfectly in this reference material, there is a major calibration problem with the Delta-B. The systematic errors are larger for the Delta-B for a range of other elements as well. A number of trace elements have a better accuracy in soil mode (30 s per beam) than in 'mining plus' mode (30 s per beam) as is to be expected; these include Co, Cu, Pb, Sn, and V. Also the

¹ Ca, Cr, K, Mg, Ni: not enough points on the graphs due to high LODs. P: laboratory geochemistry was not accurate enough to use it. Co, V: we suspect major calibration issues with the analysers for these elements in "mining plus" mode. Cu and Zn: rare grains of disseminated sulfides resulted in very different averages on some samples for the two analysers (including one more grain of sphalerite wildly influences the average, even for 30 measurement spots).

following elements were measured in soil mode but not in 'mining plus' mode: Nb, Rb, Se, Sr, Th, U.

DISCUSSION AND CONCLUSIONS

We have performed specific tests to evaluate pXRF data quality on standards and unprepared rock cores (this article), and we have acquired a substantial amount of routine *in-situ* data on cores (see the companion paper). We conclude from this experience that using pXRF *in-situ* on rocks can be very useful for a number of geoscience applications, but limitations of the technique should be understood.

The analysers are quite precise for several elements, but because the volume of rock analysed is very small, the concentrations reported are strongly influenced by the small-scale mineralogical heterogeneity of rocks, especially for coarse-grained ones. For many elements the effect of mineralogical heterogeneity, rather than the effect of instrument precision, explains much of the scatter observed in plots made from measurements on various spots from a single piece of core. This scatter can be theoretically be diminished by averaging multiple measurements made close together.

The other important limitation of using pXRF analysers on rock cores is their generally poor accuracy, and the lack of consistency between analysers, even "identical" ones. Both these problems can largely be solved by applying empirical correction factors to the raw pXRF data, to obtain elemental averages that are closer to traditional laboratory geochemistry. But in the absence of suitable standards, to obtain the correction factors, a suite of representative samples must be selected for each project and their composition determined by both pXRF and laboratory geochemistry.

Finally, with the Delta analysers from Olympus Innov-X, both the 'mining plus' and the soil modes are needed to get as many elements as possible with the best data quality possible. So a time-saving strategy when acquiring high-spatial resolution down-hole geochemical profiles on exploration drill cores would be to use two analysers, each dedicated to one mode only.

Comparison with other studies

Kenna *et al.* (2011) have performed a complete evaluation of an Alpha analyser on sediments using standard reference materials. They suggest that factory calibrations are not optimal and they obtained better results with external calibrations. They also note that their instrument drifted over the course of one year, significantly so for some elements.

Goodale *et al.* (2012) analysed unprepared fine-grained volcanic rocks by pXRF and compared the results for Rb, Sr and Zr with wdXRF. They used two

analysers from Olympus Innov-X: an Omega model and a Delta, both in soil mode. They conclude, as we do, that pXRF is quite precise for certain elements, but not accurate, and that different analysers give different compositional averages on the same samples.

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Tables

Table 1

Summary of the precision and accuracy test on SRM 2702 with the Alpha analyser (soil mode).

Element	Certified and reference values			pXRF data (Alpha)			Difference ^c ("accuracy")
	Type ^a	Concentration	Uncertainty ^b	Average ^c	SD ^d	RSD ^d (1 σ precision)	
		ppm	ppm	ppm	ppm	%	
As	C	45.3	1.8	34	3	9%	-26%
Ba	C	397.4	3.2	793	58	7%	99%
Bi	n.v.	n.v.	n.v.	8	3	44%	n.d. ^f
Co	C	27.76	0.58	29	16	56%	5%
Cr	C	352	22	437	45	10%	24%
Cu	R	117.7	5.6	101	10	10%	-14%
Fe	C	79100	2400	85252	1132	1%	8%
Mn	C	1757	58	1487	48	3%	-15%
Mo	R	10.8	1.6	9	5	56%	-14%
Pb	C	132.8	1.1	129	5	4%	-3%
Rb	C	127.7	8.8	126	3	2%	-1%
Sn	R	31.6	2.4	12	39	316%	-61%
Sr	C	119.7	3.0	120	3	2%	0%
Ti	C	8840	820	10376	346	3%	17%
Zn	C	485.3	4.2	434	7	2%	-11%
Zr	n.v.	n.v.	n.v.	304	7	2%	n.d. ^f

^a Types of values on the NIST certificate: C = certified; n.v. = no value; R = reference (see also Zeisler 2004).

^b Expanded uncertainty with a coverage factor of two (95% confidence); see Zeisler (2004).

^c Average concentration from ten pXRF measurements on the SRM with a 120 s integration time, in soil mode.

^d Standard deviation (SD) and relative standard deviation (RSD) of the ten pXRF measurements.

^e Difference = (average pXRF minus NIST value)/NIST value. This is an indication of systematic error or accuracy.

^f n.d. = no data.

Table 2

Five conventional geochemical analyses used to establish the reference composition of the basalt between 30.70 and 77.80 m in Matagami diamond drill-hole BRC-08-72.

Sample ^a	Box #	From m	To m	Fe ₂ O ₃ ^T %	MnO %	Sr ppm	TiO ₂ %	Zn ppm	Zr ppm
G0578651	1	30.80	31.00	16.7	0.20	97.2	2.01	137.3	131.0
549636	2	36.0	36.1	16.1	0.20	59	2.1	135	120
549637	7	57.4	57.55	16.4	0.23	133	2.18	122	131
G0578654	8	61.00	61.20	17.9	0.26	340.1	2.03	164.4	128.6
G0578655	11	75.75	76.00	17.5	0.25	219.5	2.02	167.5	130.3
Mean				16.9	0.23	170	2.07	145	128
Standard deviation				0.8	0.03	112	0.07	20	5
Relative s.d.				5%	12%	66%	4%	14%	4%

^a The three samples which have numbers starting with "G" were analysed at INRS-ETE by fusion ICP-AES (Fe, Mn, Sr, Ti, Zn) and fusion ICP-MS (Zr). The other two analyses were supplied by Xstrata Zinc Canada (XRF data obtained from ALS Chemex).

Table 3

Summary of 104 valid pXRF measurements using the Alpha analyser in soil mode on basalt cores between 30.70 and 77.80 m in Matagamí diamond drill-hole BRC-08-72^a.

Element/oxide	Fe ₂ O ₃ ^T %	MnO %	Sr ppm	TiO ₂ %	Zn ppm	Zr ppm
Mean	22.3	0.18	132	2.77	237	115
Standard deviation	4.6	0.05	83	0.47	142	23
Relative s.d.	21%	25%	63%	17%	60%	20%
1σ precision ^b	2%	9%	4%	7%	10%	6%

^a See text for explanation.

^b Estimated precision of the instrument for a 45 s integration time based on the relative standard deviation of a series of 30 measurements at 45.94 m (see fig. 1).

Table 4

Summary of the precision and accuracy test on SRM 2702 with the Delta analysers, in “mining plus” mode.

Element	Certified and reference values			pXRF analysis (Delta-A)				pXRF analysis (Delta-B)			
	Type ^a	Concentration	Uncert. ^b	Average ^c	SD ^d	RSD ^d (1σ precision)	Difference ^e	Average ^c	SD ^d	RSD ^d (1σ precision)	Difference ^e
<i>Major elements in %</i>											
Al	C	8.41	0.22	3.47	0.08	2%	-59%	4.18	0.11	3%	-50%
Ca	R	0.343	0.024	0.29	0.01	2%	-16%	0.30	0.01	2%	-13%
Fe	C	7.91	0.24	7.49	0.06	1%	-5%	8.21	0.04	0%	4%
K	C	2.054	0.072	1.76	0.02	1%	-15%	6.55	0.05	1%	219%
Mg	R	0.990	0.074	<LOD	<LOD	<LOD	n.d. ^f	<LOD	<LOD	<LOD	n.d. ^f
Mn	C	0.1757	0.0058	0.14	0.00	3%	-19%	0.22	0.01	3%	24%
P	C	0.1552	0.0066	0.36	0.01	2%	130%	0.44	0.01	2%	186%
S	I	1.5	n.v.	0.93	0.02	2%	-38%	0.81	0.01	1%	-46%
Si	n.v.	n.v.	n.v.	14.35	0.11	1%	n.d.	16.53	0.10	1%	n.d.
Ti	C	0.884	0.082	0.54	0.01	1%	-38%	0.58	0.02	3%	-34%
<i>Trace elements in ppm</i>											
Ag	R	0.622	0.078	171	8	5%	27344%	<LOD	<LOD	<LOD	n.d. ^f
As	C	45.3	1.8	47	4	8%	3%	38	3	8%	-17%
Bi	n.v.	n.v.	n.v.	45	3	7%	n.d. ^f	48	2	4%	n.d. ^f
Cd	C	0.817	0.011	156	10	7%	19019%	165	7	4%	20145%
Co	C	27.76	0.58	337	37	11%	1114%	443	61	14%	1495%
Cr	C	352	22	345	31	9%	-2%	373	19	5%	6%
Cu	R	117.7	5.6	134	7	5%	14%	138	11	8%	17%
Mo	R	10.8	1.6	13	2	17%	20%	13	1	6%	20%
Ni	C	75.4	1.5	68	11	16%	-10%	58	9	16%	-23%
Pb	C	132.8	1.1	112	5	4%	-15%	129	6	4%	-3%
Sb	C	5.60	0.24	212	17	8%	3688%	205	11	5%	3555%
Sn	R	31.6	2.4	163	10	6%	415%	185	14	8%	485%
V	C	357.6	9.2	520	67	13%	45%	588	53	9%	64%
Zn	C	485.3	4.2	478	13	3%	-1%	493	7	1%	2%
Zr	n.v.	n.v.	n.v.	345	5	2%	n.d. ^f	352	5	1%	n.d. ^f

^a Types of values on the NIST certificate: C = certified; I = information; n.v. = no value; R = reference (see also Zeisler 2004).

^b Expanded uncertainty with a coverage factor of two (95% confidence); see Zeisler (2004).

^c Average concentration from ten pXRF measurements on the reference material with a 60 s integration time (30 s per beam), in mining plus mode.

^d Standard deviation (SD) and relative standard deviation (RSD) of the ten pXRF measurements.

^e Difference = (average pXRF minus NIST value)/NIST value. This is an indication of systematic error or accuracy.

^f n.d. = no data.

Table 5Comparison of three XRF analysers on the same basaltic core sample¹.

	Al	Ca	Cu	Fe	Mg ²	Mn	P	S	Si	Ti	V	Zn	Zr
<i>Elemental averages</i>													
	%	%	ppm	%	%	%	%	%	%	%	ppm	ppm	ppm
Alpha	n.d.	n.d.	25	19.1	n.d.	0.14	n.d.	n.d.	n.d.	1.7	n.d.	289	130
Delta-A	6.5	4.9	94	14.2	2.2	0.15	0.06	0.52	27.7	0.8	651	804	134
Delta-B	5.7	5.8	41	12.8	1.9	0.21	0.12	0.17	27.6	0.6	384	303	198
Difference ³	-13%	20%	-56%	-10%	-13%	37%	106%	-68%	0%	-27%	-41%	-62%	48%
<i>Relative standard deviations</i>													
Alpha	n.d.	n.d.	112%	2.4%	n.d.	7.8%	n.d.	n.d.	n.d.	6.6%	n.d.	7.2%	5.8%
Delta-A	1.3%	1.0%	10%	1.3%	17%	2.4%	15%	1.6%	1.0%	2.6%	12%	2.4%	2.2%
Delta-B	1.7%	1.1%	12%	1.1%	16%	3.2%	8.1%	3.9%	0.7%	2.9%	19%	4.0%	2.7%

Abbreviations: n.d. = no data.

1. Repeat measurements made on a core sample from BRC-08-72 at 45.94 m depth. For the Alpha, 30 measurements at 60 s in soil mode. For the two Deltas, 31 measurements at 60 s (total time) for each device in “mining plus” mode.
2. For Mg, the Delta-A reports “<LOD” nine times out of 31, whereas the Delta-B always reports values, but this element is still included in the table for comparison purposes.
3. Percent difference between the averages of Delta-B and Delta-A.

Table 6

Summary of pXRF measurements using the Delta-A analyser (“mining plus” mode) on seven core samples from Matagami diamond drill-hole BRC-08-72.

	Basalt	Andesite	Gabbro	Quartz gabbro	Bracemac Rhyolite	Altered Wat. Rhy.	Watson Rhyolite
Box nb.	4	65	97	107	121	135	146
From (m)	45.28	308.91	446.11	488.99	547.35	610.50	655.80
To (m)	45.48	309.11	446.31	489.19	547.55	610.70	656.00
Nb. meas.	50	30	31	32	31	32	51
<i>Averages*</i>							
SiO ₂	54.76	55.51	48.56	55.62	74.57	63.87	76.82
Al ₂ O ₃	9.44	10.06	9.20	10.05	6.19	10.27	7.06
Fe ₂ O ₃ ^T	16.98	21.50	15.60	16.80	9.85	10.84	9.15
MnO	0.18	0.04	0.20	0.21	0.06	0.06	0.06
MgO	<LOD	6.13	4.85	3.74	<LOD	4.83	<LOD
CaO	7.14	<LOD	10.55	6.27	<LOD	<LOD	<LOD
Na ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K ₂ O	<LOD	0.55	<LOD	<LOD	<LOD	2.11	0.81
TiO ₂	1.21	0.49	0.73	1.19	0.13	0.34	0.28
P ₂ O ₅	0.36	0.11	0.17	0.35	0.11	0.23	0.13
LOI	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	0.20	0.07	0.19	0.08	0.08	0.05	0.11
Ba	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	<LOD	456	<LOD	<LOD	280	315	<LOD
Cr	<LOD	<LOD	258	<LOD	<LOD	<LOD	<LOD
Cu	57	63	161	50	47	31	44
Ni	<LOD	<LOD	91	<LOD	<LOD	<LOD	<LOD
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	491	301	464	477	<LOD	248	164
Y	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	249	1980	226	384	184	200	141
Zr	187	77	69	170	313	867	508
<i>Relative standard deviations</i>							
SiO ₂	5%	10%	9%	4%	9%	8%	6%
Al ₂ O ₃	10%	14%	12%	7%	18%	18%	12%
Fe ₂ O ₃ ^T	9%	16%	5%	6%	31%	21%	12%
MnO	7%	15%	8%	8%	28%	19%	12%
MgO	<LOD	29%	22%	31%	<LOD	43%	<LOD
CaO	30%	<LOD	9%	5%	<LOD	<LOD	<LOD
K ₂ O	<LOD	42%	<LOD	<LOD	<LOD	32%	35%
TiO ₂	13%	12%	57%	18%	18%	20%	18%
P ₂ O ₅	13%	19%	23%	12%	41%	14%	18%
S	41%	113%	29%	22%	20%	17%	48%
Co	<LOD	16%	<LOD	<LOD	18%	15%	<LOD
Cr	<LOD	<LOD	28%	<LOD	<LOD	<LOD	<LOD
Cu	26%	100%	36%	31%	24%	12%	45%
Ni	<LOD	<LOD	14%	<LOD	<LOD	<LOD	<LOD
V	13%	15%	39%	16%	<LOD	26%	22%
Zn	19%	325%	17%	34%	39%	29%	38%
Zr	16%	21%	23%	13%	10%	17%	16%

* Major oxides (SiO₂ to P₂O₅) in percent, elemental sulfur in percent, trace elements (Ba to Zr) in ppm.
Abbreviations: LOI = loss on ignition, LOD = limit of detection, n.d. = no data.

Table 7

Summary of pXRF measurements using the Delta-B analyser (“mining plus” mode) on seven core samples from Matagami diamond drill-hole BRC-08-72.

	Basalt	Andesite	Gabbro	Quartz gabbro	Bracemac Rhyolite	Altered Wat. Rhy.	Watson Rhyolite
Box nb.	4	65	97	107	121	135	146
From (m)	45.28	308.91	446.11	488.99	547.35	610.50	655.80
To (m)	45.48	309.11	446.31	489.19	547.55	610.70	656.00
Nb. meas.	51	32	30	31	31	31	50
<i>Averages*</i>							
SiO ₂	67.56	73.44	65.63	69.67	92.54	74.36	91.50
Al ₂ O ₃	11.91	14.44	13.26	13.01	8.01	14.07	8.75
Fe ₂ O ₃ ^T	17.76	23.25	16.24	18.74	11.38	12.39	9.22
MnO	0.26	0.06	0.29	0.32	0.09	0.10	0.08
MgO	3.01	5.01	4.69	2.52	1.74	4.40	1.69
CaO	7.87	<LOD	12.70	7.21	<LOD	<LOD	<LOD
Na ₂ O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K ₂ O	<LOD	<LOD	<LOD	<LOD	<LOD	7.02	2.32
TiO ₂	1.16	0.54	0.77	1.28	0.15	0.37	0.29
P ₂ O ₅	0.33	<LOD	<LOD	0.29	<LOD	0.11	<LOD
LOI	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	0.20	0.07	0.19	0.08	0.08	0.05	0.11
Ba	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	475	707	568	506	403	505	350
Cr	<LOD	<LOD	302	<LOD	<LOD	<LOD	<LOD
Cu	56	40	159	56	43	25	44
Ni	<LOD	<LOD	59	<LOD	<LOD	<LOD	<LOD
Nb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Sr	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
V	493	303	445	529	142	247	172
Y	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zn	245	590	183	450	198	223	162
Zr	189	78	67	170	320	940	522
<i>Relative standard deviations</i>							
SiO ₂	6%	8%	4%	4%	7%	10%	8%
Al ₂ O ₃	12%	11%	6%	4%	16%	12%	11%
Fe ₂ O ₃ ^T	10%	13%	4%	5%	27%	27%	12%
MnO	7%	14%	6%	7%	24%	23%	12%
MgO	25%	20%	15%	16%	43%	39%	28%
CaO	29%	<LOD	7%	7%	<LOD	<LOD	<LOD
K ₂ O	<LOD	<LOD	<LOD	<LOD	<LOD	32%	52%
TiO ₂	12%	11%	93%	16%	16%	22%	26%
P ₂ O ₅	21%	<LOD	<LOD	22%	<LOD	37%	<LOD
S	221%	117%	138%	76%	66%	53%	74%
Co	17%	16%	13%	15%	19%	19%	17%
Cr	<LOD	<LOD	25%	<LOD	<LOD	<LOD	<LOD
Cu	38%	44%	36%	42%	27%	16%	71%
Ni	<LOD	<LOD	25%	<LOD	<LOD	<LOD	<LOD
V	13%	17%	63%	14%	47%	23%	31%
Zn	23%	158%	27%	35%	33%	29%	43%
Zr	16%	17%	16%	17%	11%	21%	16%

* Major oxides (SiO₂ to P₂O₅) in percent, elemental sulfur in percent, trace elements (Ba to Zr) in ppm.

Abbreviations: LOI = loss on ignition, LOD = limit of detection, n.d. = no data.

Table 8

Laboratory geochemical analyses performed on seven core samples from Matagami diamond drill-hole BRC-08-72^a.

	Basalt	Andesite	Gabbro	Quartz gabbro	Bracemac Rhyolite	Altered Wat. Rhy.	Watson Rhyolite
Box nb.	4	65	97	107	121	135	146
From (m)	45.28	308.91	446.11	488.99	547.40	610.50	655.80
To (m)	45.48	309.11	446.31	489.19	547.60	610.70	656.00
SiO ₂	50.22	54.40	49.36	50.20	75.47	60.09	74.00
Al ₂ O ₃	11.92	13.28	12.64	12.12	7.59	14.83	8.89
Fe ₂ O ₃ ^T	16.16	19.65	15.13	18.83	10.43	11.17	8.65
MnO	0.191	0.042	0.212	0.331	0.088	0.07	0.064
MgO	4.51	6.34	6.67	4.24	3.38	6.54	3.94
CaO	6.76	0.13	11	7.16	0.05	0.33	0.07
Na ₂ O	1.78	<0.01	1.34	3.48	0.05	0.13	0.04
K ₂ O	0.09	0.64	0.2	0.17	0.58	2.17	0.92
TiO ₂	1.87	0.61	0.88	1.98	0.15	0.46	0.31
P ₂ O ₅	0.25	0.03	0.09	0.22	0.02	0.06	0.03
LOI	6.24	5.03	2.48	1.85	2.67	4.59	2.95
Total	100.0	100.2	100.1	100.6	100.5	100.4	99.9
S	0.42	<0.05	0.07	<0.05	<0.05	<0.05	<0.05
Ba	329	192	179	357	77	498	159
Co	33	19	47	37	14	16	10
Cr	<5	82	252	<5	<5	<5	<5
Cu	24	34	117	13	11	<5	8
Nb	7	2	3	7	22	39	20
Ni	10	32	66	14	-4	5	<4
Pb	9	<5	<5	<5	<5	<5	<5
Rb	3	15	5	4	11	42	16
Sr	104	8	153	149	4	12	9
V	285	212	268	337	<5	<5	<5
Y	44	14	15	44	86	214	121
Zn	141	460	91	114	100	109	71
Zr	152	70	46	138	297	848	465

^a wdXRF data from Actlabs, except sulfur by LECO at INRS. Major oxides (SiO₂ to P₂O₅) and loss on ignition (LOI) in percent, elemental sulfur in percent, trace elements (Ba to Zr) in ppm. Analyses of standards and duplicates are available upon request.

Table 9

List of correction factors for the Delta analysers in “mining plus” mode^{1,2}.

	Al ₂ O ₃	Fe ₂ O ₃	MnO	SiO ₂	TiO ₂	Zr
Delta-A	1.3156	0.9914	1.3003	0.9660	1.5234	0.9534
Delta-B	0.9757	0.9165	0.8640	0.7796	1.4888	0.8972

1. These factors are the reverse of the slope of a linear regression between the average of 30-50 pXRF measurements per sample, for each analyser, and traditional laboratory geochemistry, for seven Matagami core samples. See text and figure 5 for explanation.
2. The uncorrected pXRF concentrations can be multiplied by these factors to improve their accuracy. Note however that these corrections do not remove the effect of mineralogical variations in rocks, but the average of corrected measurements should be accurate for each lithology.

Table 10

Summary of the precision and accuracy test on the NIST 2702 standard reference material with the Delta analysers, in soil mode.

Element	Certified and reference values			pXRF analysis (Delta-A)				pXRF analysis (Delta-B)			
	Type ^a	Concentration	Uncert. ^b	Average ^c	SD ^d	RSD ^d (1σ precision)	Difference ^e	Average ^c	SD ^d	RSD ^d (1σ precision)	Difference ^e
<i>Major elements in %</i>											
Ca	R	0.343	0.024	0.40	0.01	2%	15%	0.44	0.02	4%	29%
Fe	C	7.91	0.24	8.23	0.06	1%	4%	9.03	0.09	1%	14%
K	C	2.054	0.072	2.29	0.03	1%	11%	2.74	0.04	1%	33%
Mn	C	0.1757	0.0058	0.19	0.00	2%	10%	0.20	0.00	1%	12%
P	C	0.1552	0.0066	0.46	0.03	6%	196%	0.41	0.03	7%	165%
S	I	1.5	n.v.	1.81	0.09	5%	21%	1.59	0.07	5%	6%
Ti	C	0.884	0.082	0.96	0.01	1%	9%	1.10	0.02	1%	24%
<i>Trace elements in ppm</i>											
Ag	R	0.622	0.078	<LOD	<LOD	<LOD	n.d. ^f	<LOD	<LOD	<LOD	n.d. ^f
As	C	45.3	1.8	47	3	6%	3%	48	2	4%	6%
Cd	C	0.817	0.011	<LOD	<LOD	<LOD	n.d. ^f	<LOD	<LOD	<LOD	n.d. ^f
Co	C	27.76	0.58	29	2	5%	3%	28	2	7%	2%
Cr	C	352	22	366	22	6%	4%	387	9	2%	10%
Cu	R	117.7	5.6	110	6	5%	-7%	121	4	4%	3%
Mo	R	10.8	1.6	13	1	5%	20%	10	2	19%	-7%
Nb	I	63	n.v.	63	2	3%	0%	1293	37	3%	1952%
Ni	C	75.4	1.5	<LOD	<LOD	<LOD	n.d. ^f	<LOD	<LOD	<LOD	n.d. ^f
Pb	C	132.8	1.1	120	4	3%	-10%	130	4	3%	-2%
Rb	C	127.70	8.8	130	3	2%	1%	139	2	2%	9%
Sb	C	5.60	0.24	<LOD	<LOD	<LOD	n.d. ^f	<LOD	<LOD	<LOD	n.d. ^f
Se	R	4.95	0.46	5	1	23%	-3%	6	1	14%	24%
Sn	R	31.6	2.4	44	10	22%	39%	30	2	5%	-6%
Sr	C	119.7	3	120	4	3%	1%	123	2	1%	2%
Th	C	20.51	0.96	24	3	14%	17%	72	16	22%	251%
U	I	10.4	n.v.	11	1	7%	1%	8	1	6%	-25%
V	C	357.6	9.2	380	11	3%	6%	229	9	4%	-36%
Y	n.v.	n.v.	n.v.	42	2	6%	n.d. ^f	598	24	4%	n.d. ^f
Zn	C	485.3	4.2	506	10	2%	4%	448	8	2%	-8%
Zr	n.v.	n.v.	n.v.	435	6	1%	n.d. ^f	413	9	2%	n.d. ^f

^a Types of values on the NIST certificate: C = certified; I = information; n.v. = no value; R = reference (see also Zeisler 2004).

^b Expanded uncertainty with a coverage factor of two (95% confidence); see Zeisler (2004).

^c Average concentration from ten pXRF measurements on the reference material with a 90 s integration time (30 s per beam), in soil mode.

^d Standard deviation (SD) and relative standard deviation (RSD) of the ten pXRF measurements.

^e Difference = (average pXRF minus NIST value)/NIST value. This is an indication of systematic error or accuracy.

^f n.d. = no data.

Figure captions

Figure 1: Results of a precision test on the Alpha analyser, using SRM 2702, a fine-grained marine sediment. The relative standard deviation of a series of 10 repeat measurements in soil mode generally improves as integration time is increased. Note the logarithmic scale on the vertical axis.

Figure 2: Results of a precision test on the Alpha analyser, using a basaltic core sample (see text for details). The relative standard deviation of a series of 30 repeat measurements in soil mode improves as integration time is increased. Note the logarithmic scale on the vertical axis, partly hiding the dramatic decrease in RSD as the integration time changes from 10 s to 45 s. The best compromise between precision and measurement time seems to be around 60 s for the elements Fe, Mn, Sr, Ti, Zn, and Zr taken as a group. Other elements shown cannot be determined precisely in most unmineralized rocks from Matagami.

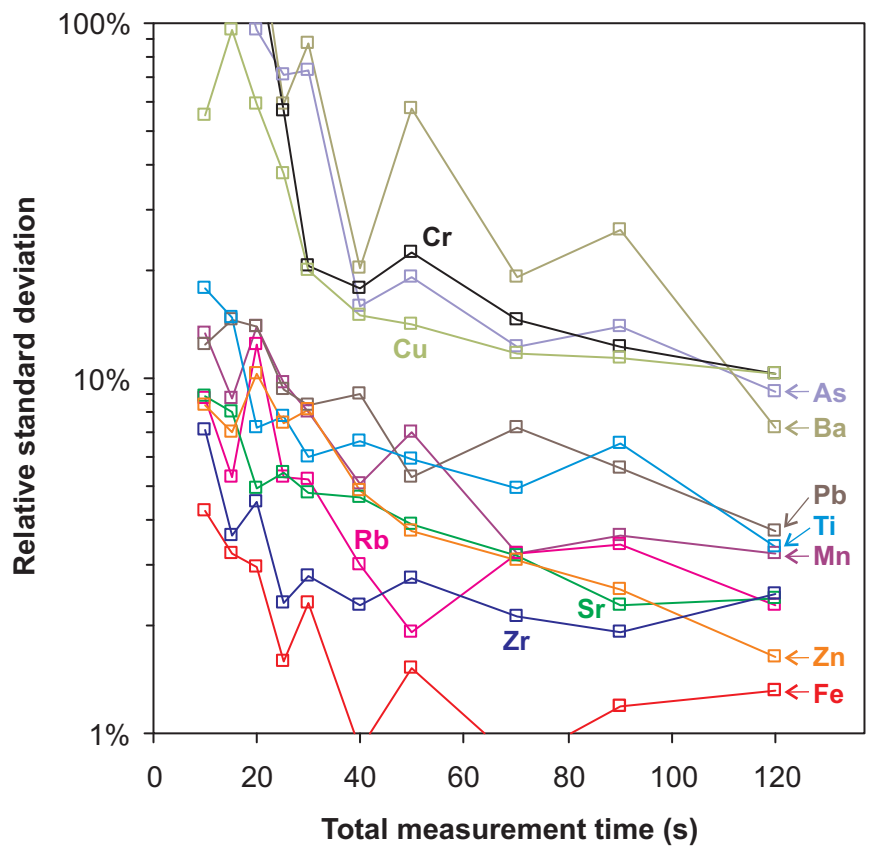
Figure 3: Comparison of five laboratory geochemical analyses from a long interval of basaltic lava with 104 pXRF measurements done with the Alpha analyser in soil mode (see text for details). (a) Raw data: Zr by pXRF is typically

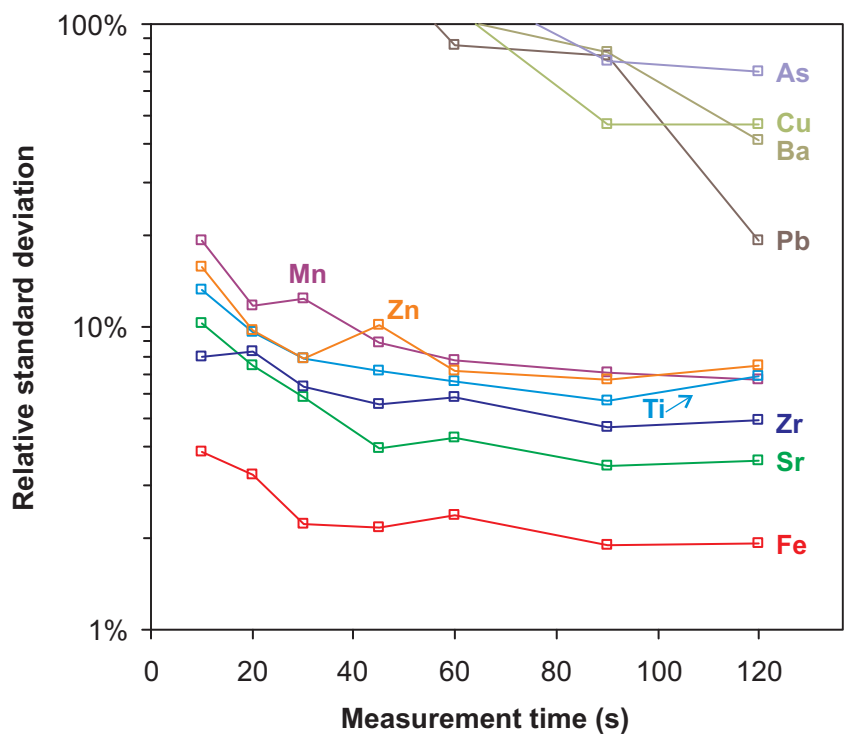
too low and Ti is typically too high; (b) corrected data: the averages are now the same for laboratory geochemistry and pXRF. The spread in pXRF data is due mostly to mineralogical variability at small scale, not to instrument precision.

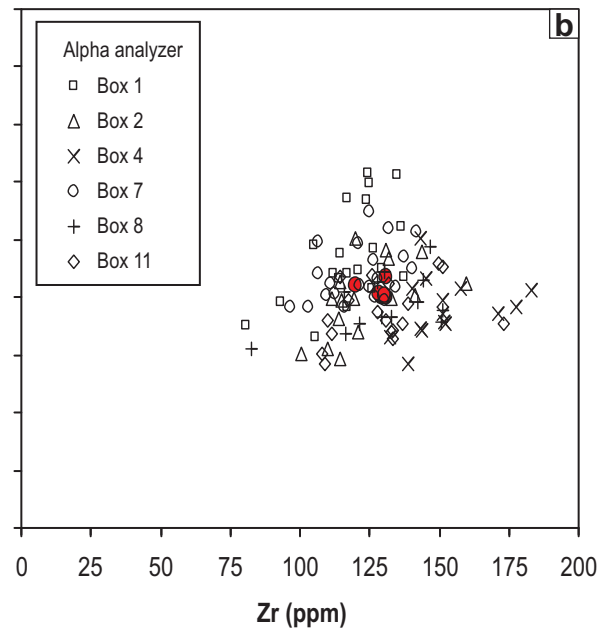
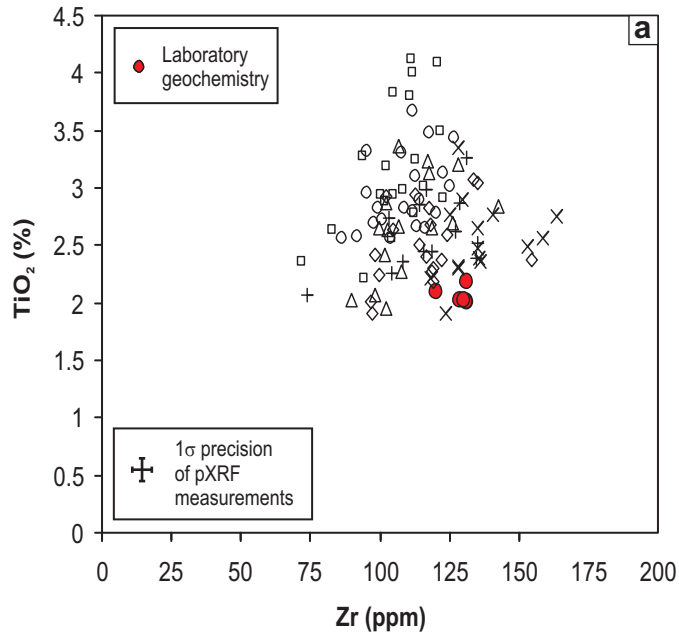
Figure 4: A precision test on the Delta-A analyser in the 'mining plus' mode, using a basaltic core sample from Matagami (see text for details). The relative standard deviation of a series of 31 measurements improves as integration time is increased. The best comprise seems to be around 60 s (30 s per beam) for the elements shown.

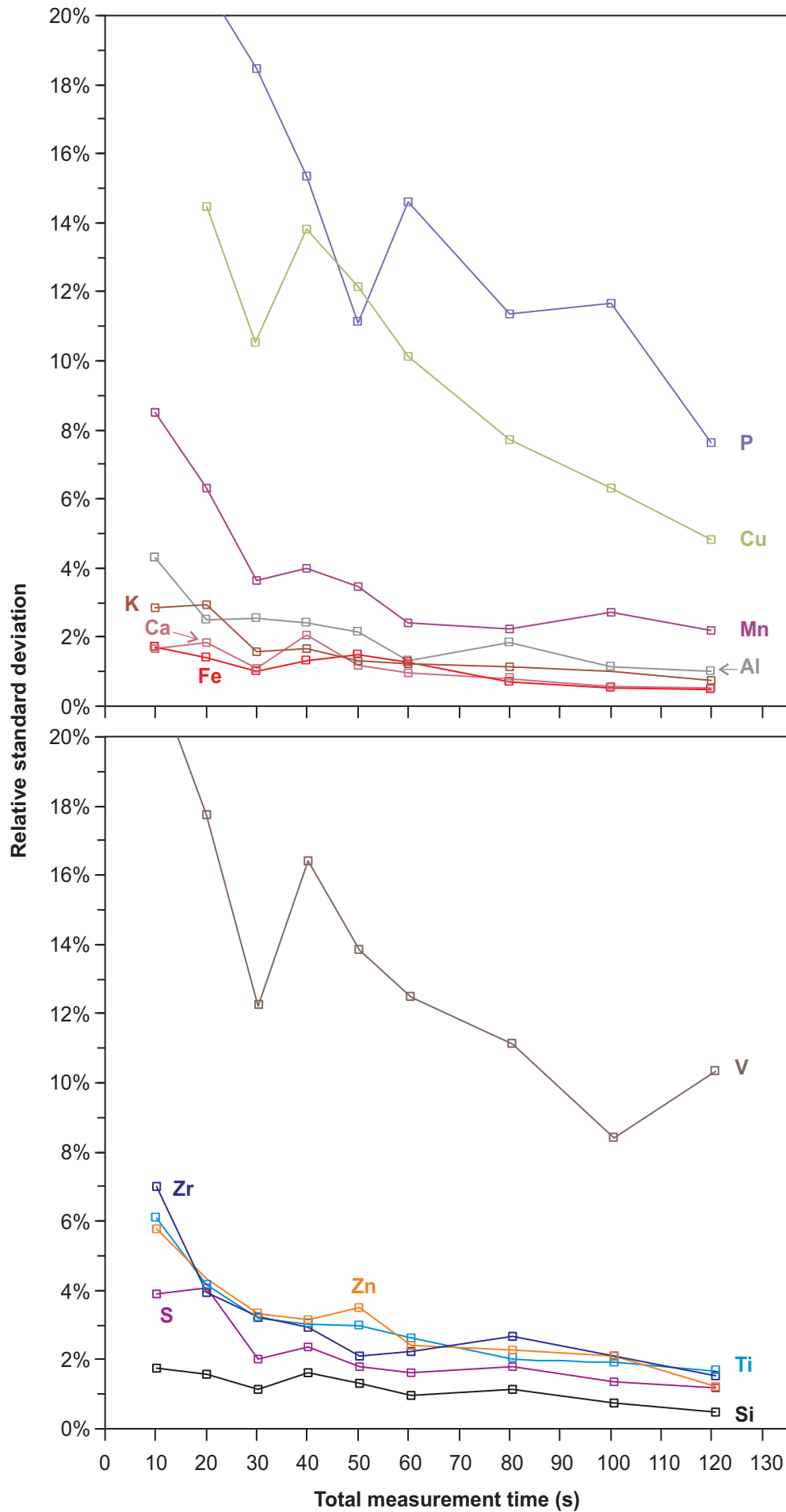
Figure 5: Comparison of laboratory geochemistry with pXRF data in 'mining plus' mode for the Delta-A analyser. (a)-(d) Average of uncorrected pXRF data versus wdXRF for seven samples from Matagami diamond drill-hole BRC-08-72, for the elements Al, Si, Ti and Zr. (e)-(f) Plots of TiO₂ vs. Zr showing uncorrected (e) and corrected (f) pXRF data for a single 20 cm-long piece of NQ core (the basalt, see Table 6).

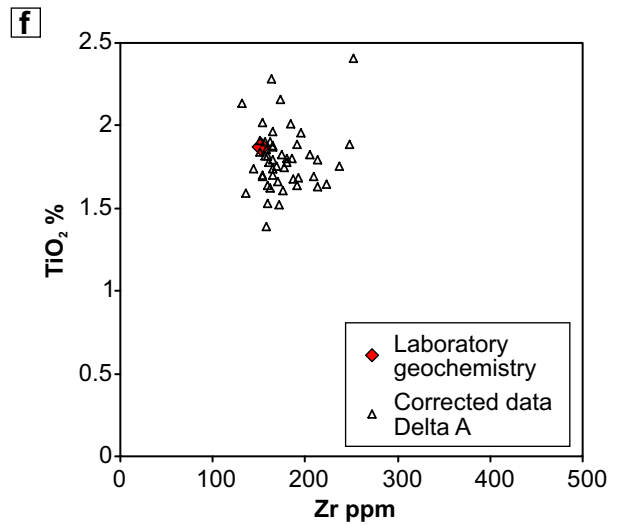
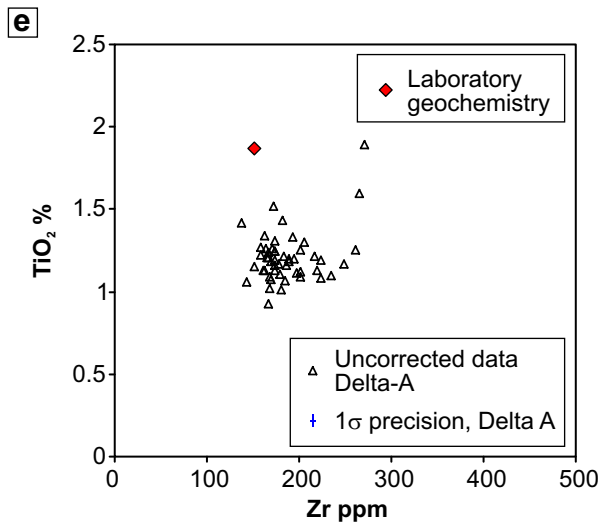
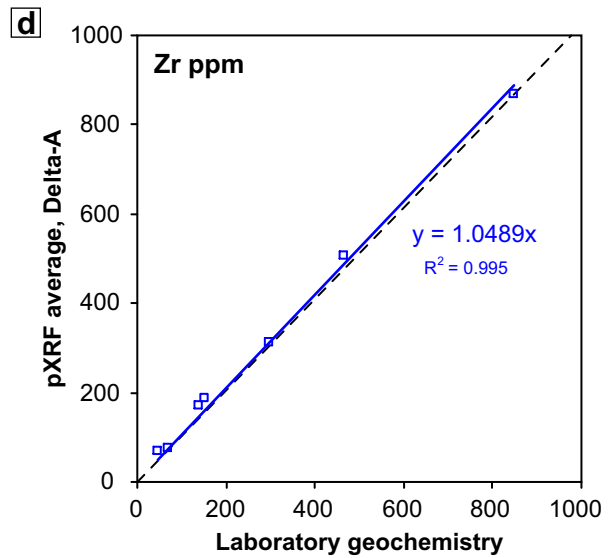
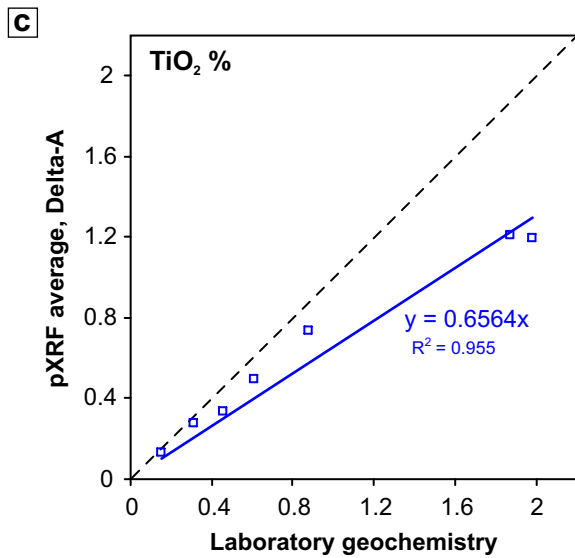
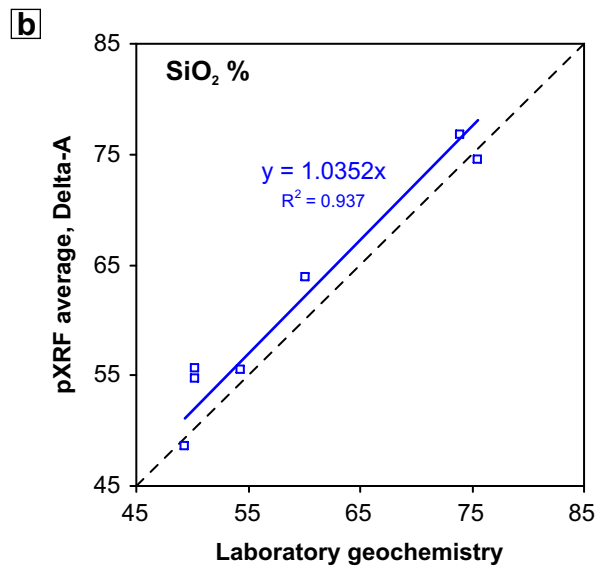
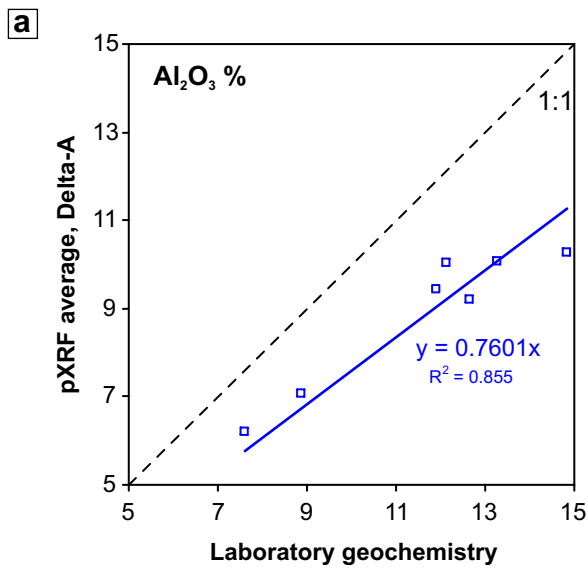
Figure 6: Uncorrected pXRF data on various spots from two 20 cm-long pieces of NQ core from Matagami diamond drill-hole BRC-08-72: the basalt (top) and the altered Watson Rhyolite (bottom; see Table 7). The Delta-B analyser was used in 'mining plus' mode with a 60 s integration time. The grey circles with error bars represent the means and standard deviations of these data. The other error bars in the upper right corner of each plot show the 1 σ precision obtained on specific spots from the same samples. Note how, for most elements, the scatter in the pXRF data is largely due to small-scale mineralogical variability, not instrument precision. For the rhyolite, the precision test yielded 'LOD' for Cu so there is no error bar for this element. Note that CaO is shown for the basalt, but K₂O is shown for the rhyolite, and that some plots of the same elements do not have the same axes.



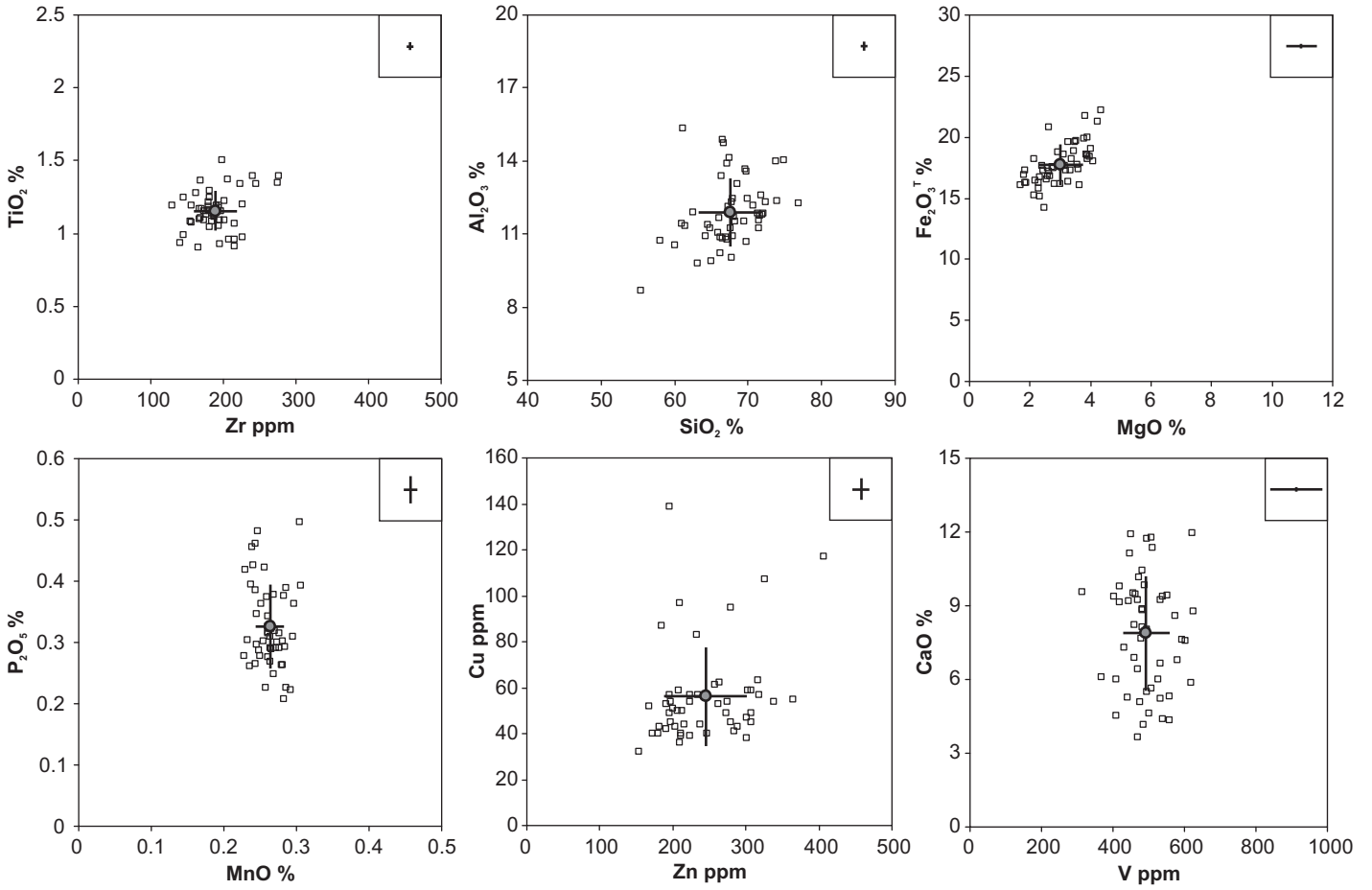








Basalt (n = 51)



Altered Watson rhyolite (n = 31)

