The use of property-scale portable X-ray fluorescence data in gold exploration: advantages and limitations

Dennis C. Arne1*, Rob A. Mackie1 & Stacie A. Jones2

1CSA Global Canada Geosciences Ltd, 610-1155 West Pender Street, Vancouver, British Columbia, V6E 2P4, Canada
2Prosperity Goldfields Corporation, 800-789 West Pender Street, Vancouver, British Columbia, V6C 1H2, Canada

*Corresponding author (e-mail: dennis.arne@csaglobal.com)

ABSTRACT: This study examines field portable X-ray fluorescence (pXRF) data for unsieved B- and C-horizon soil samples from two contrasting Au exploration programs in northern Canada and compares them to laboratory results from sieved samples to determine if a minimalist approach to sample preparation, equipment calibration and analysis produces results that are adequate for exploration purposes.

The collection of 14,651 residual soil samples on detailed grids at the Whiskey Au project in the Black Hills of the Yukon Territory, Canada during the 2011 field season allows a comparison of pXRF data from unsieved samples with inductively-coupled plasma mass spectrometry (ICP-MS) data from the <100-µm grain size fraction digested in aqua regia. XRF data were generated on two devices: an Innov-X Delta handheld and a Niton FXL desk-top unit. Data for selected elements from the pXRF units show trends in gridded percentile plots comparable to the ICP-MS data, although the continuity of these trends reflects the degree to which the pathfinder element concentrations exceed the lower orders of detection. Acceptable merged gridded images for As and Cu from the two devices were generated without data levelling, whereas the Pb, Mo and Ni data require leveling prior to gridding in order to provide a reasonable fit to the laboratory data. Data for elements that occur in concentrations close to the lower limit of detection by pXRF, such as Sb, may provide some useful information but must be used with caution. Data for Fe also show a poor correlation, possibly due to heterogeneity of Fe in the samples, as well as due to incomplete digestion of all Fe-bearing minerals in some samples using an aqua regia digestion.

A total of 680 till samples collected from regional and detailed sampling grids on the Kiyuk Lake Au property in southern Nunavut, Canada during the 2012 field season were analysed by pXRF and also by ICP-MS following an aqua regia digestion. pXRF data were generated on an Innov-X Delta using unsieved samples for comparison with ICP-MS data from the <70-µm grain size fraction. The pathfinder element As shows good agreement with the laboratory data, whereas Ni, Mo and Sb data give poor matches due to proximity of the data to the lower orders of detection by pXRF.

The use of pXRF data on soil samples with no sample preparation other than drying and no instrument calibration is a robust approach for Au exploration using particular elements, such as As and Cu, provided the data are monitored for consistency. Even greater compatibility between pXRF and laboratory data would be expected where sample preparation and site-specific calibrations are implemented. Other pathfinder elements for Au, including W, Sb, Bi, Ag and Te, as well as Au itself, typically occur at levels in soil either close to or below the lower order of detection of the current generation of field-portable analytical devices. The use of pXRF in Au exploration allows for quick decision-making and provides near-real time sampling guidance in the field where ‘fit for purpose’ data for suitable pathfinder and lithologically-controlled elements can be obtained.

KEYWORDS: Yukon Territory, Nunavut, portable X-ray fluorescence, pXRF, Au, mineral exploration, pathfinder elements, geochemistry
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Field portable X-ray fluorescence (pXRF) has almost become a routine semi-quantitative analytical tool in the environmental and resource industries. In spite of its near ubiquitous presence, there appear to have been only a handful of application case studies published following on from the pioneering work of Potts et al. (1995), and few of these post-date the introduction of silicon drift detector (SDD) technology. Some of the few published studies to directly compare pXRF data and laboratory analyses of soil include the work of Argyraki et al. (1997) and Wu et al. (2012), although this is certainly common practice. Much of the early work focused on variability introduced by surface irregularities and the effects of different moisture contents in soils measured in situ. Houlanan et al. (2003) demonstrated improved accuracy and precision through crushing and pulverizing mineralized samples prior to analysis for grade control purposes in mining. Morris (2009) emphasized the importance of adequate count times and the potential effects of different sample bag materials on results. Wu et al. (2012) noted that those elements at concentrations well above the lower limits of detection for the device (e.g. Ni, Cu, Pb, Zn) fared better than those at concentrations closer to their respective lower limits of detection (e.g. Cd, Cr, Hg, As) when compared to laboratory analyses. This raises the question as to whether the lower orders of detection quoted by manufactures are realistic or comparable to lower limits of detection used by geochemical laboratories. While the important variables that affect data quality are well established, the application of methodologies for their minimization and correction are applied inconsistently in practice.

In both mineral exploration and environmental assessments, it is often not the absolute value of a particular element that is of significance, but rather the relative contrast of 'anomalies' and 'hotspots', respectively, to local or regional background that is of interest (e.g. Vanhoof et al. 2004; Peinado et al. 2010). Excessive sample preparation and prolonged counting times in these situations can prove unnecessary and costly, particularly when samples may ultimately be analysed at the laboratory. Recognition of the cost-effectiveness of different methodologies in the field versus the final use to which the data will be put has led to the concept of whether the pXRF data are 'fit for purpose'.

In this contribution we present soil geochemical data from two Au exploration programs in northern Canada (Fig. 1) where sample preparation was limited to drying of the samples. The samples were then analysed directly through their woven polyester sample bags using factory calibrations immediately prior to shipment from the field. In other words, the pXRF analyses were integrated into the sample stream from field to charter aircraft with minimal disruption or delay to what the normal routine would be in the absence of pXRF. All samples were ultimately analysed at the laboratory for Au and a suite of 36 other elements, as the identification of suitable pathfinder elements that could be used as a surrogate for Au had not yet been established in both cases. Those trace elements that are associated with Au in these areas are arguably not reliable enough to preclude laboratory analysis even after the collection and interpretation of a considerable amount of geochemical data. It will be demonstrated that relative differences in pXRF data from some important pathfinder elements for Au are remarkably similar to the trends generated for the same elements using laboratory results. These data are therefore 'fit for purpose' of identifying trends and areas of elevated concentration worthy of immediate follow-up. Therein lies one of the major advantages of pXRF – the ability to generate data quickly in remote areas and to modify sample collection strategies accordingly while sampling crews are still available. However, there are limitations to and indeed, pitfalls, in pXRF data produced for some typical pathfinder elements for Au that could have detrimental effects to an exploration program if not recognized.

GEOLOGICAL SETTING

Geology of the Whiskey property, Yukon Territory

The Whiskey property is located in the Black Hills c. 95 km SW of Dawson City in the recently discovered White Gold district (MacKenzie et al. 2010), which is part of the Tintina Au Province (Hart et al. 2002). The property extends north of the Stewart River along Black Hills Creek (Fig. 2). A second claim block extends south of the Stewart River along Barker Creek but was not sampled in any detail during the 2011 exploration program and will not be discussed further.

The region is underlain by Palaeozoic basement rocks of the Yukon-Tanana Terrane. Within the Whiskey property boundary the basement consists of greenschist to amphibolite grade meta-sedimentary and meta-igneous rocks intruded by late metamorphic felsic dykes, mafic intrusions and granitic

Fig. 1. Map showing the locations of the Whiskey and Kiyuk Lake properties.
bodies of inferred Early Jurassic age (MacKenzie et al. 2013; Fig. 2). The Palaeozoic schists and gneisses experienced multiple phases of deformation, with ductile folding and shearing believed to have occurred during the Late Permian, and subsequent semi-ductile shearing and thrust faulting in the Jurassic (Jones 2011). Palaeozoic basement rocks consisting of quartzite, felsic orthogneiss, amphibolite gneiss and marble are unconformably overlain by early Cretaceous alluvial gravels of the Tantalus Formation and late Cretaceous Carmacks Volcanics. These Cretaceous units are approximately flat lying and provide a reference elevation for the pre-Cretaceous land surface, as well as constraining the amount of post-late Cretaceous tilting and erosion on the property.

Late Cretaceous igneous activity associated with north–south- and east–west-orientated brittle faults may have provided the impetus for Au mineralization in the region, as it is clear that at least some of the Au mineralization post-dates the emplacement of the mid-Cretaceous Coffee granite (Wainwright et al. 2011; Mckenzie et al. 2013). However, the main phase of Au mineralization in the district is constrained to have occurred during the Jurassic on the basis of Re-Os age determinations of molybdenite associated with Au mineralization in the White Gold District (Allan et al. 2013).

The Au mineralization identified on the property to date appears to be localized along sheared lithological margins broadly associated with elevated As and Sb in graphitic quartzite. Mineralized quartz veins are variably associated with elevated Bi, Te, Mo, Pb and Ag, with distinct geochemical populations evident depending on the host rock. The mineralization style has been likened to orogenic quartz veining in the Klondike goldfield by MacKenzie et al. (2013), although the overall pattern of geochemical zoning on the property may be related to elevation and some vein textures are suggestive of low-sulfidation epithermal systems. Scattered, well mineralized boulders have been located that give Au values in excess of 1 g/t and thin mineralized zones associated with quartz veins, breccia and quartz-sericite alteration have been intersected in drill-holes (e.g. 0.37 g/t Au and 15.1 g/t Ag over 4.3 m; DDH WH11-08). The Black Hills and Barker Creeks support active alluvial Au mining operations (Lowey 2004), leading one to speculate that more significant bedrock mineralization remains to be found on the property.

The Quaternary geological history of the SW Yukon Territory is unique for Canada in that some areas were not glaciated during the Pleistocene (Lowey 2004). Elevations on the Whiskey property range between c. 750 and 1500 m and...
vegetation consists of spruce, birch, poplar, alder and willow, much of which had recently been affected by forest fires. High-level terraces consisting of fluvial and probable glacio-fluvial sediments occur along the Stewert River (Fuller 1993), which bisects the property, but do not appear to extend to any significant degree away from its banks. Bedrock ridges generally have convex profiles and valleys are filled with colluvium and recent alluvium. In general, the highest metal concentrations in residual soil are found in the deepest C-horizon samples (Hart & Jober 1996). However, permafrost is widespread and north-facing slopes have been disturbed by cryoturbation. Mass wasting due to land slips, particularly after forest fires, is common. Residual profiles may also be covered by a thin layer of loess formed during the last glaciation in the region (Bond & Lipovsky 2011) and volcanic ash (Robinson 2001). Incorporation of these exotic materials into the soil profile through cryoturbation and mass wasting results in dilution of the primary geochemical signal in the residual soil (Bond & Sanborn 2006). In order to avoid some of the complexities associated with soil profiles in the Black Hills, grid soil sampling was generally restricted to south facing aspects and avoided steep colluvium-dominated slopes and valley bottoms. However, it must be stressed that down-slope creep is active in such periglacial areas even on the shallowest of slopes (i.e. 5°) and that considerable movement of soil has undoubtedly occurred away from the ridges.

Geology of the Kiyuk Property, Nunavut

The Au mineralization discovered to date at Kiyuk Lake in southern Nunavut is hosted by Palaeoproterozoic upper Hurwitz Group and lower Kiyuk Group meta-sedimentary rocks of the Poorfish-Windy Belt in the Hearne Domain of the western Churchill Province. The Kiyuk Group contains arkose sandstone and distinctive polymictic conglomerates that unconformably overlie continental to marine platform meta-sedimentary rocks of the Hurwitz Group, which in turn unconformably overlie Archean basement rocks consisting of felsic gneiss, plutons and supracrustal rocks of the Rankin Inlet-Ennadai greenstone belt (Aspeter et al. 1989). U-Pb dating of detrital zircon grains indicates a maximum depositional age of 1911 +/- 7 Ma and 1898 +/- 28 Ma for sediments of the Tavani Formation (Hurwitz Group) and K2 Member (Kiyuk Group), respectively (Davis et al. 2005). Both the Hurwitz and Kiyuk Groups at Kiyuk Lake were folded into a NE-striking regional syncline disrupted by NW-verging thrust faults during the Trans-Hudson Orogeny around 1.8 Ga (Aspeter et al. 2002). Infolding of the cover rocks and basement is thought to have occurred during this period, resulting in the formation of several structural ‘basins’ or outliers of Proterozoic meta-sediments. The Hudson felsic magmatic suite was emplaced at mid-crustal levels from 1845–1795 Ma during the final stages of the Trans-Hudson Orogeny, followed by intrusion of high-level A-type granites of the Nuelint suite from 1765–1760 Ma (Van Breeman et al. 2005). Both types of intrusions are located c. 10–15 km east of Kiyuk Lake along the eastern margin of the property, and are indicative of significant exhumation of the region during the 50 Ma interval between emplacement of the two intrusive suites. The age of the alteration and Au mineralization at Kiyuk Lake has not yet been determined, though it can be postulated that one of these two igneous events provided the necessary heat (and potential sources of metal) to circulate the hydrothermal fluids ultimately responsible for Au mineralization on the property.

Gold mineralization at Kiyuk Lake was initially discovered in gossanous boulders by prospectors investigating elevated arsenic levels in regional lake sediment samples collected by the Geological Survey of Canada in 1976 (Fig. 3). Bedrock exposure on the Kiyuk property is poor, as there is covered with an extensive thin veneer to locally thick (i.e. > 10 m) blanket of ribbed moraine, streamlined till and glacio-fluvial sediments deposited to the south of the Keewatin ice divide (Aylsworth 1986; Aylsworth & Shilts 1989; Stea 2012). The direction of glacial transport is to the SW, between 185° and 210° (Shaw et al. 2010). The terrain is gently undulating with variable tree cover. Vegetation tends to be shrubs and tree stands dominated by small black spruce, pine and birch. Topographic highs in the area are mainly formed by accumulations of till and other glacial debris, and outcrop ridges are scarce. Glacial cover has hindered exploration of the property, but significant bedrock Au mineralization was eventually discovered in albite-actinolite-carbonate-quartz altered and brecciated sandstones by Prosperity Goldfields Corporation in 2011 (e.g. RU11-001 – 37.8 m @ 4.18 g/t from 2.4 m). Prosperity has therefore confirmed dispersion of Au from bedrock sources in a southwesterly direction. Anomalous Au in till has been traced down-ice from known bedrock sources using both geochemistry and mineralogical analysis of heavy mineral separates.

METHODOLOGY

As previously discussed, sampling in 2011 on the Whiskey property was focussed mainly on ridges and south-facing slopes. Thick accumulations of colluvium and permafrost areas were intentionally not sampled where recognized, as the target was residual bedrock material. The samples were collected using a 1-m long soil auger and were not sieved in the field, although large rock clasts were removed prior to placing c. 1 kg of soil into Hubco woven polyester sample bags. The samples were dried in a heated tent at camp for several days until completely dry and then analysed by pXRF. If the samples were cemented by clay on drying, they were hammered a few times to make sure they lay flat on the analysers. Once analysed, the samples were then immediately prepared for transport to the laboratory. A total of 14,651 residual soil samples from the Whiskey property were analysed by both pXRF and at the laboratory in 2011.

Sampling of till at Kiyuk Lake in 2012 was done using shovels and metal bars, as the till locally contained large boulders. Although the C-horizon was the target horizon for sampling, many samples collected were transitional between the B- and C-horizons. Approximately 2 kg of material was collected in Hubco polyester sample bags because of the sandy nature of the till. Larger pebbles were removed by hand but the samples were not sieved. The samples were also dried for several days in a heated tent prior to analysis through Hubco woven polyester sample bags. A total of 680 till samples were analysed by both pXRF and laboratory methods. Till samples were taken on a regional grid having a density of approximately one sample per km². Sampling was focused onto till-covered ridges because low-lying areas were often covered in glacial boulders that had accumulated following down-slope movement (Stea 2012).

Two pXRF analysers were used at Whiskey during the 2011 field program. A Niton FXL benchtop analyser and an Innov-X Delta Premium handheld with a Rh anode in a test stand configuration were used at different times in the program and sometimes concurrently. A total count time of 120 seconds in soil mode was used on the FXL, with 60, 30 and 30 seconds on the main, high and low ranges, respectively. The Delta was used in 3-beam soil mode for a total count time of...
90 seconds, but with durations of 45, 30 and 15 seconds on beams 1, 2 and 3, respectively. The counting times were modified from factory settings to provide more counts for the main trace elements of interest. The variance associated with a spot analysis of an unsieved soil sample will no doubt greatly exceed that introduced by the count times that were used. Although no calibration was undertaken, the accuracy of As levels in particular was monitored using a combination of certified reference materials (CRM; Canmet Till-3, Canmet stream sediment STSD-3, marine sediment NIST 2702, ferruginous soil Oreas 42P) and a series of representative soil samples from the project area. The resolution of the analysers was also monitored on a daily basis during the system checks, and the units were allowed to warm up for c. 15 minutes before analyses began. Only the Innov-X Delta Premium in a test stand was used for analyses at Kiyuk, using operating procedures similar to those previously described for the Whiskey project.

Similar QA/QC protocols were employed for both projects. Prior to analysing any samples, a silica blank was run, as were two CRMs. The silica blank and two different CRMs were analysed at the end of the day. The CRMs were selected to provide a range of anticipated As values, and the expected values were checked against the reading to ensure they were within c. 10% of the certified total As values. Duplicate analyses were meant to be performed on every 50th sample after removing, adjusting and replacing it on the analyser, but fewer duplicate analyses were undertaken than prescribed. Data were downloaded on a daily basis and any numbering errors corrected in the data spreadsheet before being uploaded into a project Access database. This process allowed for analysis of between 150 and 200 samples per day, depending on the unit used given different count times.

All samples were subsequently shipped to Acme Analytical Laboratories for analysis. The Whiskey samples were sent to the preparation facility in Whitehorse, Yukon Territory where they were dried further and dry-sieved to <150-mesh (<104-µm). The Kiyuk samples were shipped to the preparation facility in Timmins, Ontario where they were dry-sieved to <230-mesh (<70-µm). The pulps were then shipped to the Acme facility in Vancouver where the pulps were re-mixed, a 30-g split digested in aqua regia, and the solution analysed by ICP-MS for Au plus 36 other elements (Method ‘1F-MS’).

RESULTS

Quality assurance and quality control

Quality control on pXRF data generation focussed on As given its common association with Au mineralization in a wide variety of geological environments and deposit types. The accuracy of As determinations in the range 10 to 150 ppm was determined using a selection of commercially-available certified reference materials (CRMs) and near-total (4-acid) digestion soil data from samples previously collected from the property. The pXRF values were similar to the expected values and so no calibration of the pXRF units was undertaken, although it must be kept in mind that these CRMs do not take into account any attenuation of secondary X-rays by the soil sample bags (e.g. Morris 2009). The accuracy of the As data was confirmed by the routine analysis of the CRMs on a daily basis during analysis of the soil samples. Data from both pXRF instruments are shown in Figure 4. Although the Niton FXL began with consistently accurate results for the CRMs, it began to show an increasing negative bias as the program progressed. It was pulled from service and replaced by the Innov-X Delta. The latter displays a slight negative bias with respect to Canmet STSD-3, but the results are more consistent than those obtained from the FXL, and so the Delta was used to complete the program. This experience highlights the importance of
having access to a readily available back-up analyser where the data are integral to the sampling program, as it can be difficult to repair or obtain a replacement unit during short field seasons in remote areas. Alternatively, the CRM data could have been used to correct the bias observed in the data, but this would have been time-consuming given the number of elements being evaluated and the need for multiple CRMs to monitor consistency.

Duplicate analyses were not undertaken as frequently as desired, and the random nature of the data collection means that most data for As are within an order of magnitude of the lower limit of detection and so are inherently imprecise (Fig. 4). For example, the average coefficient of variation (CV) for As calculated from 82 duplicate analyses using the root mean square method (RMS; Stanley & Lawie 2007) is 22%, whereas for Cu it is 27%. These values emphasize the need to obtain large duplicate pair data-sets to constrain variations in error at different concentrations.

Not shown are the results for the daily analysis of a silica blank. In general, the majority of readings for As and Cu are below the lower orders of detection (LOD) for the analysers, with only occasional readings over an order of magnitude above the anticipated lower detection limits. The silica blank data illustrate general cleanliness of the work environment during analysis, as well as good data management, as blanks are easily recognizable within the database.

Direct comparison of pXRF and laboratory data

Some filtering of the data has been undertaken prior to comparing the pXRF and ICP-MS data. Only data above the LOD quoted by the pXRF manufacturers have been used on the basis that data near or below these values are inherently imprecise and unsuitable for statistical assessment. Data below the LOD have been given null values, thus precluding some statistical tests for data comparison. The best-case LOD values are generally in the range 2 to 4 ppm for the trace elements of interest (As, Cu, Mo, Pb, Sb) in a silica matrix. Actual lower limits of detection have not been calculated for the pXRF data from this study. Any pXRF readings for which the full count time was not achieved have also been removed from the data-set, as these data are clearly erroneous. Only elements for which an aqua regia digestion would be expected to give a near-total value are valid to compare in this fashion. Elements such as Cr, Ti and Zr may be significantly under-reported in aqua regia data compared to a total analysis from pXRF.

Comparisons of pXRF and ICP-MS data for As, Cu, Sb and Fe from the Whiskey property are shown in Figure 5. The resulting graphs allow an assessment of accuracy, based on the slope of the regression line, as well as goodness of fit, based on the coefficient of determination. In the case of As and Cu, the pXRF data consistently underestimate the As and Cu levels determined by ICP-MS. This is probably due in part to the attenuation of X-rays by the sample bag material (e.g. Morris
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2009) and in part to a systematic negative bias in the pXRF data compared to the laboratory data for these elements. However, the small degree of scatter in the data is remarkable, particularly given that the laboratory data are from a sieved and homogenized pulp compared with a single pXRF analysis through the sample bag, and that the data are for instruments from two different manufacturers.

However, the Sb data are not at all reliable, reflecting the fact that they are at least an order of magnitude lower than concentration data from either As or Cu and therefore much closer to their respective lower LODs. Although this observation is not unexpected, the determination of pXRF Sb values that would be considered to be highly anomalous from an exploration perspective in samples containing little or no Sb (i.e. false positives) can lead to wasted effort. A similar conclusion can be drawn for Mo, Hg, Te, Pd, Ag and Bi pXRF data, demonstrating one of the limitations of pXRF in Au exploration using soil data.

Data from the two devices have not been separated in Figure 5 for As, Cu and Sb, but would need to be distinguished should the data be used to derive calibration factors (i.e. slope and Y-intercept) for use on the individual devices. Data for Fe have been differentiated, and both devices show a similar degree of scatter, although it must be kept in mind that use of fundamental parameters for internal calibration may have resulted in a better fit to the ICP-MS data on both instruments. The poor correlation between pXRF and laboratory data may reflect heterogeneity in the samples, as well as incomplete digestion of all Fe-bearing minerals in an aqua regia digestion for some samples (e.g. chrome).

Spatial comparisons of pXRF and laboratory data

Ultimately, it is the similarities and differences in the spatial patterns obtained from pXRF data compared to laboratory data that are significant for mineral exploration. In this regard, the use of percentile thematic plots or gridded images is more relevant than plotting absolute values. The gridded images presented here were generated in ioGAS™ exploratory data analysis software using the maximum value of 20-m cells with a capture radius of 100 m. Percentile ranges are unequal and are designed to emphasize the upper, 90th, 95th, 98th and 99th percentiles. The gridded images are not continuous because, as previously described, sampling was designed to generally avoid colluvium-filled valleys and north-facing slopes affected by permafrost.

The pXRF and ICP-MS data for As from the Whiskey property are compared in Figure 6. The similarities in the percentile gridded images for the two data-sets are striking, particularly given that pXRF devices from two separate manufacturers were used to collect the data. Contour intervals for the two grids reflect the negative bias in the pXRF As data previously illustrated in Figure 5. Of particular note is the concentration of As along the north to NE-trending contact with hornblende gneiss in the west-central portion of the map area. The quartzite in this area is graphitic, brecciated and locally contains trace disseminated pyrite. Portable XRF analyses of representative hand samples demonstrate that the As content of the graphitic quartzite is generally less than 10 ppm in the absence of sulphide minerals, but increases significantly where pyrite has been precipitated, indicating interaction with mineralizing fluids. A similar conclusion was reached by MacKenzie et al. (2010) for the White Gold district.

Data for Cu from the Whiskey property are compared in Figure 7. The agreement between the pXRF and ICP-MS data is also good, although there are differences in detail. Copper values appear to be highest in portions of the hornblende gneiss, suggesting the presence of distinct phases within this unit. Similar spatial differences also exist for Ni, Mg, Cr and Co in the hornblende gneiss, suggesting the presence of a geochemically more primitive phase not distinguished in the mapping.
Unlike data for As and Cu, the Pb, Mo and Ni data from the two different instruments are significantly different. However, the data have been median-levelled to account for this difference to produce the gridded image for Pb presented in Figure 8 as an example (data for Ni and Mo not shown). The pXRF data provide a reasonable match with the ICP-MS data, but there are some significant variations that appear to be artifacts of the levelling process and the subtle trends apparent in the ICP-MS data are not visible in the pXRF data.
Background soil Sb levels are generally quite low in most geological environments and therefore at or below detection for most pXRF devices. ICP-MS and pXRF data for Sb are compared in Figure 9 for the Whiskey project. The pXRF data show an irregular pattern over most of the grid, characteristic of imprecise data near the lower limit of detection. However, in spite of the high level of background noise, most of the areas highly anomalous in Sb are apparent in the pXRF data, even
though the relative ranking of these elevated areas differs with the ICP-MS data. Even some of the subtle trends apparent in the ICP-MS data are apparent in the pXRF data. Overall, the pXRF data have some merit in delineating highly anomalous areas in spite of the poor correlation shown in Figure 5 between the ICP-MS and pXRF data. However, the Sb data must be used with caution as there are highly anomalous pXRF values that are not supported by the ICP-MS data (i.e. false positives).

ICP-MS and pXRF data for As in till samples from the Kiyuk Lake property are presented in Figure 10. Data for these samples were generated using a single hand-held device. Again, the agreement between the pXRF and laboratory data is good when compared using percentile gridded images. Areas of anomalous As do not align well with the dominant ice flow direction due to the coarse nature of the sampling grid (1 km²). More detailed sampling in the immediate vicinity of known bedrock Au occurrences indicates that trends in elevated pathfinder elements are aligned sub-parallel to the ice flow direction. It is also apparent from Figure 10 that not all Au occurrences at Kiyuk Lake are associated with elevated As levels, nor have all areas of elevated As been tested by exploration.

DISCUSSION

Most published studies on the use of pXRF to analyse soils have involved *in-situ* measurements (e.g. Argyraki et al. 1997; Peinado et al. 2010) and the ability to link pXRF devices directly to a GPS receiver further facilitates this approach in mineral exploration and environmental site assessments, it is the repeatability of the measurements over time that is important. Where absolute values are required, either a calibration using matrix-appropriate CRMs or project-specific standards should be applied, either on the pXRF directly, or within a database. The latter has the advantage of retaining the original data so that adjustments to the calibration can be made and the corrected data re-calculated.

Although the use of several instruments within a single survey is not recommended, it is at times unavoidable, either due to instrumental problems or the need to process large numbers of samples in a short period of time. Even different models of the same device from a single manufacturer may produce slightly different data. It is possible to level data from two instruments where necessary in the same way that geochemical data from different laboratories can be levelled when merging surficial survey data-sets. This has been demonstrated for Pb
in this study, and was also necessary for Ni and Mo, whereas As and Cu data from the two devices used were similar enough to obviate the need for levelling, even though analyses of the same CRM by the two instruments indicate slightly different biases (Fig. 4). Where the sampling precision greatly exceeds differential biases, this issue is not considered to be significant.

This study has demonstrated that the use of pXRF with no sample preparation other than drying and minimal disruption to the work flow of large-scale soil sampling campaigns can successfully provide data for some elements as long as they are encountered at levels well above the lower LODs of the pXRF devices. The additional cost of incorporating pXRF into these field programs was minimal – on the order of $5/sample, considering only employment costs and pXRF rental. Sample preparation increases these costs significantly, on the order of 2 to 3 times depending on the thoroughness of the preparation, and so is a significant cost factor for programs where thousands of soil samples may be collected. However, should the samples not be destined for laboratory analysis, then the extra cost associated with thorough sample preparation might be warranted.

A final consideration is the importance of data management in the field. Data should be downloaded from the devices on a daily basis and edited immediately to correct any data entry errors that may have occurred during data collection. Depending on how the data have been collected, it is possible to calculate realistic lower detection limits for individual elements for an entire data set. Lower limits of detection must be either calculated or arbitrarily set prior to exploratory data analysis. The high volumes of data generated by large soil programs using pXRF must be well managed in order to maximize the usefulness of the results.

CONCLUSIONS

The use of pXRF data in mineral exploration is an attractive proposition because results can be obtained within a few days of collecting and drying soil samples. This immediacy is of great value, particularly in remote locations with short summer field seasons, as it provides timely feedback on survey design while crews are on site. Acceptable data for some important pathfinder elements for Au exploration, such as As, Cu and Pb can be obtained from soil samples in the field with little or no sample preparation and calibration of pXRF instruments as long as the purpose of the data is to provide indications of relative abundances rather than accurate values. These data are best compared to laboratory results through the use of percentile thematic plots and gridded images. While such data may be ‘fit for purpose’ during exploration programs, greater care in sample preparation and calibration is required for other uses in mining, such as grade control. Common pathfinder elements for Au, such as Ag, Sn, Bi, Hg, Te and Ag, as well as Au itself, generally occur at levels in soil too close to or below the lower limits of detection for the current generation of pXRF instruments to provide reliable results and must be interpreted with caution.

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