

Status and New Developments in Field Portable Geochemical Techniques and On-Site Technologies for Mineral Exploration

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ABSTRACT

There is an ongoing need to be innovative with the way we undertake mineral exploration. Recent technological advances that have enabled successful mineral exploration include on-site or portable instruments, on-site laboratory technologies, various core scanners, and technologies for fluid analysis. Portable or field technologies such as pXRF, pXRD, pNIR-SWIR, μ Raman, and LIBS aid in obtaining chemical and mineralogical information. Spectral gamma tools, a well-known technology, recently took advantage of improved ground and airborne (drone) instruments to complement hyperspectral imagery. Novel, ground-breaking technology Lab-at-Rig® was developed by CSIRO, Imdex and Olympus at the Deep Exploration Technologies CRC, and is currently being retrofitted to diamond drilling. Cuttings are separated from drilling fluids in a Solid Removal Unit (SRU), producing one metre composite mud which is sub-sampled, dried and analyzed by both X-ray Fluorescence (XRF) and X-ray Diffraction (XRD) sensors that deliver the chemistry and mineralogy of a sample, respectively. These data are automatically uploaded to a cloud-based storage platform and subjected to a range of statistical analyses with results returned to the geologist in a matter of seconds, allowing decisions to be made in near real time. At a mine site, core scanners become a useful tool to analyze metres of core as it is being drilled. Core scanners include hyperspectral and XRF systems, such as Corescan, HyLogger and Minalyzer, for example. Fluid analyses are not as common as analyses of solid materials, but there are advances in such technologies as ASV, polarography and ion exchange electrodes aiming for analysis of commodity or environmentally important elements.

With all available portable, field and on-site technologies it is now possible to collect data at the exploration site or while drilling. Certainly, field and on-site analyses cannot yet compete with laboratory analyses in terms of sensitivity, precision and accuracy due to compromises in sample preparation, instrument performance and work environment. However, field and on-site results must only achieve the level of confidence expected from the decision. Most mineral exploration decisions are based on flexible thinking rather than on a pre-set framework of investigations. One of the key benefits of real-time analyses, or short delay analyses (less than a day), is the possibility to adjust sampling plans, test hypotheses based on ongoing results, and make fast decisions on the exploration process - especially drilling and sampling. This is particularly important for remote locations, where sample logistics to the laboratory may become long and demanding.

ON-SITE TECHNOLOGIES: WHY?

Field portable technologies have seen rapid development over the past two decades, and especially in the last one. This is the result of recent technology advances, that made on-site analysis possible and a credible alternative to laboratory work.. We provide here a review of the main technologies involved. However, application of field technologies was slower in the more regulated exploration industry, because there were quality compromises compared with conventional laboratory technologies, and therefore the same accuracy was not achievable initially.

By offering analytical results on the spot, in almost real time, on-site technologies fit the increasing needs of exploration teams for fast information that provides decision-making support during field work and drilling operations, and sample screening before laboratory requests.

The gain in time and flexibility, even without any consideration of lower analytical costs, has a significant impact on the

efficiency and cost-effectiveness of field operations, especially in remote areas. For instance, field analyses allow the selection of the most promising formations (Galuszka et al., 2015; Zhang et al., 2017), stream or soil areas, and to focus immediately on potential targets. At a drill site, they help the geologists to identify target formations, to sample mineralized sections more precisely, and to stop drilling when necessary. Benefits are therefore expected for field costs and the length of operations. But the most important benefits are for exploration efficiency, and for improved chances to hit targets, due to continuous feedback of information.

ON-SITE TECHNOLOGIES: CURRENT STATUS

Analytical technologies designed for the laboratory are increasingly adapted for on-site use, in order to address mineral exploration needs for faster or more efficient decision making (Lemiere, 2015). This includes elemental and mineralogical solids analysis, water analysis, and other more integrated strategies. The scope of this paper covers handheld instruments,

able to operate in the field, and site portable instruments, able to operate at remote sites, with limited logistics. All should provide decision-making results within minutes or on the same day as sampling and analysis. The fast evolution of technology implies that many of them were far less advanced or even non-existent at the time of Exploration '07.

ANALYTICAL TECHNOLOGIES FOR SOLIDS

Analyses for exploration include:

- elemental analyses for commodity elements, for major and trace elements to distinguish rock types and style of alteration,
- mineralogical analyses to constrain rock-forming, ore and alteration minerals.

They are used on mostly solid samples (soil, stream sediment, rock, ore, either at outcrop, or on drill-core, or drilling cuttings). Beyond exploration, they can be used at mine sites for exploitation, for ore processing and for waste management.

Portable X-Ray Fluorescence Spectroscopy

Origin and Early Exploration Applications

Portable or handheld X-ray fluorescence (pXRF) spectroscopy is the most frequently used elemental analysis technique. It appeared in exploration in experimental form before 1997 and was already considered to be of key interest in 2007 (Ge et al., 2005; Glanzman and Closs, 2007). Prototypes appeared as early as 1979 and were tested for exploration, followed by small scale production of heavy commercial devices, but with no documented success or usage (Glanzman and Closs, 2007). Outside of the USA, one of the earliest documented applications of pXRF in exploration was published by Konstantinov and Strujkov (1995) who recognized buried Au-Ag mineralization by the content of associated elements (As, Cu, Pb, Zn, Sn) in crosscutting dikes. This was achieved with a long forgotten, pioneer instrument developed in Russia in the early days of pXRF history, the RRK-103 "Poisk".

An intense development activity took place in China between 1984 and 2000, with the IED-2000P pXRF analyzer incorporating a ^{238}Pu isotope source. Examples include Zhou et al. (1992) in a copper prospecting area in China, using Pb and Zn as tracer elements, and a summary is given by Ge et al. (2008).

The experimental use of modern instruments for grade control was documented by Houlahan et al. (2003) at Ernest Henry Copper/Gold and Highway Reward Copper Mines in North Queensland and the Falconbridge Koniambo Nickel laterite deposit in New Caledonia.

Mainstream applications came later, mainly after 2007. Glanzman and Closs (2007) describe a case study in Northern Colorado, unpublished at the time, where the spatial

geochemical structure of the explored area was recognized in an extremely short time.

Fajber and Simandl (2012) demonstrated that pXRF could reliably analyze P from a phosphate deposit (exploration for phosphate \pm yttrium and REE), and provide a quantitative but biased, or semi-quantitative estimation for Nd, Ce, La, Zr, W and Al. Durance et al. (2014) used pXRF for litho-geochemistry at gold camps that enabled precise identification of host formations. Gazley et al. (2014) used pXRF in gold exploration for the recognition of host lithologies in drill-cores, but also for the quantification of sulphide content and of hydrothermal alteration with associated elements (As, Cu, K, V). A similar approach was used by Zhang et al. (2017) at the Mount Pleasant deposit (Fire Tower Zone, W-Mo-Bi, and North Zone, Sn-Zn-In). They deduced mineralization signatures (As and Mo, along with K, Rb, Fe and Mn depletion, interpreted as the W-Mo mineralization, and Sn, Zn, Cu and S with slightly negative Sr and Ba, representing Sn-Zn mineralization) from principal component analysis (PCA) of the multi-element pXRF data.

At the same time, pXRF was used by the environmental business as early as 1995 (Bernick et al., 1995), and extensively since 2000 (Kalnicky and Singhvi, 2001), following the publication of US-EPA standard method 6200. Even if this method was designed for RCRA¹ needs, nothing prevents its use for mining needs. This large lag time (a decade!) cannot be explained by technical reasons alone, and points to the reluctance of the exploration business to use this new technology. This would deserve a full discussion by itself, and might be difficult as it has not been documented by journal or conference papers. Quality issues are discussed below, but business practice and tradition played a role too.

An extensive description of the pXRF principle and devices (then called FPXRF) was given by Glanzman and Closs (2007) at the Exploration '07 conference. Most of it is still valid today, and the present chapter reports only updates within the last decade.

The ability of pXRF to provide reliable simultaneous measurements of many elements with Z ranging from 19 (K) to 82 (Pb) (Young et al., 2016; Ryan et al., 2017, and Figure 1) gave it the potential to locate ore elements at various scales, from the exploration lease down to the drill-core sample. It also provides reliable information on rock-forming elements, such as Al, Si, K, Ca, Fe or Ti, to better recognize host lithologies (Gazley et al., 2014) and hydrothermal alterations. Transition elements are most favourable for pXRF analysis (Ryan et al., 2017), but heavier elements are also efficiently analysed: U-Th (Tuovinen et al., 2015), Hg (Brent et al., 2017) and obviously Pb, for which pXRF was designed.

However, numerous reliability issues from expedited measurements and insufficient supervision by geochemists led to controversy and slow acceptance by the exploration world.

¹ Resource Conservation and Recovery Act (RCRA) is the USA public law that creates the framework for the proper management of hazardous and non-hazardous solid waste.

Elements for pXRF analysis																		
H																		He
Li	Be																	Ne
Na	Mg																	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Rn	
			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

cannot be analysed by pXRF
 difficult analysis with pXRF
 can be analysed by pXRF if abundant
 can be analysed by pXRF in most cases
 can be detected but cannot be analysed

Figure 1: Current pXRF elemental capabilities for handhelds.

Recent Developments

Recent developments massively increased pXRF potential for exploration teams. The analysis of lighter elements such as Al, Si or even Mg was made possible by the introduction of improved detectors (West et al., 2015) and spectrometer geometry. This proved to be more efficient and convenient than flushing the measurement area with helium, a technique that was introduced a decade ago (Berger et al., 2008). Detection limits for heavier elements were improved simultaneously, allowing recent high-end spectrometers to break the 10 mg/kg limit in favourable lithologies.

The replacement of radionuclide sources by X-ray tubes facilitated pXRF management, but reduced further its shallow depth of analysis in the sample.

Surface irregularity, mineral heterogeneity and matrix effects were soon identified as major sources of error in quantitative pXRF analysis. (Ge et al., 2005). The first one applies to measurements carried out directly on the rock face or core surface. It was addressed by Esbensen et al. (2015) by a field abrasion device (Figure 2 **Error! Reference source not found.**). This does not solve the mineral heterogeneity issue but improves measurements dealing with it.



Figure 2: Abrasion surface for pXRF measurements (photo K. Esbensen).

The small X-ray beam size makes pXRF sensitive to spot sample heterogeneity (Potts and West, 2008), but this turned to be an advantage to evaluate matrix heterogeneity (Glanzman and Closs, 2007; Gałuszka et al., 2015).

In order to cope with mineral heterogeneity, on-site sample preparation (Figure 3) was introduced to allow analysis of pulps closer to laboratory practice. In mineral exploration, this

approach is much more reliable than point-and-shoot on rock faces.



Figure 3: On-site battery-operated sample milling device.

Flexibility in spectral post-processing was introduced by one manufacturer (Bruker), while the other ones focussed on improving embedded processing algorithms built on fundamental parameters. Most instruments available from major manufacturers do not provide access to raw counts or spectra, but only to calculated concentrations, from standard or custom calibrations, and a proprietary program. Bruker offered the possibility to download raw data, for processing offline by another spectral analysis program. This may promote further development by users, but complicates the routine use of the instrument and increases the need for proper user expertise.

Matrix-specific spectral analysis and dedicated calibration are not offered as standard by instrument providers, because they are not compatible with pXRF use on varied material. They can be developed on a narrower matrix compositional range with better accuracy and lower analytical limits. This will improve pXRF performance within a specified host formation (Steiner et al., 2017).

Specific calibration schemes can also be designed to cope with interferences by an abundant element (for instance Fe, Cr) affecting the detection and accuracy of other elements within the same spectral region (Ni, Co, V).

More generally, pXRF development was led with "black box" spectral processing, favouring all-terrain versatility. Continuous development by manufacturers since 2007 improved performance over variable media using beam conditions (voltage, amperage and filters) across the entire spectral range (from 8 to 50kV). Issues with overlapping elements or specific matrixes in soil (Compton normalization mainly) or mining (fundamental parameters) modes were addressed in recent user

programs, aimed at optimizing performance for a large range of matrices, of operating conditions - and of users.

Specific calibrations or spectral post-processing require geochemical expertise. Once validated, these calibrations may be implemented on each instrument for routine use within a single exploration camp. This is a significant step forward for the technology in improving data quality.

Regardless of the processing option, it is essential that the raw data are stored intact with complete chain of custody, without any user intervention, along with processed data.

The now widespread use of pXRF analysers, especially by junior companies, sparks further innovation. For instance, Brand and Brand (2016) showed how to profit from the multi-element capabilities of pXRF and of geochemical signatures to overcome its limitations with light elements, predicting Li concentrations with elements that can be analyzed by pXRF. A combination of heavier elements, geochemically associated with lithium, can be correlated with laboratory Li analyses with an acceptable level of confidence.

The use of PCA and other multivariate methods on elements that can be analyzed by pXRF allows prediction of elements that cannot be analyzed by pXRF, or not reliably (Zhang et al., 2017)

Precision, Accuracy and Relationship with Laboratory Results

The consistency between field measurements and laboratory analyses is frequently discussed for pXRF, which is the most documented technique to date. Most laboratory analyses for exploration are however performed by ICP or AAS spectrometry after acid sample digestion. In favourable cases, field measurements and these laboratory analyses show a good correlation (Figure 4). In other cases, reproducible field measurements and laboratory analyses show a biased correlation (Figure 5). Such a bias happens more frequently for elements which are more difficult to analyze for spectral reasons, even by laboratory XRF, or by pXRF for instrumental compromises. However, a bias may be the result of spectral interference by a locally abundant element, hampering the analysis of an otherwise easy element. This is particularly true with iron, a ubiquitous element in exploration, which tends to interfere with other transition elements. Bias is not only element-specific but also matrix-specific. For instance, Zn can be well correlated between pXRF and laboratory analyses in a sandstone, and slightly biased in a limestone. From the authors' experience, some elements are more prone to bias (Al, Si, P, S, Ti, V, Cr, Co, Ni, Se, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Ba, W, Hg, Bi), and some are more often well correlated (K, Ca, Mn, Fe, Cu, Zn, As, Rb, Sr, Pb), but there is no systematic rule pertaining to this.

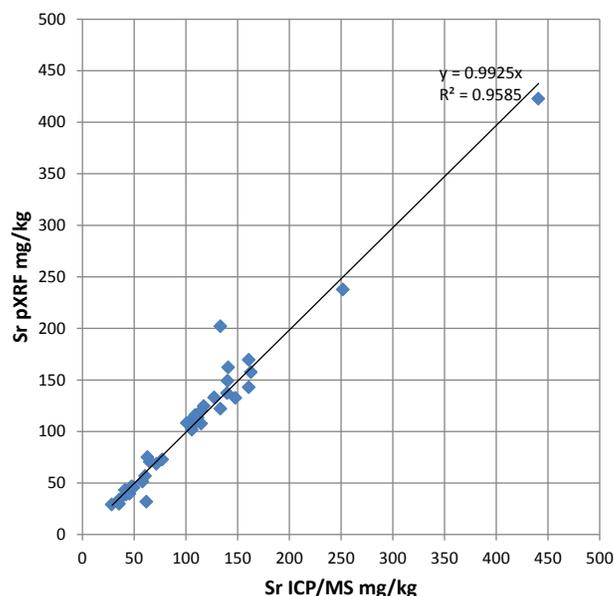


Figure 4: Correlation between laboratory and pXRF data, on a favourable case (strontium in sandstone).

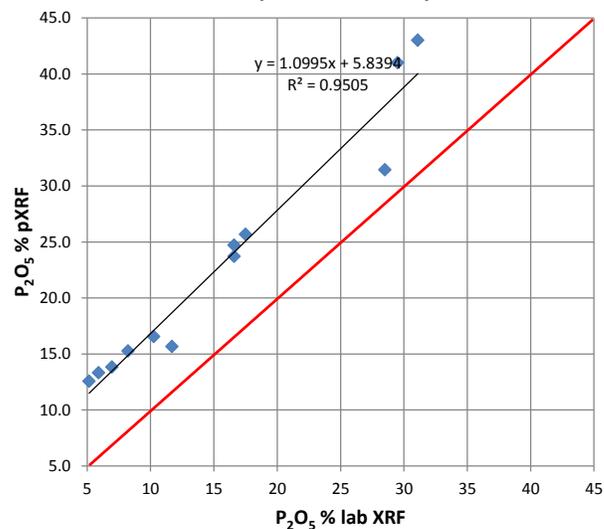


Figure 5: Correlation between laboratory and pXRF data, on a less favourable but viable case (phosphorus in carbonate rocks).

Bias depends also on the type of digestion to which pXRF results are compared. Results obtained by pXRF are often higher than laboratory results based on the standard aqua regia digestion (Figure 6), especially for refractory minerals such as cassiterite (Sn), wolframite (W) or rutile (Ti). In this case, pXRF analyses carried out on laboratory standard pulps will often be more accurate than standard laboratory analyses, unless total digestion techniques are used (Figure 7).

The comparison between field and laboratory analyses should strictly speaking be made with laboratory XRF, which is based on the same principles as pXRF but benefits from better instrumental and laboratory conditions. However, a large part of

geochemical exploration is based on wet chemical methods, especially ICP/AES, ICP/MS and AAS. This has led to improper bias controversy when laboratory results based on partial digestion were opposed to pXRF total analyses. Any reported bias should be first checked using total digestion techniques such as HF-based digestion or alkali sintering.

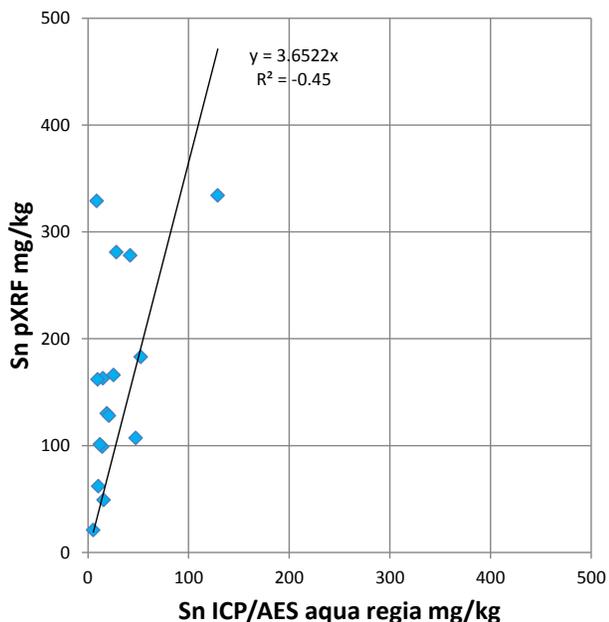


Figure 6: Correlation between aqua regia ICP and pXRF data.

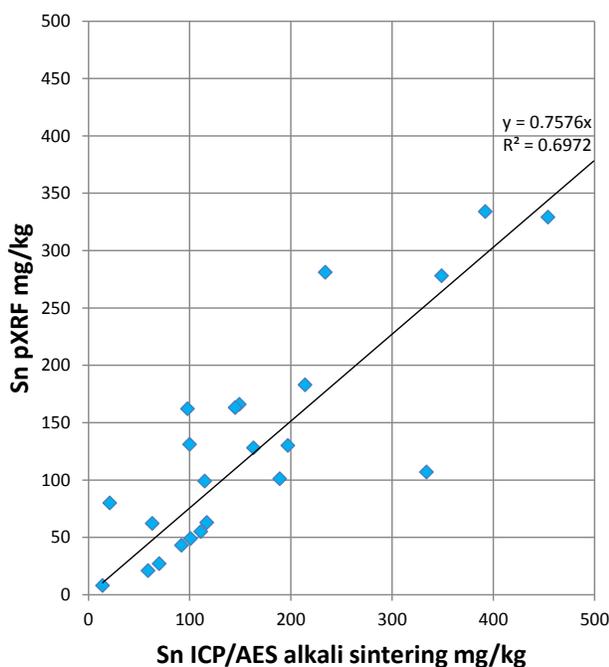


Figure 7: Correlation between alkali sintering ICP and pXRF data.

Field analyses and on-site analyses cannot compete with laboratory analyses in terms of sensitivity, precision or accuracy, due to compromises in sample preparation, instrument performance and work environment. From this perspective, field and on-site results must always be controlled by a subset of laboratory samples. However, ultimate laboratory accuracy is not generally required for exploration decisions.

Field and on-site results must only achieve the level of confidence expected from the decision. Bias can be corrected for with the use of appropriate standards or with site samples already analyzed by a laboratory. Precision is usually at least acceptable and the only real issue is sensitivity for ultra-trace or nugget commodities. This issue may be often overcome using companion or trace elements in combination. A careful confidence evaluation is always necessary, based on field and laboratory analyses, before field or on-site methods are used for decision-making.

pXRF Quality and Exploration

The introduction of robust procedures and QA/QC schemes (Hall et al., 2013; Gazley and Fisher, 2014) helped pXRF to overcome its controversial reliability issues. A critical review of expedited but inadequate field practice is also given by Durance et al. (2014).

Unlike laboratory analyses, which may be produced by a single instrument, field analyses are often produced by several instruments within one team. This may lead to minor drift between instruments, and even between batteries (Chang and Yang, 2012). This issue is easily dealt with using instrument traceability procedures and standards. Durance et al. (2014) recommended the use of site-specific calibrations rather than general purpose CRMs, and warned against measurements through paper bags.

Matrix specific issues may also require geochemical expertise for the reliable interpretation of field data.

Close cooperation between the field analysis team and the laboratory tends to improve significantly the quality of the former and the cost-effectiveness of the latter, with an improved performance of geochemical surveys as a result.

QA/QC good practice is the condition for field measurements gaining acceptance in press releases with respect to JORC or NI 43-101 regulations. These aspects were investigated by Arne and Jeffress (2014) and Arne et al. (2014) who concluded on the acceptability of pXRF under strict QA/QC conditions: "A robust sampling methodology with a suitable quality assurance/quality control program should produce pXRF data of sufficient quality for public reporting purposes, provided that the data are presented using appropriate cautionary language and adequate supporting information". Besides common sense evidence on sample preparation and sample containers, these authors insisted on the necessity of implementing a QA/QC scheme similar to that used by laboratories, and on the relevance of pXRF data for supporting exploration results as long as QA/QC results were satisfactory.

Stoker and Berry (2015) showed through two examples that reporting of exploration results, mineral resources and ore reserves based on pXRF were acceptable, as long as pXRF use complied with good laboratory practice.

Laser-Induced Breakdown Spectroscopy

Laser-induced breakdown spectrometry (LIBS) is a recent competitor of pXRF for elemental analysis (Fortes and Laserna, 2010). The first prototype appeared in 1995 (Cremers et al., 1996), but handheld instruments (Figure 8) did not reach the market until 2010. It does not face the limitations of pXRF for light elements ($Z < 14$) (Harmon et al., 2013). LIBS offers an efficient and powerful method for simultaneous multi-element analysis of materials. Elements that can be detected and theoretically quantified span the majority of the Periodic Table, including light elements such Li, Be, B, Na and Mg.

In principle, LIBS is a form of atomic emission spectroscopy, relying on characteristic spectra emitted from plasma generated by a high-energy laser pulse striking a sample (solid, liquid or gas). Each pulse produces a high-intensity plasma that is detected by a series of spectrometers, and the resulting emission spectrum contains atomic emission lines from the atomic species present in the plasma. The spectrometers are able to measure, with varying degrees of sensitivity, almost every element in the periodic table within each laser pulse. Quantitation is achievable either by conventional calibration methods using defined standards, or by numerical methods (e.g., chemometric methodology of Death et al., 2009).



Figure 8: LIBS spectrometer (photo IVEA).

Laser-induced breakdown spectroscopy is not currently widely used in the mineral industry, however, one should keep in mind that LIBS has advantages over many other microanalytical tools, such as little to no sample preparation required, accommodation of small sample sizes, detection of trace elements to ppm levels, and its modular and readily configurable nature in terms of instrumentation (cf. Harmon et al., 2009; Hark and Harmon, 2014). It also produces little damage to samples, consuming nanograms of sample material per laser pulse. Each laser pulse has the potential to detect nearly all elements in a mineral with a suitably configured instrument. These advantages should be contextualized by the disadvantages of LIBS, with reference to

physical and chemical matrix effects, the inherent shot-to-shot variability in LIBS experiments, and a level of precision of ~5–20% RSD (Hark and Harmon, 2014; Rossi et al., 2014). The technique still needs development of protocols and exploration-oriented standard libraries.

Besides this, LIBS is still lacking sufficient case studies for exploration, which makes it a pioneer's choice, requiring geochemical expertise. It was recently offered as a complement to pXRF, with both instruments in the same case, sharing sample preparation.

Spectral Gamma

Spectral gamma analysis is an age old technology used for precise mapping of radioactive elements (K, Th, U) in drill-holes, but also on outcrops with handheld instruments. It recently took advantage of improved ground and airborne (drone) instruments to complement hyperspectral imagery (Bharti et al., 2015). It has great development potential as a field instrument, if used as a complement to imagery and/or other handheld instruments (pXRF, LIBS, IR). It was recently used with success by us for heavy mineral level detection in sandstone, in combination with pXRF (Figure 9). In this case, U+/-Th anomalies were recorded on the outcrop using a handheld RS-300 portable gamma spectrometer (Radiation Solution INC) and further investigated by pXRF.

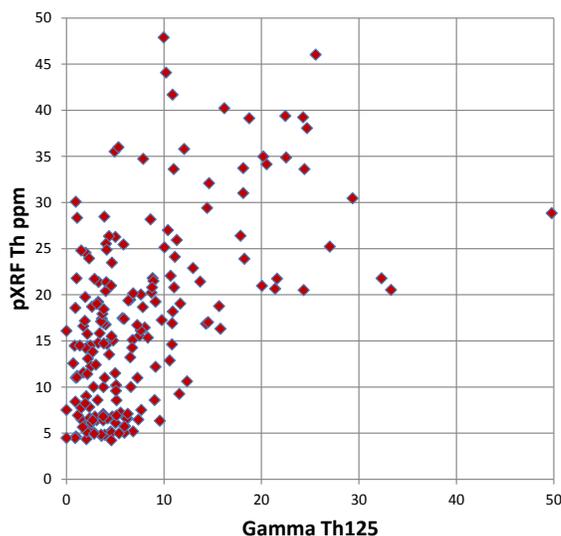


Figure 9: Example of correlation between spectral gamma and pXRF data in sandstone.

Portable X-Ray Diffraction

With the advancement in hardware technology, namely X-ray tubes, detectors and processors, and more powerful and sophisticated software packages, X-ray diffraction (XRD) has become a qualitative and quantitative tool for the identification of crystalline materials and has tremendous potential applications in exploration and mining. Until now XRD has been a laboratory technique used mainly in exploration for specific investigations. With automation of the data processing,

XRD has the potential to become a routine technique for systematic analysis of geologic materials.

Field-portable X-ray diffraction (pXRD) instruments appeared during the last decade. They can be operated in the field, despite being heavier than handheld pXRF analysers. Portable XRD instruments aim to fill a critical role in exploration mineralogy (especially the recognition of hydrothermal alteration zones and secondary minerals, and also lithologies or ore types (Uvarova et al., 2014; Burkett et al., 2015)). Portable XRD analysers have a unique piezo-harmonic, Vibrating Sample Holder (VSH), which vibrates the sample without macroscopic movement of the holder (Sarazzin et al., 2005). This exposes crystallites in each sample to the X-ray beam in random orientations, thus helping to reduce orientation effects and allowing for superior particle statistics (Sarrazin et al., 2005). In field conditions, no additional sample preparation is required for a pXRD instrument other than crushing the dry sample down to particle size of less than 130 μm , and very little sample is required (a few mg). However, a finer grain size will improve the quality of analyses. Similarly to pXRF, a laboratory-type sample preparation will provide the best results, but a simplified preparation will provide quickly useful information.

In an exploration context, pXRD does not require breakthrough thinking like LIBS or pFTIR. The type of information provided does not differ fundamentally from laboratory XRD. The limitations to be taken into account result from the instrument size and X-ray source. It is expected that technology improvement will continue and use of XRD-based mineral information in exploration data will be more common.

pFTIR

Handheld near-infrared (NIR) instruments are routinely used for humidity measurements (Minasny et al., 2011) and for asbestos detection (US-DOE, 2009), and also for mineralogy investigations (Shankar, 2015). Middle infrared (MIR) instruments are used for extended mineralogy and organic compounds, but NIR range instruments are still the most frequently used pFTIR in mineral exploration. Neither provide quantitative information easily. Field portable units (Figure 10) operate usually in diffuse reflectance, but attenuated total reflection (ATR) can be also used for spot surficial measurements.

There is a need for a chemometrics approach to process the data and for the development of exploration-oriented standard libraries. pFTIR spectrometers have a proven potential for hydrothermal alteration recognition and mapping (Chang and Yang, 2012; Zadeh et al., 2014; Huang et al., 2017), identified before field technology was easily accessible (Thompson et al., 1999). They can therefore complement elemental analyses (pXRF, LIBS) for target identification and delineation.



Figure 10: pFTIR spectrometer (photo Agilent).

Besides hydrothermal alteration studies, pFTIR measurements may help characterization of carbonate horizons (Ji et al., 2009) or identification of supergene minerals (Velasco et al., 2005).

μRaman

Field-portable Raman instruments (see Figure 11) appeared in the last decade, whereas previously Raman spectrometry was a specialist technique confined to the laboratory. The affordability of handhelds opened this technology to non-specialists, and signal processing was focussed on positive identification, rather than on spectral resolution, which is best achieved with larger and more stable laboratory spectrometers. It is currently used for extended mineralogy recognition (Jehlička et al., 2011; Bersani et al., 2014) and for organic molecule detection. Most Raman handheld spectrometers operate at 532 nm, 785 nm or 1064 nm wavelengths. Despite real field successes, they still need the development of protocols and exploration-oriented standard libraries. Like pFTIR, they have a significant potential for hydrothermal alteration recognition (Culka et al., 2015) and mapping. They are less sensitive than pFTIR spectrometers to water contents in samples, but they may be affected by ambient light conditions and by cosmic ray interference. The interpretation of Raman spectra is not yet a routine process.



Figure 11: μRaman spectrometer (photo J. Jehlička).

ANALYTICAL TECHNOLOGIES FOR WATER

Water analysis in the field is not as widespread as solids analysis in mineral exploration, but commodity element or trace element analysis is now possible. This allows field screening for hydrogeochemical exploration, either with commodity elements (Cu, Zn, Pb, etc.) or trace elements (As), with sensitivity depending on the analysis technique. Most are electrochemical instruments, more sensitive and precise than colorimetric or immuno-assay field kits.

Voltammetry and Polarography

Field applications of voltammetry and polarography are based on miniaturized laboratory instruments. They were developed decades ago, as this technology was known for a long time, but did not reach widespread use due to troublesome electrode operation. Anodic stripping voltammetry (ASV) uses a novel electrode printing technology (Pérez-Ràfols et al., 2017) to become field portable (Figure 12). It allows on-site trace level analysis in water for commodity (Cu, Zn, Pb, and also Ni, Co, Au, Sn) and environmental/trace (As, Cd, Hg, Mn, Se) elements down to 1 ppb in favourable conditions.



Figure 12: ASV printed electrode.

Polarography is a traditional but highly sensitive electrochemical technique, similar to ASV (Mann and Lintern, 1984), but perhaps more flexible and allowing precious metal detection. It is also more experimental in its field application and demands care and skills to operate.

Voltammetry was used by Idronaut (IT) to develop a large multiparametric probe, with profiling abilities for metals and metalloids (Buffle and Tercier-Waeber, 2005). It is a bulky instrument (Figure 13), unable to be used in observation wells due to the size of the sensors. Its main applications are oceanography and lake monitoring, but it might be used in mine pits.

Unfortunately, the current miniaturization efforts on this technology do not yet allow its implementation on standard 2" or 4" multiparametric probes. Such an advance would open

doors for metal monitoring and groundwater hydrogeochemical exploration.



Figure 13: Voltammetric VIP probe (photo Idronaut).

Ion Selective Electrodes

Ion selective electrodes (ISEs) are inexpensive and simple to use, with a wide concentration range for several chemical and physical water parameters. They each have a sensitive membrane through which theoretically only the specific ion can pass. The ions diffuse through the membrane until equilibrium is reached, building up a charge proportional to concentration. The ISEs commonly available to date are designed for pH, NH_4^+ , Ba^{2+} , Br^- , Cd^{2+} , Ca^{2+} , Cl^- , Cu^+ , CN^- , F^- , I^- , Pb^{2+} , Hg^+ , NO_3^- , NO_2^- , ClO_4^- , K^+ , Na^+ , Ag^+ , S^{2-} , and SCN^- .

CSIRO within Deep Exploration Technologies CRC developed a fluid management system that has a peristaltic pump and 12 ISEs measuring pH, Eh and concentrations of a number of cations and anions (Figure 14). This system pumps the fluid and continuously measures 12 parameters. The system can fit into a medium size Pelican case, and hence is transportable



Figure 14: Fluid Management System consisting of a peristaltic pump and 12 ion selective electrodes (photo Nathan Reid, CSIRO).

The fluid management system underwent a field campaign during Mineral System Drilling Program in South Australia, where it was installed next to the drill rig and measured pH, Eh and 10 cations and anion concentrations of drilling fluids in real-time.

ON-SITE LABORATORY TECHNOLOGY

We do not address here fast response field laboratories using regular lab equipment, as these tend to be present mainly at operating mine sites rather than in grassroots exploration.

Drilling On-site Instrumentation

The Lab-at-Rig® analytical system developed by CSIRO, Imdex and Olympus within Deep Exploration Technologies CRC is a novel analytical technology applicable to exploration camps. The system provides the analysis of drill powders (drill fines) extracted from drill fluid that is returned during drilling. This novel sample medium records cm-scale changes in geochemistry of rock being drilled through. In addition to being an ideal sample medium (~78% of particles are <38 µm; cf. conventionally pulverized samples where ~42% of particles are <38 µm) that is ready for analysis once dried, diamond drill fines may produce a larger sample per metre drilled than recovered by the core itself, and thus be a better representation of the rock that has been drilled through. For an HQ hole size (for rocks with specific gravity = 3100 kg/m³), the weight of drill fines produced in 1 m of drilling is 12.5 kg, whereas the weight of the 1 m in length of core for the same interval is 9.7 kg. The Lab-at-Rig® system is part of the Assay While Drilling (AWD) suite of products offered by REFLEX. It currently integrates pXRF and pXRD sensors. Lab-at-Rig® is not only offering results in real time to improve the efficiency of exploration during drilling operations, but it combines chemistry and mineralogy to offer an opportunity for enhanced field interpretation and more relevant exploration decisions. Specific attention to sampling and preparation issues allows improvement in the level of confidence of data and in subsequent decisions. A case study of applying Lab-at-Rig® system was conducted during the drilling of DETBrukunga2 drill-hole from the DET CRC Drilling Research and Training Facility, located at the old Brukunga sulphur mine in the Adelaide Hills, South Australia (Uvarova et al., 2016). It was demonstrated that high-resolution (≤5 cm resolution) geochemistry and mineralogy could be obtained with sampling resolution and depth fidelity. The approach undertaken in the study by Uvarova et al. (2016) was to collect diamond drilling cuttings brought up to the surface with drilling fluids from well constrained depth intervals, separate the drill fines from the drilling fluid using a Solid Removal Unit, dry the drill fines and analyze them with portable XRF and XRD analyzers which are part of the Lab-at-Rig® system. The sample has proven to be homogeneous (at the cm-scale) and any observed heterogeneity was within analytical precision. The physical nature of the drill fines and their upward velocity are enough to avoid any lag that can potentially create smearing in the data, especially with normal 1 metre composite sampling. Moreover, the sampling depth can be determined accurately and precisely within a narrow range. In the first instance we suggested analyses by a combination of XRF and XRD, as these portable sensors are well developed, have an excellent performance and produce data

of high quality. Comparison of XRF and XRD results for drill fines with existing logging of the corresponding core showed that drill fines are consistent with the lithologies intersected by the drill-hole. Comparison of pXRF results from drill fines are comparable with assay results by a commercial laboratory on corresponding core (Figure 15). The approach suggested in the study of combined pXRF-pXRD analyses can be performed on a large set of complex geological samples and the techniques complement each other (Uvarova et al., 2016)). Portable XRF results can be used to verify the results of portable XRD and vice versa. A small amount (less than 5–10 g) of sample is required for coupled pXRF-pXRD analysis that can be performed with currently available portable instruments in <15 minutes for both measurements. Drying of this amount of material requires little time (<30 minutes). Application of the Lab-at-Rig® workflow results in full chemical and mineralogical analyses by the time the drill-hole is completed, providing ‘objective logging’ and an opportunity to make real time decisions during the course of a drilling campaign. It was also demonstrated that the analysis of drill fines extracted from drill fluid is an excellent sample medium; this is critical as rapid drill technologies, such as coil tube drilling (Hillis et al., 2014), will only return a powdered sample to the surface.

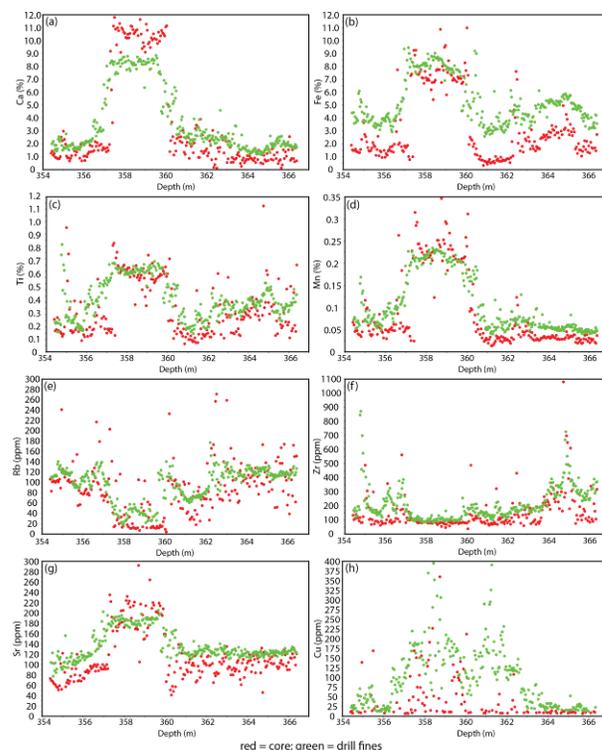


Figure 15: Comparison of selected elemental concentrations determined by pXRF in drilling fines and the corresponding core.

Core Scanners

X-Ray Fluorescence core scanners are not portable but can be installed on-site in a tent or shipping container. They provide rapid core scanning on a core that is just extracted from the drill-hole. Other sensors can be combined with XRF, for instance

spectral gamma, NIR or LIBS. It can be beneficial to acquire simultaneously elemental and mineral information, and to combine both to build a mineral chemistry map of the core. They also collect high resolution photo images that can be used for structural analysis, and even for remote or routine logging. They allow creating a 3D model of the core tray with the core in it, allowing structural logging applications.

Though these instruments are not truly field portable, they provide on-site and real time information, and contribute to exploration efficiency in the same manner as field devices.

GEOCHEMISTRY IN THE FIELD, GEOCHEMISTRY AT SITE

The first requires handheld instruments, or at least field-portable, battery-operated instruments. It operates on outcrops, on soil surfaces, on sieved sediments, or on samples submitted to a very basic preparation, using field-portable devices such as battery-operated mills.

The second uses transportable laboratory instruments, or any type of rugged equipment that does not require a laboratory-controlled environment. It operates usually on 100/250V power provided by site generators, and may be hosted by portable cabins or laboratory trucks. It may become a full mine site laboratory when the prospect becomes a mine. Exploration for orebody extensions of a mine is often supported by the mine site laboratory.

Both approaches provide geochemical information much more quickly than samples sent to a regional or international laboratory. They support decision-making on site, and sampling plans based on measurement results.

The first approach provides invaluable services in remote areas, where shipping samples to a laboratory may face long delays and severe logistical difficulties. It is also essential support for mobile teams involved in regional and grassroots exploration.

REAL TIME DECISIONS BASED ON FIELD ANALYSES - BENEFITS FOR EFFICIENCY AND COST-EFFECTIVENESS

Most mineral exploration decisions are based on flexible thinking rather than on a preset framework of investigation.

One of the key benefits of real-time analyses, or short delay analyses (less than a day) is a possibility to adjust sampling plans, test hypotheses based on ongoing results, and make fast decisions for exploration work. Examples of such include:

- decisions on further drilling and/or sampling, based on commodity element concentrations or on key geological markers, more easily recognized than by the geological logging work on its own;
- increasing sample density in the most promising parts of a looser grid, allowing deployment of sampling staff or analytical resources where it matters;
- exploring promising areas beyond the original grid without extending the whole grid too far;

- applying further field techniques or more focused calibration schemes on identified targets to gain quickly a better knowledge of them.

This is particularly important for remote locations, where sample delivery logistics to a laboratory may become time-consuming and laborious. This may also apply in highly competitive situations, where the exploration team wishes to keep as much as possible of the information internal before a decision is made or publicized.

This is similar to strategies such as ASAP (Adaptive Sampling and Analysis Programs (US-DOE, 2001) and Figure 16), dynamic workplans (Robbat, 1997) or TRIAD (US-EPA, 2008) in environmental investigations. The cost-effectiveness of these strategies was demonstrated in comparison to predetermined sampling strategies.

Besides their use for immediate decisions, field analytical techniques also offer cost-effective screening capabilities while selecting the samples to be submitted to a laboratory for conventional analysis. They significantly improve the efficiency of smaller sample sets on a more limited budget.



Figure 16: Adaptive Sampling and Analysis Program design and execution (from US-DOE, 2001).

DATA QUALITY VS. DATA DENSITY: WHICH IS BETTER FOR EXPLORATION EFFICIENCY?

The reliability of a professionally sampled, professionally analyzed (laboratory) data set should be better than the reliability of a data set collected with field portable techniques,

due to limitations in sample preparation and field analysis. This was discussed mainly for pXRF, which is currently the main technology for on-site analysis. The lessons in its deployment can be applied to the other techniques described here.

However, budget and delay constraints imply that the data set generated by the former may be much smaller than the latter, with a much lower data density. The number of data points for a given budget may be up to ten times smaller when using a conventional laboratory analysis instead of a field or on-site analysis. The cost ratio depends actually on the sampling strategy. On a preset sampling plan such as a regular grid, with strict sampling procedures, the cost of sampling may exceed by far the analytical budget, even with shipping costs, and the benefit of field analyses will not be obvious. Benefits from on-site analyses can be expected for flexible sampling plans, or where sampling procedures can be simplified for on-site analysis.

Data quality, or fit-for-purpose ability (Ramsey and Boon, 2012), is a measurement of how far the geochemical data set will be representative of the explored object, and how far exploration decisions based on it will be reliable, in terms of effectiveness and financial consequences. The usually lower quality of field analyses is more than balanced by the much larger number of analyses made possible by on-site methods. For instance, a target may be missed by a less dense laboratory sampling grid, because it was either too small or its definition was not sharp enough. This can happen with deep targets or targets under cover.

The benefits of larger or denser data sets are observed also during later data processing and modelling. The application of geostatistics to on-site data, especially from pXRF (for instance Eze et al., 2016), is facilitated by their higher spatial density, by their multielement coverage, and by their more detailed uncertainty data matrixes. The same applies to geometallurgy (Gazley and Fisher, 2014), taking advantage of multielement data for several different applications of the information system (geologic model, ore reserves, mechanical stability, waste management, all used for profitability optimization), and for spatial modelling.

It is also more than balanced by the better relevance of the field data set, resulting from dynamic sampling and faster decision making. Being able to resample or refine the sampling pattern on site gives the opportunity of pre-processing on-site data and provides more focused exploration information before the team actually leaves the site.

THE PLACE OF ON-SITE TECHNOLOGIES IN EXPLORATION TOMORROW

In the early 2000s, most on-site technologies were not offering the level of reliability, and thus confidence, required for making sound exploration decisions. Despite the advantage of quick analysis, they were not often developed, or even used. They became increasingly popular after 2007 in exploration camps and even at mine sites, despite some reluctance within the industry to deploy these innovative methods.

Use of on-site analytical methods in site operational automation depends on the physical characteristics of the technique. pXRF and pXRD need a proximal contact with the sample and cannot be easily adapted to a material flow analysis process, unless an automatic sample preparation scheme is considered. XRF and XRD sensors implemented over conveyor belts are usually heavier and more powerful than handhelds. These sensors are therefore modified laboratory devices. LIBS, pFTIR and μ Raman accept greater distances and may be incorporated in a sample monitoring scheme if a signal processing chain is used. Water samples cannot yet be analyzed in-situ in most cases, this requires subsampling from a flow derivation.

Exploitation of complex spectra (especially for pFTIR and μ Raman) may need mathematical techniques such as chemometrics, rather than direct calibration with standards. Alternative approaches to analytical calibration may be based on comparative or differential techniques, but they will require further critical reviews. Direct quantification of minerals by pFTIR and μ Raman are not yet available routinely, as is the case for pXRF. They are not, however, out of reach, and we may hope to see mineral quantification reach the market before Exploration '27. This quantification is expected to be based on larger databases, with pure mineral and alteration assemblage spectra. It will also require patient research using chemometrics and possibly other approaches (e.g., machine learning) to unlock the apparent complexity of spectra. Calculation capabilities implemented in the field instruments can be an attractive option—in the same way as for Positive Material Identification, but it may lead to "black box" machines with little user control on the diagnosis. On the other hand, increasingly easier and more powerful calculation capabilities will offer advanced exploration staff the opportunity to maximise the value of their data with post-processing and data integration. The "black box" approach is often favoured by manufacturers, while the "big data" approach gives users a better control of their results.

Most of the further development of on-site analysis is expected to be based on its integration with laboratory methods and on sound QA/QC practice, allowing a precise evaluation of its confidence level and uncertainties.

This is applicable to elemental analyses, on which official exploration results are based. The constraints on mineralogical analyses, used mainly to guide exploration campaigns, are not as restrictive.

It will be also possible to reach better global confidence levels using large data sets generated by field instruments than with budget-restricted laboratory programs. In order to increase the role of field analyses in exploration, the efforts must be focused on increasing the level of confidence in field results. This can be achieved through a stricter application of laboratory principles to field analyses, and through the development of robust and reproducible sampling and measurement protocols. Such protocols can be shared between exploration geologists, mining engineers and field analysis technicians/chemists, with large benefits for data consistency.

Instrument performance will improve too, but it is more likely to improve detection limits or element selectivity, to overcome

interferences. New instruments may appear, either from less documented spectral areas or from a different approach to spectra, like in Raman analysis.

This wealth of field-generated information also has to be taken in consideration by laboratory-based programs. These often overlook potential issues on sample representativeness, sample heterogeneity and sample digestion, while field measurements offer representativeness monitoring and physical analyses without digestion. Discrepancies between field and laboratory results obtained with the standard aqua regia digestion may point to unexpected refractory mineral phases and suggest the use of total digestion techniques instead.

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