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► To cite this version:

Bruno Lemiere, Y Uvarova. Introduction: New developments in field portable geochemical techniques and site technologies and their place in mineral exploration. . Exploration 17, Field Analysis Workshop , Oct 2017, Toronto, Canada. hal-01740971

HAL Id: hal-01740971

<https://hal-brgm.archives-ouvertes.fr/hal-01740971>

Submitted on 22 Mar 2018

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Introduction: New developments in field portable geochemical techniques and site technologies and their place in 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 meter 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 analyse meters of core as it is being drilled. Core scanners include hyperspectral and XRF systems, such as Corescan, HyLogger and Minalyzer CS, 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.

In this session we will introduce some techniques which appeared since 2007 or underwent major progress and discuss their benefits, challenges and pitfalls, why use them and what to expect from them.

WHY USING FIELD TECHNIQUES, WHAT TO EXPECT FROM THEM

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 (Gałuszka 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 mineralised 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.

SOME TECHNIQUES WHICH APPEARED SINCE 2007 OR UNDERWENT MAJOR PROGRESS

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 presentation 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 for 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 & Closs, 2007). At the same time, pXRF was used by the environmental business as early as 1995 (Bernick et al., 1995), and extensively since 2000 (Kalnicky & Singhvi, 2001), following the publication of US-EPA standard method 6200. Even if this method was designed for RCRA 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. Quality issues were raised, but business practice and tradition played a role as well.

Principle and current applications

An extensive description of the pXRF principle and devices (then called FPXRF) was given by Glanzman & Closs at the Exploration'07 conference. Most of it is still valid today, and this presentation reports only updates within the last decade, with summaries by Hall et al. (2013, 2014), West et al. (2015) and Young et al. (2016).

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 recognise 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.

Elements for pXRF analysis																						
H																		He				
Li	Be																B	C	N	O	F	Ne
Na	Mg																Al	Si	P	S	Cl	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						
			Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn					
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 technology 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. 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 **Erreur! Source du renvoi introuvable.**). 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, but this turned to be an advantage to evaluate matrix heterogeneity (Glanzman & 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

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).

Laser-Induced Breakdown Spectroscopy

Laser-induced breakdown spectrometry (LIBS) is a recent competitor of pXRF for elemental analysis (Fortes & Laserna, 2010). The first prototype appeared in 1995 but handheld instruments (Figure 4) 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 chemometrics methods.



Figure 4: LIBS spectrometer (photo IVEA)

Laser-induced breakdown spectroscopy is not currently widely used in the mineral industry, however, it has advantages 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). 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 5). In this case, U \pm -Th anomalies were recorded on the outcrop using a handheld RS-300 portable gamma spectrometer (Radiation Solution INC) and further investigated by pXRF.

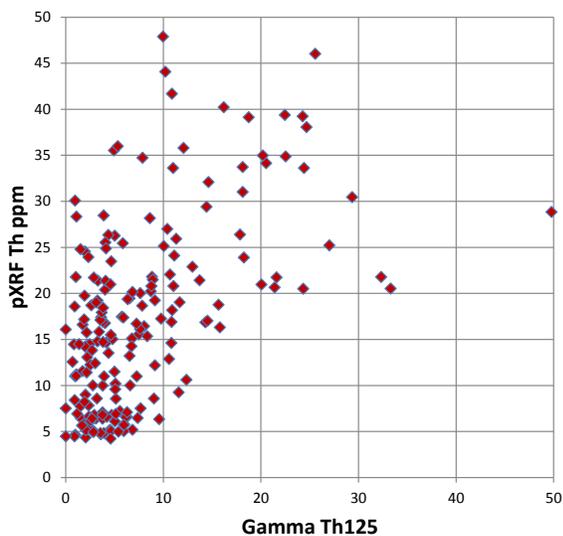


Figure 5: Example of correlation between spectral gamma and pXRF data in sandstone

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, but also lithologies or ore types, Uvarova et al., 2014 and 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 (Sarrazin 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 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), but also for mineralogy investigations (Shankar, 2015). Middle infrared (MIR) instruments are used for extended mineralogy and organic compounds, but the most frequently used pFTIR in mineral exploration are still NIR range instruments. Neither provide quantitative information easily. Field portable units (Figure) 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 & 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 4: pFTIR spectrometer (photo Agilent)

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

μ Raman

Field-portable Raman instruments (see Figure) 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 7: μ Raman 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 miniaturised 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-Ráfols et al., 2017) to become field portable (Figure). It allows on-site trace level analysis in water for commodity (Cu, Zn, Pb, and also Ni, Co, Au, Sn) and environmental/trace elements (As, Cd, Hg, Mn, Se), down to 1 ppb in favourable conditions.

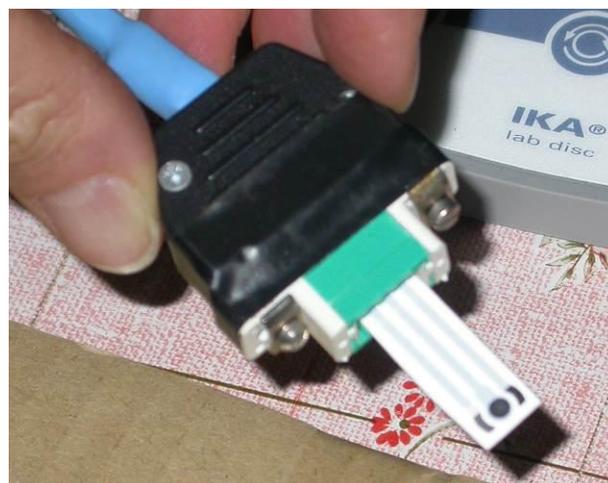


Figure 8: ASV printed electrode

Polarography is a traditional but highly sensitive electrochemical technique, similar to ASV, 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 & Tercier-Waeber, 2005). It is a bulky instrument (Figure), 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 miniaturisation 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 9: 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). 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 10: 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. The Lab-at-Rig® system is part of 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 analyse them with portable XRF and XRD analysers which are part of the Lab-at-Rig® system. 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 assays results by a commercial laboratory on corresponding core (Figure). 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.

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.

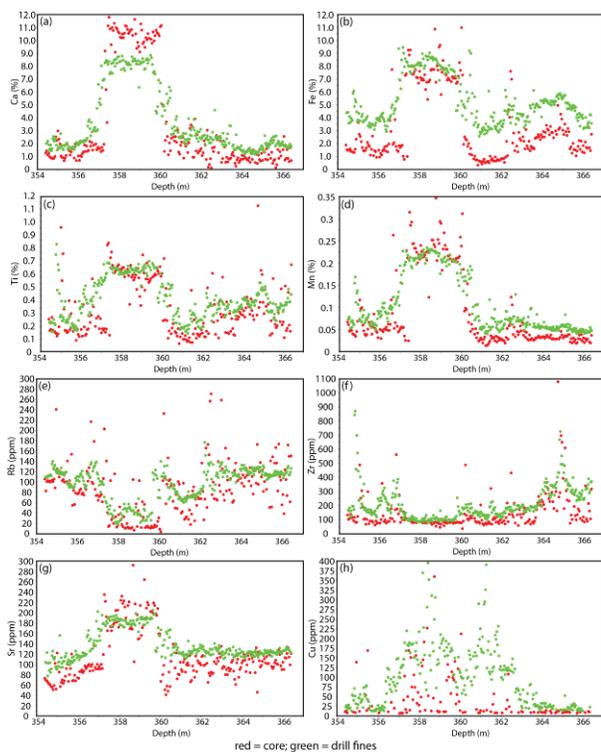


Figure 11: Comparison of selected elemental concentrations determined by pXRF in drilling fines and the corresponding core

BENEFITS, CHALLENGES AND PITFALLS

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 lab instruments, or any type of rugged equipment which does not require a lab-controlled environment. It operates usually on 100/250V power provided by site generators, and may be hosted by portable cabins or lab 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 lab.

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.

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