

Coupled XRF and XRD analyses for rapid and low-cost characterization of geological materials in the mineral exploration and mining industry

INTRODUCTION

Portable X-ray fluorescence (pXRF) spectrometry has numerous applications in a wide range of studies, including: non-destructive analyses in the alloy metals industry, particularly scrap metal sorting and material identification; archaeometry (Longoni et al. 1998); environmental sciences for conducting contamination characterization, removal, and remedial operations at hazardous waste sites (Kalnicky & Singhvi 2001; Melquiades and Appoloni 2004), archaeology (Romano et al. 2006; Phillips & Speakman 2009; Tantrakarn et al. 2009; Shakley 2010; Shakley 2011; Liritzis & Zacharias 2011); non-invasive analysis of museum artefacts (Karydas 2007; Uhlir et al. 2008); rapid screening of toxic elements in various products, goods and media (Ashley et al. 1998; Palmer et al. 2009); and, soil analysis and agriculture (Clark et al. 1999). In the last decade, portable XRF analysis has emerged as an important analytical technique for exploration and mining (Figueroa-Cisterna et al. 2011; Fisher et al. 2013; Gazley et al. 2011a, 2011b, 2013; Gazley & Fisher in press; Le Vaillant et al. in press). Portable XRF offers rapid, accurate and cost-effective analysis of geologic samples and provides data of high quality where appropriate calibration and quality assurance and quality control (QA/QC) protocols are followed.

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 technique that is used mainly in research, but with automation of the data processing, XRD has the potential to become a routine technique for analysis of geologic materials. Ultimately, combined portable XRF and XRD instrument analyses will allow rapid chemical and mineralogical characterization of a sample, which in turn

allows discrimination of lithologies, hydrothermal alteration and ore types. Coupled portable XRF-XRD analyses will pioneer a new paradigm in greenfields and brownfields exploration and geometallurgy. Here, we give an example of the application of coupled pXRF-pXRD analysis and software packages for data processing currently available on the market to a set of geologic samples.

SAMPLES AND ANALYTICAL TECHNIQUES

Samples

The samples studied here are from a diamond drill hole at the Brukunga pyrite mine, South Australia, closed in 1970s and currently being used as a Deep Exploration Technologies Cooperative Research Centre Drilling Testing and Training Facility. It is located 47 km east from Adelaide (Fig. 1).

The rocks intersected by the drill hole are metasediments of the Nairne Pyritic Formation comprised of fine-grained greywackes, quartzites and siltstones and pyrite- and pyrrhotite-bearing beds siltstones of Cambrian age (Skinner 1958; Graham 1978). The drill hole intersected the main ore body from 130 to 280 m, and a number of thin zones with iron sulfide veins. The rocks of the Nairne Pyritic Formation are intruded by dolerite dikes. In this study we analyzed a set of 200 pulps by portable X-ray fluorescence (pXRF) spectrometry and lab-based and portable X-ray diffraction (XRD). The corresponding diamond drill core was logged and the analytical data were interpreted in light of the logging data.

Portable X-ray fluorescence spectrometry

Portable XRF analyses were performed on powdered material using an Olympus X-5000 (25 mm² detector, 50kV, 10Watt Ta anode) and an Olympus Delta Premium (30 mm² detector, 40kV, 4Watt Rh anode) instruments. Samples were analyzed in Soil, Mining Plus and Geochem modes. Prior to use, the instruments were standardized using a 316-steel plate. An instrument check was done prior to



Figure 1. Schematic map showing location of the Deep Exploration Technologies Cooperative Research Centre Drilling Testing and Training Facility at Brukunga, Australia.

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measurement and then after every 15 samples using standards NIST2702, NIST2709, NIST 2781, NIST 2710a, NIST 2711a and a SiO₂ blank. Detection limits were estimated of the basis of reproducibility of the measurements for certified reference materials (NIST standards). The pulverized samples were placed in plastic vials, with the opening covered with Kapton tape. A small amount of material is required for this analysis, for the studied samples 5 to 10 g were used. The vial was then placed on the instrument window (tape side down) and analyzed with reading time on each beam of 60 seconds. Both Mining Plus and Geochem modes have two beams, and the Soil mode has three beams, with the beam energy stepping down with each subsequent beam. Beam run time can be chosen to vary from 10 to 60 seconds, but as it was shown that the analytical precision improves and the analytical error is reduced with longer counting time (Fisher et al. in press), the counting time was set up at 60 seconds. This resulted in total run times of 120 seconds for the Mining Plus and Geochem modes, and 180 seconds for the Soil mode. The data were processed off-line by QA/QC procedures based on the standard performance and application of appropriate calculated correction factors (Gazley & Fisher in press). The correction factors were developed based on the analysis of certified reference materials NIST2702, NIST2709, NIST 2781, NIST 2710a, NIST 2711a, and comparison of the expected and measured concentrations for each standard (Gazley & Fisher in press).

Powder X-ray diffraction

The same pulps were subsequently analysed by X-ray diffraction (XRD) using two instruments: (1) a lab-based Bruker D4 Endeavor AXS instrument, operating with Co radiation; data collection range of 2θ angle from 5 to 90°, with step size of 0.02°; data collection time of 7 minutes per sample; and (2) an Olympus Terra portable XRD instrument, operating with Co radiation; data collection range of 2θ angle from 5 to 55°, with increment of 0.25°; data collection time of 10 minutes per sample. Sample preparation for the analysis on the Bruker instrument required the material to be mixed with ethanol to form a paste and applied to a glass slide in order to obtain random orientation of mineral

crystallites, particularly of platy shape. No additional sample preparation was required for the Terra pXRD instrument as the particles were less than 130 μm, and the pulps were loaded into the piezo-harmonic, Vibrating Sample Holder (VSH) of the Terra instrument (Sarazzin et al. 2005). The vibration frequencies are within the kHz range (Sarazzin et al. 2005). For both Bruker and Terra XRD analyzers 100 to 200 mg of material were used. Quartz contained in all analysed samples was used as an internal standard to verify mineral peak positions and correct for any displacement if required.

The XRD patterns obtained from both instruments were processed and mineral assemblages were quantitatively estimated using two different software packages: Bruker DIFFRAC.EVA which is based on the Reference Intensity Ratio (RIR) method (Smith et al. 1987), and SIROQUANT which is based on the Rietveld method (Rietveld 1967, 1969). Each peak above the background was examined and mineral identification in the analyzed samples was done manually to ensure that all components present in the multiphase mixtures are identified and accounted for, as the quantification data are normalized to 100%.

In addition, two artificial mixtures were prepared by weight using well-characterised mineral standards (i.e., quartz, albite, muscovite, biotite, hornblende and pyrite). Mixtures A and B were analyzed using the same procedures as the samples. The obtained diffractograms were processed with both DIFFRAC.EVA and SIROQUANT software packages, mineral abundances were estimated and compared to the expected percentages (Table 1).

RESULTS

Selected elemental contents determined by pXRF are shown in Figure 2 and are correlated with the lithologic log for the drill hole. The drill hole from which the samples were collected for this study intersected a zone of stratiform sulfide mineralization from 130 to 260 m, a few narrower intervals (5 cm to 1 m) with sulfide veins (e.g., at 65, 100, 103, 275 - 285, and at 300 m) and a few dolerite dikes (48 - 50, 288 - 291, 292 - 293, 295 - 298, 302 - 304, and 315 - 318 m) (Fig. 2). The pXRF data show that sulfide veins and main

Table 1. Mineral percentages obtained for prepared standard mixtures using Bruker and Terra instruments and DIFFRAC.EVA and SIROQUANT software packages.

Mineral	Actual %	Refined % Bruker+EVA	Refined % Terra+EVA	Refined % Bruker+Siroquant	Refined % Terra+Siroquant
Mixture A					
Quartz	25	15	24	24	27
Albite	25	22	28	21	24
Biotite	25	30	22	29	24
Muscovite	25	33	26	26	25
Mixture B					
Quartz	40	40	41	41	42
Albite	40	38	41	37	37
Hornblende	10	14	10	14	11
Pyrite	10	8	8	8	10

mineralization are evident as sharp increases in Fe and S contents, whereas dolerite dikes are distinguished by well-defined peaks in Ca (Fig. 2).

XRD analysis employing lab-based and portable instruments and subsequent data interpretation with two software packages based on Reference Intensity Ratio (RIR) and Rietveld methods resulted in four datasets:

(1) Data collected with the lab-based Bruker instrument and processed with DEFFRAC.EVA

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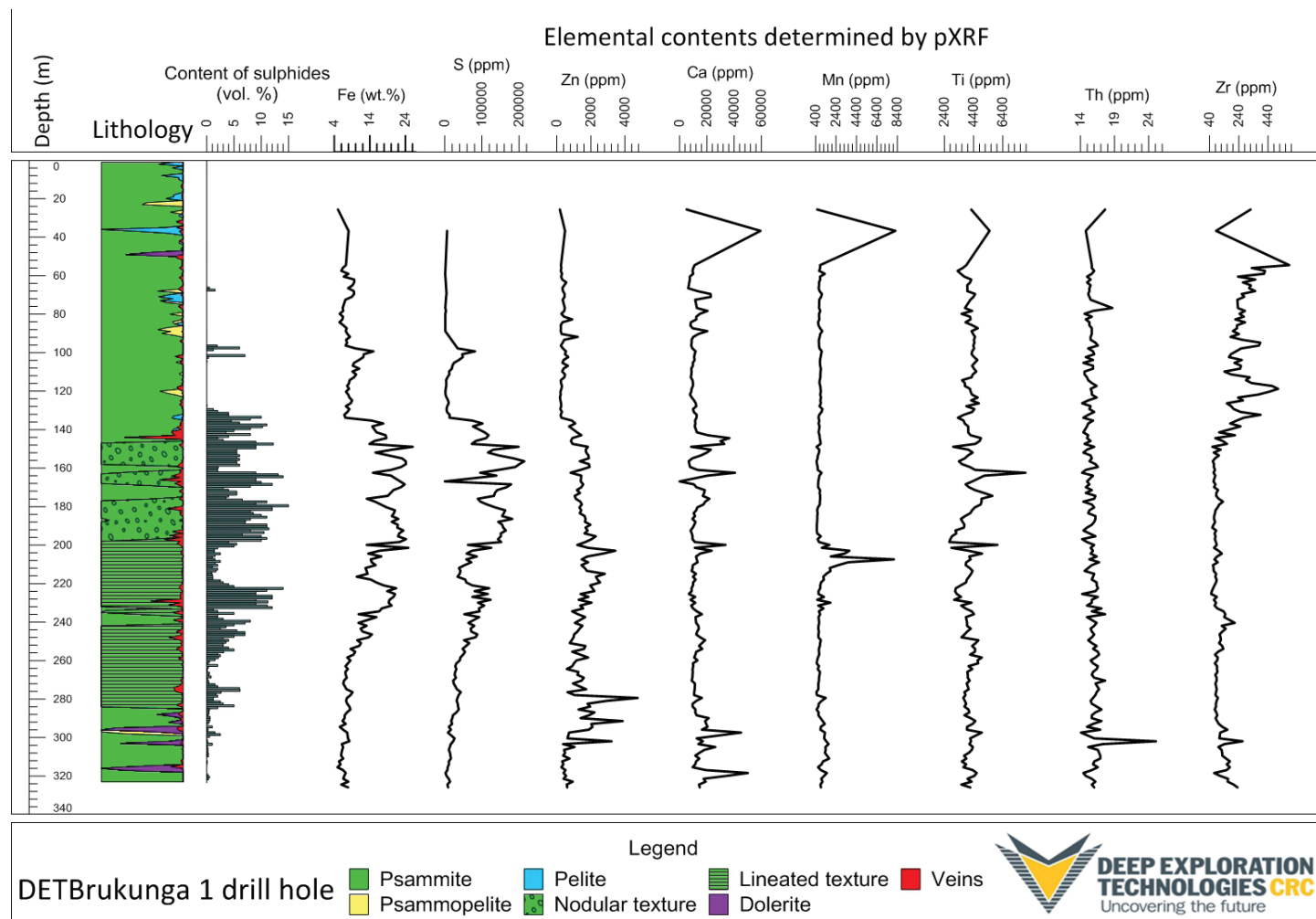


Figure 2. Lithology, sulphide distribution and content logged in the drill core and selected elemental abundances for the pulps from the DETBrukunga1 drill hole analysed by pXRF.

- software (RIR method);
- (2) Data collected with the lab-based Bruker instrument and processed with SIROQUANT software (Rietveld method);
- (3) Data collected with the portable Terra instrument and processed with DEFFRAC.EVA software (RIR method);
- (4) Data collected with the portable Terra instrument and processed with SIROQUANT software (Rietveld method).

The final outcome of XRD analysis and processing of the data with both instruments and software packages is the identification of all detectable mineral phases in the sample and an estimate of their abundance. Independent of the instrument or software used, the following minerals were identified by XRD in pulp samples: quartz, feldspar, biotite, muscovite, actinolite, chlorite, pyrite, and pyrrhotite. Figure 3 shows the mineral percentages for four combinations of the instrument and software package used for data collection and processing.

The analysis of artificial standard mixtures shows that all minerals in them are correctly identified, however

estimated abundances of each mineral, vary depending on the type of the instrument used for data collection and software used for data processing (Table 1). Thus, percentages of mica-group minerals are overestimated with the use of the lab-based instrument and DIFFRAC.EVA software (Table 1). This, in turn, results in underestimation of other phases in the mixture. If SIROQUANT software is used for processing of the same data collected with the lab-based instrument, the abundances are much closer to the expected ones (Table 1). The data collected with a portable XRD analyser independent of the software used gave phase abundances closer to the expected (Table 1). This can be explained by two issues: sample orientation and availability of an option to refine for preferred orientation in the refinement method. For the lab-based Bruker XRD instrument, sample preparation requires either a back-packed powdered sample loaded in a holder or a small amount of material put on a glass slide. In both cases, sample preparation results in platy crystals creating the preferred orientation which is common for mica-group minerals, chlorites, amphiboles, etc. Portable XRD Terra

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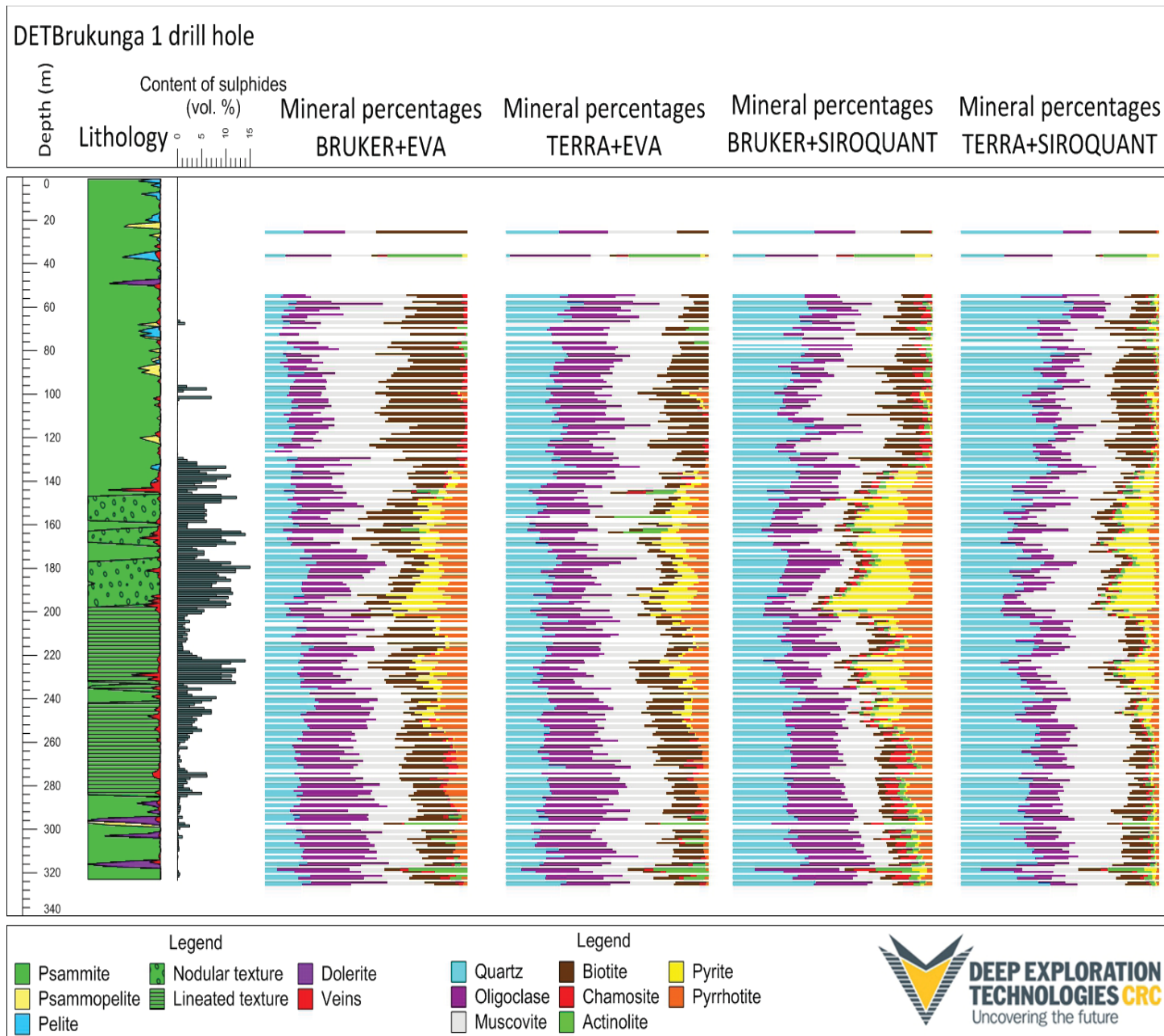


Figure 3. Lithology, sulphide distribution and content logged in the drill core and mineral percentages quantified from the XRD data collected with the portable Terra and lab-based Bruker instruments and processed with SIROQUANT and DIFFRAC.EVA software packages.

instrument has a convectional sample chamber in which the sample resonates during data collection, and it allows random orientation of all crystallites in the sample. Moreover, processing of XRD data in the DEFFRAC.EVA software which is based on the RIR method does not include refinement for preferred orientation. The SIROQUANT software based on the Rietveld method, on the other hand, allows the refinement for preferred orientation of platy minerals.

To verify the results of XRD analysis in a separate way, pXRF data were used and a normative content of pyrite and pyrrhotite was calculated, based on S contents determined and on the reasonable assumption that the only S-bearing minerals present are sulphides (no sulphates are present).

Figure 4 compares the total sulfide (pyrite and pyrrhotite) percentages quantified from the XRD data with the portable Terra and lab-based Bruker instruments and processed with SIROQUANT and DIFFRAC.EVA software packages.

DISCUSSION

Portable XRF is becoming routinely used in mineral exploration (Figueroa-Cisterna et al. 2011; Fisher et al. 2013; Gazley et al. 2011a, 2011b; Gazley & Fisher in press; Le Vaillant et al. in press). With the currently available portable instruments, data collection takes on average 120 seconds to achieve the best analytical precision and minimal

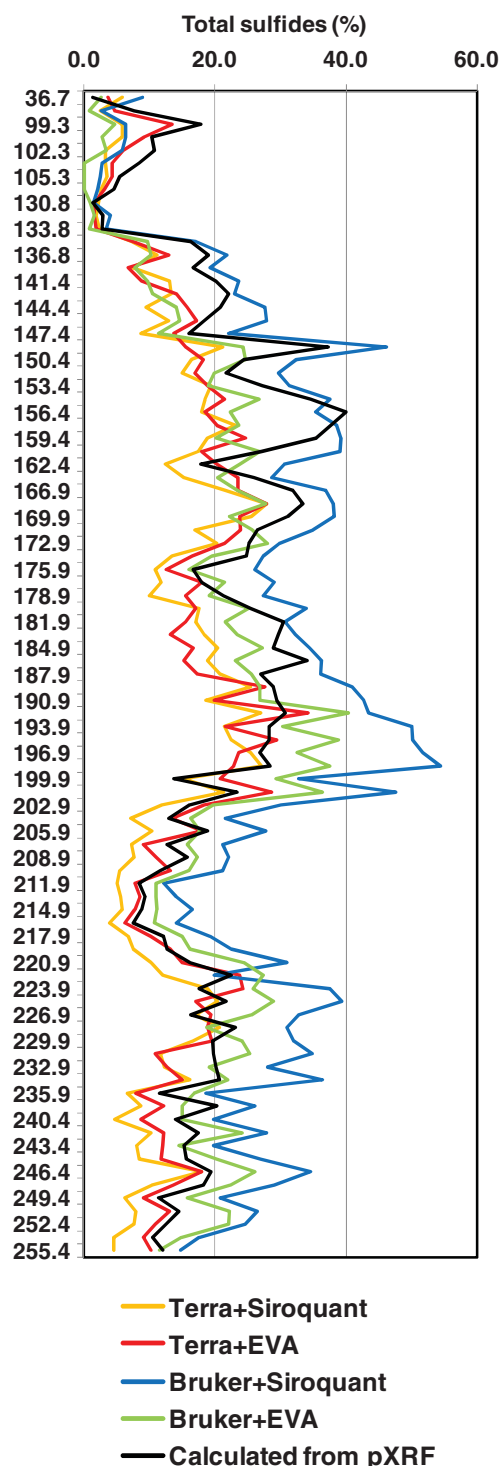
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analytical error. Portable XRF analysis thus allows for the characterization of a large number of samples within a single day at low cost and of high quality where proper QA/QC protocols are followed. In the current study, pXRF data clearly identify the various metasedimentary, the sulfide mineralization and the dolerite dikes and can be used to distinguish between them (Figure 2).

The assemblage quartz – feldspar – biotite – muscovite $\pm$ actinolite $\pm$ chlorite $\pm$ pyrite $\pm$ pyrrhotite was identified in all samples studied, but there are differences in the mineral abundances determined by which instrument and data processing software is used (Fig. 3). Accordingly, Figures 5a and b illustrate the downhole abundance variations in biotite and muscovite (respectively) for the different instruments and data reduction software used. Figure 5a shows that biotite abundances determined by the lab-based instrument and RIR method of quantification are greater than those obtained using the lab-based instrument and Rietveld refinement data reduction or with the portable Terra instrument, as the former allows for refining of the preferred orientation and the latter has a convectional sample chamber and reduces the effect of preferred orientation during data collection. Muscovite abundances show similar features amongst the instruments and the data reduction software used (Figure 5b). This is similar to the results obtained for the artificial standard mixtures, where abundances of mica-group minerals were overestimated with the lab-based instrument and RIR refinement (Table 1). Underestimation or overestimation of any mineral affects calculation of percentages of others as the data are normalized to 100%. Thus, for the standard mixture containing quartz, feldspar and mica-group minerals, in cases where mica-group minerals were overestimated, quartz and feldspar abundances were underestimated (Table 1). In the case of the studied samples, percentages of quartz and feldspar were underestimated with the lab-based instrument or RIR refinement because the amount of mica-group minerals overestimated (Figures 5c and d). Chlorite and actinolite abundances quantified with the pXRD analyzer and processed with the SIROQUANT software are lower than those obtained with the lab-based



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Figure 4. Comparison of total sulphide (pyrite and pyrrhotite) percentages quantified from the XRD data collected with the portable and lab-based instruments and processed with SIROQUANT and DIFFRAC.EVA software packages and theoretical amount of sulphides calculated from pXRF sulphur content in the samples.

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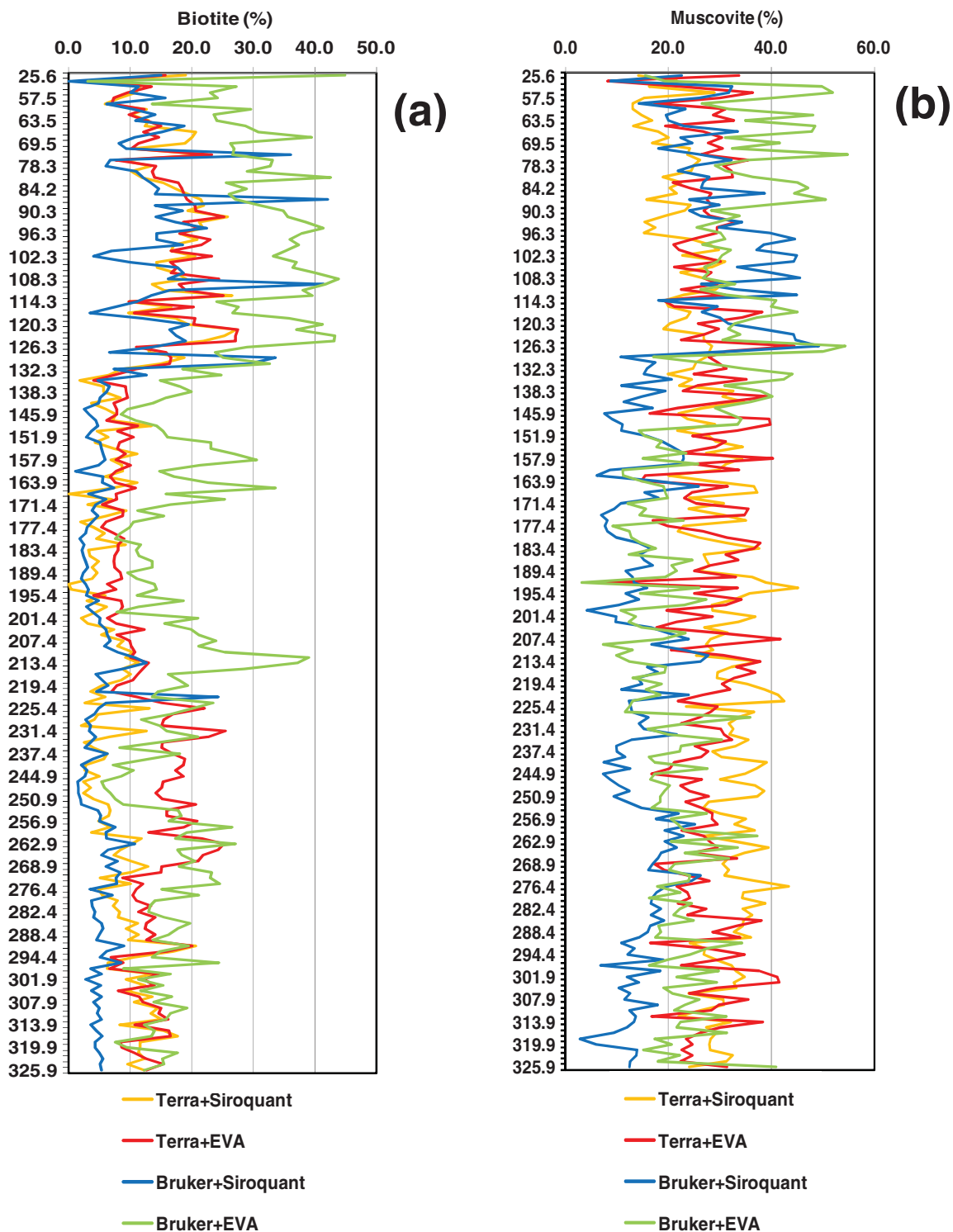
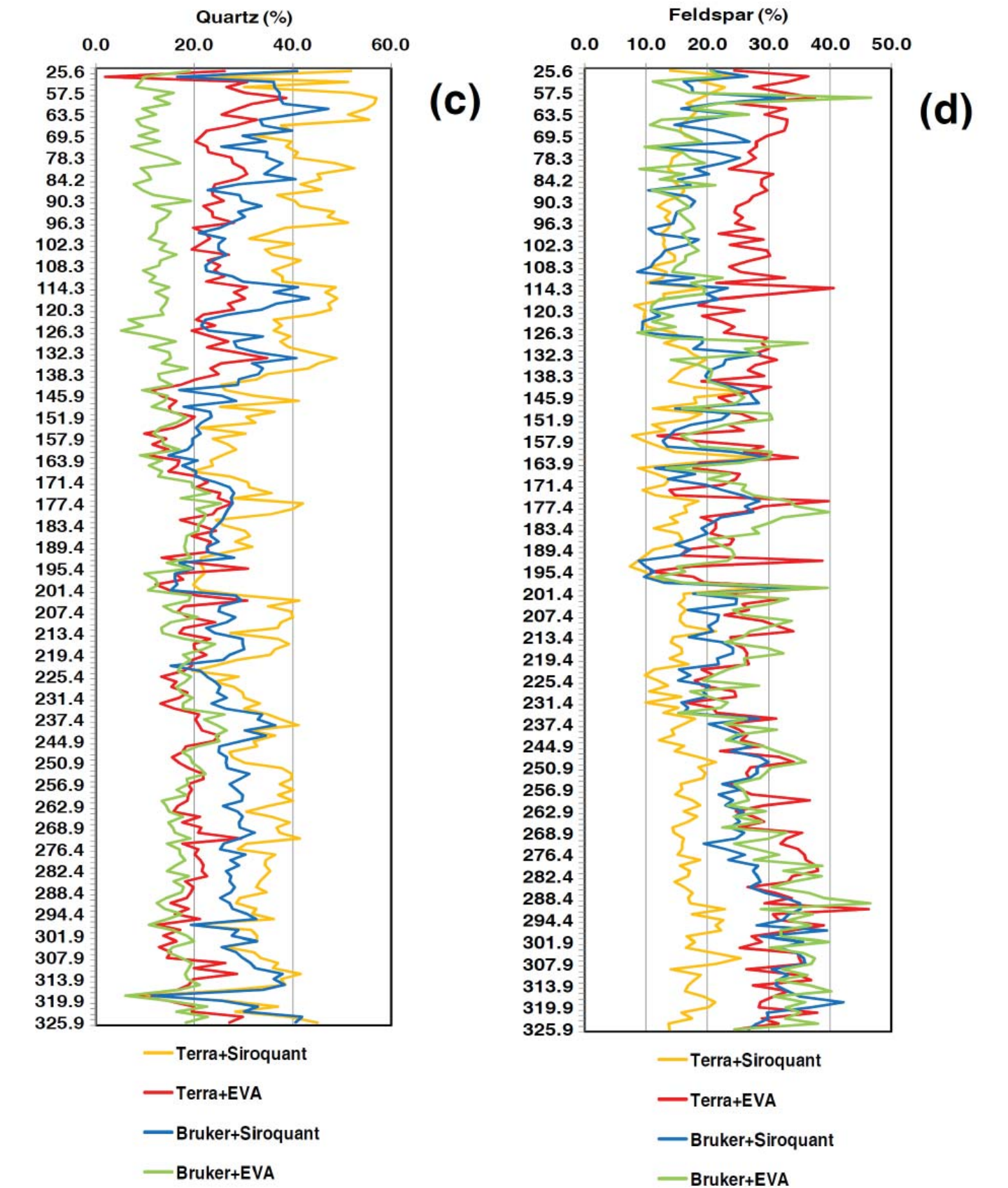


Figure 5. Comparison of (a) biotite, (b) muscovite, (c) quartz, (d) feldspar, (e) chlorite and (f) actinolite percentages quantified from the XRD data collected with the portable Terra and lab-based Bruker instruments and processed with SIROQUANT and DIFFRAC.EVA software packages.

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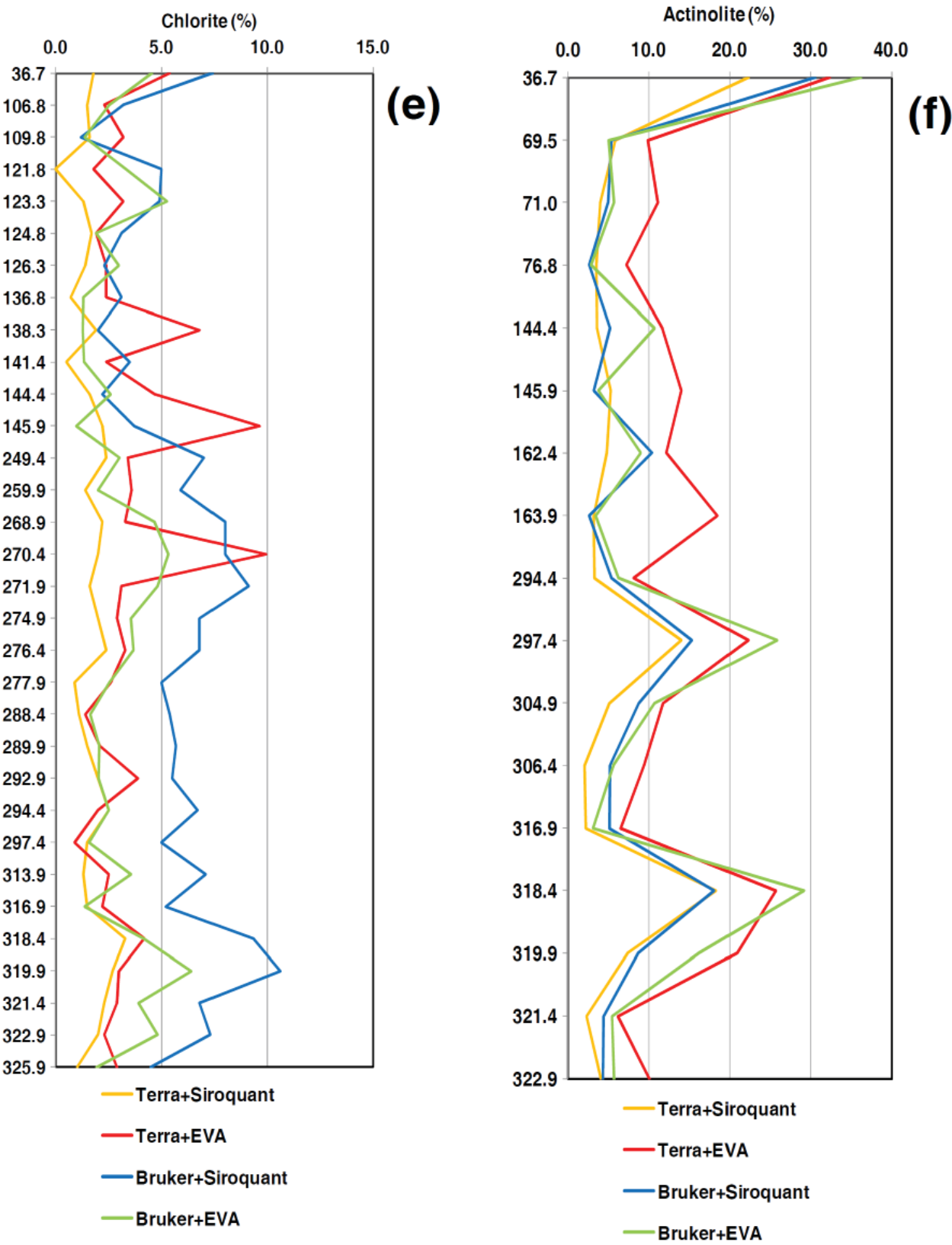
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instrument and the DIFFRAC.EVA software (Figures 5e and f). The observed results are similar to the results for biotite and muscovite, and are most likely due to overestimating of chlorite and actinolite percentages obtained with the lab-based instrument and DIFFRAC.EVA software as a result of the preferred orientation.

The sulfide abundances were estimated using the S contents determined by pXRF and an assumption that pyrite and pyrrhotite occur in ratio 1:1 supported by observations in the core. The results agree reasonably well (R^2 varies between 0.76 and 0.85, depending on which data sets are compared) with the total sulfide amounts determined by XRD (Fig. 4), which validates the results obtained by both techniques.

Overall, our data clearly show that mineral mixtures in the studied rocks can be identified and quantified using existing XRD technologies and software packages, and the portable and lab-based instruments give comparable results. However, the convectional sample chamber of the portable XRD Terra instrument provides an advantage in the analysis of samples containing minerals that form platy crystals, as it eliminates preferred orientation. The Rietveld method of data processing solves this problem as well by refinement for the orientation effect (Bish & Post 1993); however, the use of any software package based on this method requires some expertise in XRD and a background in crystallography. In contrast, the RIR method is user-friendly for the non-specialist. Although it does not allow for refinement of the preferred orientation, its use for processing of the data collected with the portable XRD analyzer equipped with the vibrating sample holder gives results that are comparable with those obtained by the refinement with the Rietveld method. For “rapid” data collection and processing, we recommend the use of the portable XRD Terra instrument and data processing using software that is based on the RIR method. For this combination, 10 minutes of data collection time and 10 to 20 minutes for data processing are required per sample. The time for data processing can be significantly decreased with a batch-processing option, which allows simultaneous refinement of a large number of patterns. Therefore, with the use of new instruments that are capable of rapid data collection and batch-processing options in the software, XRD has a strong potential to become a routine technique for analysis of geological materials and become widely applied in mineral industry.

Coupled pXRF-pXRD analysis of the same samples provides chemical and mineralogical data that can be used for discriminating lithologies, alteration and ore types. An example is the sharp increase in Ca contents between the following intervals: 295-298 m, 302-304 m and 315-318 m (Fig. 2); one possible interpretation of this is that they are due to the presence of Ca-bearing carbonate. Light elements (below Mg, atomic number 12 on the periodic table), including C, cannot be analysed by pXRF (due to tube voltage and power restrictions because of safety concerns), and as such the pXRF data cannot provide sup-

port for this possible interpretation. However, the pXRD data do not indicate the presence of Ca-bearing carbonate in these intervals, but do indicate the presence of a calcic amphibole actinolite (Fig. 3), which is associated with the dolerite dikes.

CONCLUSIONS

The current study illustrates that combined pXRF-pXRD analysis can be performed on a large set of complex geological samples and the techniques complement each other. Portable XRF results can be used to verify the results of portable XRD and vice versa. Our study also shows the viability and usefulness of portable XRD analysis that is currently underused. Portable XRD analysers can provide data comparable to modern lab-based instruments and the novel, innovative, and unique convectional sample chamber of the Olympus Terra analyser is ideally suited for analysis of samples with minerals with preferred crystallographic orientation such as mica-group minerals, chlorites, and amphiboles. 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 less than 15 minutes for both measurements. Combined portable XRD-XRF analysis, therefore, offers rapid and low-cost characterization of geologic materials for mineral exploration and mining industry and delivers elemental and mineralogical information of high quality where appropriate QA/QC protocols are followed. The integrated data can then be used to constrain lithologies and contacts between various units, hydrothermal alteration and ore types.

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