

Application of rapid field analysis techniques to the exploration of battery commodity minerals

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SUMMARY

Rapid, field-portable analytical instruments provide potentially powerful tools to support exploration for so-called battery and other critical minerals, but the effectiveness of particular techniques for identifying specific mineral species or elements is not well understood.

We have undertaken case studies of graphite, Li- and Ni-mineralized rocks in drill core and hand specimens, comparing and contrasting results from infrared reflectance (IR) spectroscopy, X-ray diffractometry (XRD) and X-ray fluorescence spectroscopy (XRF). The results allow us to recommend analytical workflows that integrate IR, XRD and XRF techniques for the most appropriate detection of a suite of battery and other critical minerals.

Key words: Infrared spectroscopy, XRD, XRF, Mineralogy, Geochemistry

INTRODUCTION

The increasing adoption of battery-based energy storage systems and electric vehicles will require increasing amounts of commodities such as graphite, alumina, lithium, transition metals (e.g. V, Co, Mn, Ni) and rare earth elements (REE) (Beardmore, 2018; DJTISI, 2019). Meeting the demand for these commodities will in large part come from discovering new resources of minerals containing these elements, which to be time and cost-effective will require rapid identification of the respective ores and indicator minerals in drill core and hand specimens.

There are a variety of well-established techniques for rapid, objective mineral identification and/or geochemical analysis, many of which are available as field-portable tools – for instance infrared (IR) spectrometers, X-ray fluorescence (XRF) spectrometers and X-ray diffractometers (XRD). Each technique has specific strengths and inherent limitations, and to be effectively used in support of mineral exploration they should be integrated collectively into routine workflows that reduce uncertainties in mineral identification and geochemical analyses.

We have undertaken a laboratory-based investigation of the effectiveness of IR, XRD and XRF techniques using graphite, Li- and Ni-mineralized rocks in drill core and hand specimens from several known mineral deposits, and used the results to make recommendations for integrated analytical workflows

tailored to specific minerals diagnostic of particular battery commodity deposits.

METHOD AND RESULTS

Samples of graphite and particular Li- or Ni-bearing minerals were obtained from diamond drill core from the Erayinia base-metal project in the Eastern Goldfields (hole EC157D), the Greenbushes Li-Ta mine in the South West Terrane (hole C3DD024), and the Mt Finnerty Ni-Cu-Co project in the Youanmi Terrane (hole GDD001; Figure 1; Table 1). All cores are archived at the Geological Survey of Western Australia's (GSWA) Perth Core Library.

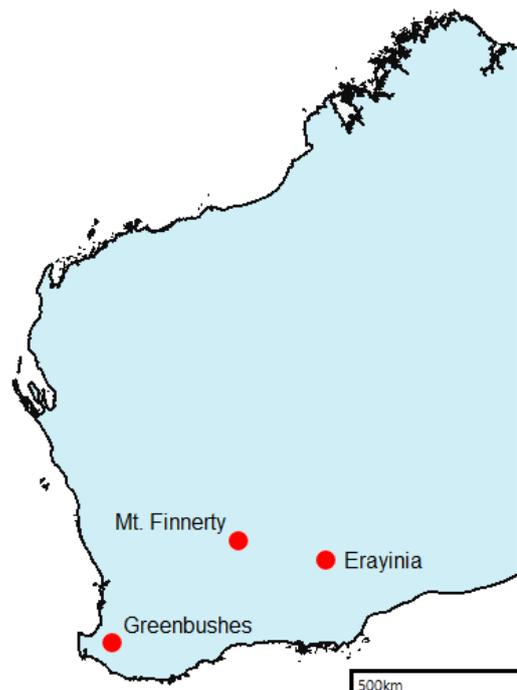


Figure 1. Simplified map of Western Australia, showing the locations of mineral deposits from which drillcore was sampled for this study.

Targeted drillcore intervals were analysed using the GSWA HyLogger-3 hyperspectral system (for IR spectroscopy) and an Olympus BTX-II benchtop diffractometer (for coupled XRD and XRF spectrometry). These rapid, non-destructive laboratory-based techniques are deemed suitable for identifying the “battery minerals” of interest, and are also regarded to provide data equivalent to that collected by field-portable instruments such as ASD, FTIR, pXRF, and pXRD.

Infrared reflectance spectroscopy measurements were made in the visible-near infrared (VNIR, 380–1000 nm), shortwave infrared (SWIR, 1000–2500 nm) and thermal infrared (TIR, 6000–14500 nm) regions using the HyLogger, and the data interpreted using *The Spectral Geologist* (TSG) software and the methodology described by Hancock *et al.* (2013). Automated mineralogical identifications were initially made using the inbuilt spectral reference library, and subsequently refined by manual identification of spectral features.

Hyperspectral results were validated using small (~1 g) samples of drill core crushed to a powder and sieved to >150 µm, that were analysed by XRF and XRD using GSWA's benchtop diffractometer. Semi-quantitative, relative-intensity-ratio analyses of diffraction patterns were made using the *XPowder* software package and its incorporated crystal structure database. Semi-quantitative analyses of the XRF spectra were performed manually by matching the energy of observed fluorescence peaks to known characteristic elemental X-ray energies.

Summary results for three case studies analysing graphite, Li phosphate and Ni sulphate are presented in Table 1.

EC157D drillcore case study (graphite)

EC157D is an Exploration Incentive Scheme (EIS) co-funded multi-commodity metal exploration hole drilled by Black Raven Mining in 2014 through a greenstone belt in the Archean Youanmi Terrane, Eraynia project (Table 1). A thin package of black shale at 105.65 m was analysed to determine the bulk mineralogy.

The SWIR spectra were highly noisy, due to the low reflectiveness of the core, but automated TSG-based mineralogical interpretations of SWIR and TIR data did indicate the core section primarily comprised of Al-rich white mica, albite and quartz, with a sharp absorption feature observed at 433 nm consistent with the presence of jarosite. Graphite has no diagnostic absorption features in the measured wavelength ranges, and was not detected.

Semi-quantitative XRF analysis of the sample indicated the presence of Fe, Ti and K, but carbon (graphite) lies outside the detection range of the instrument, and was not detected.

Analysis of the XRD pattern confirmed the presence of quartz, mica, kaolinite and pyrite, and also graphite. The latter was observable due to the elevated intensity of the 3.34 Å diffraction peak beyond that explainable purely by quartz. XRD is thus demonstrably a valuable exploration tool for graphite.

C3DD024 drillcore case study (Li minerals)

C3DD024 is a Li exploration hole drilled by Talison Lithium in 2014 that intersects the lithium mineralisation zone in the Archean Greenbushes granitic pegmatite Li-Cs-Ta deposit (described by Partington, 2017). The core was analysed at 37.9 m to identify a pink crystalline phase (Table 1).

Automated TSG-based mineralogical interpretations of SWIR and TIR data indicate the phase comprises a mix of quartz, spodumene (Li pyroxene, automatically interpreted as augite), andesine, apatite, montmorillonite and Al-rich white mica. Nothing of note was observed in the VNIR region.

Semi-quantitative XRF analysis of the sample indicated the presence of Mn, Ca and Cs (peaks at 4.29 and 4.62 keV), with the bright pink colour likely caused by the presence of Mn. Although XRF cannot detect Li, other detectable elements were useful for identifying unusual mineral phases.

The XRD pattern indicated the presence of quartz, spodumene, mica/illite, montebasite (LiAl(PO₄)(OH,F)), analcime (Na zeolite), and traces of smectite. The Cs detected by XRF is likely present in the analcime, rather than the Cs-ore mineral pollucite (with which it forms a solid solution series), because XRD data show a large analcime 211 peak at ~5.60 Å and no large pollucite 321 peak at ~3.66 Å.

Thus, the Li minerals in Greenbushes core were detected by IR and XRD analysis.

GDD001 drillcore case study (Ni sulphate)

GDD001 is an EIS co-funded nickel exploration hole drilled through ultramafic komatiite units of the Archean Youanmi Terrane by Reed Resources in 2013 (Mt Finnerty project). The core was analysed at 159.5 m downhole depth (Table 1) to determine the mineralogy of a soft, powdery blue-green mineral that is present on the surface of the core.

Automated TSG-based mineralogical interpretations of TIR data indicated the core was composed primarily of enstatite, edenite, actinolite, jarosite and carbonates. Spectra in the SWIR wavelength range were interpreted as aspectral, but a broad and deep absorption doublet (660 and 716 nm, shoulders at 570 and 820 nm) in VNIR is consistent with a transition metal-derived electronic transition absorption (Klein and Dutrow, 2007).

Semi-quantitative XRF analysis of a scraping of the surficial mineralisation indicated the presence of significant Ni, the likely cause of the observed broad VNIR absorption feature.

The XRD pattern from this scraping confirmed the presence of reigersite (NiSO₄·6H₂O), a hydrous Ni-sulphate mineral that forms in low temperature, hydrothermal, Ni-bearing mineral deposits. The presence of this Ni-bearing mineral is consistent with the detection of Ni by XRF, and elevated Ni content reported in drilling assays.

In this case study, an uncommon Ni sulphate was visually identified in drillcore by its blue-green colour and was validated by XRD in combination with XRF and VNIR data.

CONCLUSIONS

The combination of IR, XRF and XRD analytical techniques as part of a routine workflow provides a powerful tool for mineral identification and classification. Combining these analytical methods can reduce the uncertainty in phase identification, and allowed rapid detection of a wide range of battery commodity ore minerals.

XRD was found to be suitable for detecting mineral ores for Li and transition metals, and proved to be the only reliable method for detecting and quantifying graphite. XRD is also widely known to be suitable for the analysis of other major battery commodity minerals. Rapid IR analysis is found to be suitable for detecting some ore minerals of Li and transition metals, and is also known to be suitable for alumina ores and REEs. XRF is

reportedly suitable for detecting transition metals, as well as for detecting REEs and Al (Morris, 2009). However, it is not capable of being used to detect minerals containing light elements such as C (graphite) and Li.

These rapid and low cost methods can be applied outside of a laboratory environment to support greenfield and brownfield exploration activities, including regolith mapping and drilling programs. The techniques are also particularly useful in a laboratory setting to test historical core and soils, with the objective of evaluating previous interpretations and evaluations of potential resources. The ability of software to automate analytical interpretations of these methods provides a simplified and objective data collection technique that can supplement current exploration practices.

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Table 1. Summary mineralogy of drillcore samples from reported case studies

	Graphite	Lithium	Nickel
<i>Drillhole</i>	EC157D	C3DD024	GDD001
<i>Location</i>	Eastern Goldfields, Yilgarn Craton	South West Terrane, Yilgarn Craton	Youanmi Terrane, Yilgarn Craton
<i>Project</i>	Erayinia	Greenbushes	Mt. Finnerty
<i>Latitude (GDA94)</i>	-31.252066	-33.859204	-30.615281
<i>Longitude (GDA94)</i>	122.829813	116.065128	120.060528
<i>Sampled depth, m</i>	105.65	37.9	159.5
HyLogger (TSG) data			
<i>VNIR</i>	433 nm jarosite feature		Broad absorption doublet at 660 and 716 nm
<i>SWIR</i>	Al-rich white mica	Montmorillonite, Al-rich white mica	Aspectral
<i>TIR</i>	Albite, quartz	Quartz, spodumene, andesine, apatite	Enstatite, edenite, actinolite, jarosite, carbonates
XRD (X Powder) data			
	Graphite (major), mica/illite (major), quartz (minor), kaolinite (accessory), pyrite (accessory)	Montebrasite (dominant), mica/illite (minor), analcime (minor), spodumene (accessory), quartz (accessory), smectite (trace)	Retgersite (dominant)
XRF data			
	Fe, Ti, K	Mn, Ca, Cs	Ni