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Development of a model for serpentine quantification in nickel laterite minerals by infrared spectroscopy

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ABSTRACT

An investigation into the possibility of using infrared techniques to quantify serpentine in nickel laterite ores was carried out. Results obtained from this preliminary study confirmed that high confidence in serpentine content prediction is possible obtaining RMSEP and R^2 values of 1.76 and 0.97 respectively.

One hundred and forty mineral mixtures simulating limonite, transition and saprolite horizons of a Western Australian nickel laterite deposit were prepared. Diffuse reflectance infrared Fourier transform spectroscopy spectra obtained from these mixtures were used as a training set to prepare a quantitative model for serpentine content using Partial least squares multivariate analysis.

The model in turn was validated by predicting the serpentine content of 20 synthetic mixtures with confidence. The model was applied to 10 natural ores from various deposits, diversity between the synthetic and natural ore assemblages meant the analysis was qualitative. Model development using real ore samples would be required to enable incorporation of the intrinsic properties of the natural serpentine and the ore mineralogy in general.

1. Introduction

Serpentine ($(\mathrm{Mg,Fe^{2+}})_3\mathrm{Si_2O_5(OH)_4}$) is an important constituent in nickel laterite deposits that bear significant amounts of nickel. Quantification of serpentine within nickel laterites is essential for selecting optimal processing conditions for these ores as serpentine consumes acid during leaching. Whilst detailed methods such as Quantitative XRD, Automated SEM (MLA, QEMSCAN) and chemical analysis exist to characterise ores, they have a number of drawbacks in characterising nickel laterite ores. This is especially the case with low grade and/or non discrete ores. Methods such as XRD, Automated SEM and TGA require lengthy analysis time and are relatively expensive to run and maintain. These techniques also have their own accuracy limitations with respect to laterite mineral characteristics (e.g. serpentine crystallinity and a generally fine grain size). Elemental abundance methods such as XRF also are unable to provide a complete phase analysis of the deposit. Hence, there is significant interest in developing a method that is accurate, robust and cost effective for quantifying serpentine.

Oxide nickel ore deposits are steadily becoming more prospective for mining as the technology and knowledge required to extract nickel from these ores continues to improve (Johnson et al., 2005). Novel methods to quantify nickel laterite mineralogy are required to maximise extraction efficiency and reduce the cut off grade for economical extraction of nickel falls.

Data provided by infrared analysis, then modelled via chemometrics, has the potential to provide rapidly acquired information of sufficient precision. This has been a common analysis tool, for example the alumina industry employs IR based techniques to analyse bauxite ore for alumina content viable to mine (Jonas et al., 1974).

Whilst the mineralogy and chemistry of bauxite and nickel laterite deposits are distinct from one another, the weathering processes responsible for their geology produces broad similarities (e.g. grain size, phyllosilicate/iron oxide species, textural complexity). Being subject to localised heterogeneity (e.g. parent rock geology, topography and climate), there can be significant differences between separate deposits and indeed within single ore bodies. Hence, an accurate technique to determine processing related variables such as serpentine content is required. It is believed that a similar method used by the alumina industry may prove to be equally successful for serpentine quantification in nickel laterite deposits.

Many nickel laterite minerals are IR active, and have been studied qualitatively (Azevedo, 1985; Farmer, 1974; Narasimhan et al., 1989; Post and Borer, 2000). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is the most appropriate IR technique due to its ease of use, minimal sample preparation, small training requirements, relatively low capital investment and

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running costs. DRIFTS also lends itself to automation, with robotic systems developed to perform analysis of multiple samples. FTIR in conjunction with other established techniques may prove to be extremely supportive to understand the complex mineralogy of nickel laterite profiles.

It is predicted that in the near future the amount of sulphide sourced nickel supplied will remain constant and that laterite-sourced nickel supplies will increase (Moskalyk and Alfantazi, 2002). Thus there is a real opportunity to take advantage of Australia's large deposits of nickel laterites (Elias, 2006). A rapid and reliable method of characterising these ores is an essential component of this development.

2. Experimental

2.1. Materials

Natural minerals typical of a nickel laterite assemblage were used as component standards within synthetic mixtures (Table 1). Each component was kept within typical ranges of a naturally formed Western Australian nickel laterite deposit.

An experimental design composed of 140 experiments was developed, with varying quantities of the ten mineral standards as components for each experiment. An 'experiment' involved preparing a sample with mixture compositions calculated by the design. Antigorite was the serpentine mineral used in the model samples. The prepared mixtures were separated into three divisions, according to typical arid-type nickel laterite horizons; Limonite with 60 samples, transition (or clay rich) with 20 samples and saprolite with 60 samples.

An experimental design utilising distance optimality spreads samples uniformly over the design space with equal 'distance' between component values. The design maximises the information retained whilst minimising the number of experiments to a manageable number. In this case the design chose 140 differing mixtures of the 10 components which best represent the various component abundances in a natural deposit. This is especially useful when attempting to create complex mixture designs as there are fixed abundance ranges for each component. The mixture design was developed using Minitab® v 15 (Minitab Inc©). To prepare this training set each sample mixture was manually weighed into a 20 mL screw top vial to a total mass of approximately 3 g. A selection of 30 synthetic validation samples was also prepared. Five compositions of mixtures which had not already been prepared through use of the experimental design were created. These samples were still within the ranges of a typical nickel laterite assemblage shown in Table 1 and were prepared using the antigorite serpentine used in each sample of the training set (Antigorite A).

A further five mixtures with the same concentration of components as previously described were prepared using an alternate antigorite serpentine standard, (Antigorite B). This was in order to determine whether the model created through multivariate analysis can compensate for different serpentine minerals.

To validate for ruggedness of the model ten samples from the training set were re-analysed. Ten natural laterite ores were also used as a validation set. The exact component abundance was not known, although the particular horizon from where the mineral was mined had been recorded.

Each sample was analysed using a Perkin Elmer Spectrum 100 FTIR with DRIFTS attachment. A variety of different chemometrics algorithms were employed to assist in determining whether the serpentine content of nickel laterite samples could be predicted and if so, to what degree of accuracy. Spectral data is highly collinear, which causes issues with conventional regression techniques. For this reason a number of multivariate techniques were employed, including principal components analysis (PCA), regularised discriminant analysis (RDA) and partial least squares (PLS). PCA was carried out using Minitab v.15 (Minitab Inc©), RDA was performed using SCAN© v1.1 (Minitab Inc©) and PLS with The Unscrambler® v9.8 (CAMO).

2.2. Principal component analysis (PCA)

PCA is an unsupervised technique, the algorithm attempts to condense the data set to a reduced set of Principal components (PCs). These PCs include relevant data and less of the redundant data which hamper a technique's model development. Each PC is orthogonal to its predecessor, i.e. the second PC is orthogonal to the first PC, etc. By reducing the data into uncorrelated PCs and rotating the data matrix, maximum variance can be achieved (Adams, 2004).

PCs with the largest proportions of relevant data are then plotted against each other producing a Score plot. Score plots can reveal inherent structures in the data that may not have been elucidated otherwise. The score plot projects the data onto two dimensions using the PCs with uncorrelated variables which best carry the variation in the original data, which allows for the clustering of similar samples.

Score plots are commonly used to classify outliers and groupings of samples, as samples in a data set tend to cluster according to relationships between their variables, leading to the identification of either similarities or differences between samples.

Prior to performing PCA, two types of pre-treatment are commonly used, standardisation or mean-centring. Mean-centring is the method commonly used for spectral data as all the variables share the same units (wavenumbers) and did provide a better

Table 1
Minerals used to prepare synthetic mixtures.

Mineral	Typical abundance per horizon			Formula
	Limonite (%)	Transition (%)	Saprolite (%)	
Chlorite	0–5	0–10	0–10	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$
Chromite	1–6	0–3	0–1	$Fe^{2+}Cr_2O_4$
Dolomite	0–2	1–10	0–20	$CaMg(CO_3)_2$
Kaolinite	0–5	1–20	2–35	$Al_2Si_2O_5(OH)_4$
Hematite/goethite	20–60	10–50	4–20	$Fe_2^{3+}O_3$ and $Fe^{3+}O(OH)$
Pyrolusite	0–2	0–2	0	$Mn^{4+}O_2$
Serpentine	0–15	5–35	10–80	$(Mg,Fe^{2+})_3Si_2O_5(OH)_4$
Smectite	0–5	1–15	2–45	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)$
Talc	0–5	1–10	2–20	$Mg_3Si_4O_{10}(OH)_2$
Quartz	20–80	10–60	0–40	SiO_2