A NEW LIBRARY OF THERMAL INFRARED REFLECTANCE SPECTRA OF ROCK-FORMING MINERALS AND ROCKS

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ABSTRACT:

A new library of thermal infrared (TIR) reflectance spectra of rock-forming minerals (silicate, carbonate, sulphate, sulphide, phosphate, oxide minerals etc.) as well as common rocks is being compiled. The focus of the work was to build up a spectral reference dataset for qualitative and quantitative analysis of bi-directional TIR reflectance spectra acquired from rock drill cores by the TIR-HyLogger[TM] (developed by CSIRO Exploration and Mining) regarding abundances and the chemical composition of certain minerals. Pure and solid samples (as opposed to particulate samples) of representative mineral specimens were collected to be representative of the target samples (solid core samples). All spectra are acquired as radiance in the wavelength range from 5 to 14.6 µm (5000 to 14600 nm) and are calibrated to absolute radiance. The calibration process is based on blackbody measurements at different temperatures and on a Planck-function approximation and was required to remove sample heating effects within the spectra during spectral acquisition. The reflectance data was calculated relative to a 100% diffuse reflecting gold standard. For a 100% reflecting diffuse target, the SNR rises from about 400 at 7 µm to about 850 between 9 µm and 12 µm, falling again to about 400 at 14 µm. A high level of reproducibility of multiple measurements of same samples was achieved. The standard deviation over the mean of the quartz reflectance feature at 8.625 µm is 0.03, calculated from 128 spectra over 32 days. The library is available on request and the geoscience community is invited to submit characterized samples for expansion of the library, which will continue to grow as new material comes to hand.

Introduction

In recent years CSIRO Exploration and Mining has developed hyperspectral drill core logging systems based on spectral reflectance technology using the VNIR (visible and near infrared) to SWIR (shortwave infrared) wavelength range. These HyLogging™ machines scan spectrally and continuously full and cut drill core and enable the operational detection and mapping of the abundance of OH-bearing silicates which show significant spectral features in the wavelength range from 1.0 to 2.5 µm. Now the mining industry is more and more interested in mapping non OH-bearing framework silicates such as quartz, feldspars or garnets etc. which display their mineral specific spectral features solely in the longer wavelength range of the thermal infrared (TIR) between 8 and 14 µm. To fulfil industrial requirements CSIRO developed a new prototype, the TIR-Logger, which covers the wavelength region from 5 to 14.6 µm. The goal of the present work is to compile a new library of representative thermal infrared reflectance spectra of rock-forming minerals and rocks to make the TIR-Logger sufficiently robust for routine operations in core libraries to map framework silicates within drill core. Many studies have already been carried out on thermal infrared spectroscopy, e.g. dealing with spectral behaviour dependencies on grain sizes, identification and quantification of minerals and their chemical components or mapping rocks and analysing their mineral composi-

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tions (Lyon et al., 1963; Lyon, 1965; Walter and Salisbury, 1989; Salisbury et al., 1991; Thomson and Salisbury, 1993; Christensen et al., 2000; Hamilton et al., 2000). Two considerable spectral libraries for minerals in the TIR have been compiled so far - one by Salisbury et al., 1991 from the John Hopkins University (JHU) and the other one by Christensen et al., 2000 from the Arizona State University (ASU).

Why do we need a new library? Depending on the method used (reflectance or emittance) and different instruments, spectral differences may occur due to different measurement geometries. Thus for this study it has been important to collect suitable representative spectra as references using the same system as used for core logging to ensure an accurate and reliable spectral and mineralogical identification of drill core.

Instrument

The TIR-Logger is designed to continuously log drill cores spectrally and spatially (core mode) and to acquire static measured spectra of single samples for library purposes (library mode).

The spectrometer used is a rapid-scan Fourier transform infrared type from Designs and Prototypes using a rotating optical mirror producing 12 spectral scans per second. The spatial resolution (spot size) is nominally 10 by 10 mm. Each spectrum covers the range from 5 to 14.6 µm (5000 to 14600 nm). The spectral resolution in the wavelength domain varies continuously from 21 nm at 7 µm to 170 nm at 14µm. The Wavelength calibration is done by comparison with the significant quartz reflectance minimum at 8.625 µm and a number of well-known features in a polystyrene plastic film over all the whole wavelength range.

All spectra are measured in "double" bi-directional reflectance by permanently illuminating the sample using two heat sources with an angle of ~30° each. Each spectrum is acquired as radiances and is an average of 100 single scans to increase the SNR (SNR: 850 for a 100% reflecting target in the wavelength range from 9 to 12 µm). The spectra are highly reproducible which is shown by a standard deviation of 0.02 to 0.03 over the mean tested against 7 minerals measured 4 times a day over 32 days. The reflectance spectrum is calculated relative to a calibrated diffuse reflecting gold standard.

Samples and reference data

The specimens for this work have been kindly provided by the Australian Museum of Sydney, CSIRO Exploration and Mining, the University of New South Wales and the Macquarie University. The sample sizes varied from fist size to 1 x 1 x 1 cm and shapes varied from ideal crystal shapes to massive lumps without any preferred cleavage surfaces. Most of the samples are monomineralic. Only non-destructive sample preparation was applied for spectral library measurements, such as dust removal from surfaces and equilibration of sample temperature to the temperature of the spectrometer and the laboratory environment. To achieve the latter samples were stored in the laboratory for at least 24 hours before spectral acquisition.

The validation of the samples has been undertaken using macroscopic analyses, spectral comparison with existing spectral libraries or chemical analyses. The latter are still underway for certain samples. Additionally each sample has been tested for impurities with OH-bearing minerals by reflectance spectroscopy covering the VNIR–SWIR wavelength range using ASD FieldSpec Pro and PIMA-2 spectrometers. The validation of rock samples has been conducted determining the modal composition based on the thin-section point counting method.

All spectra and metadata are collated in a database. Digital pictures of the samples have been taken for each measured spectrum and each sample has been macroscopically described.

Calibration

Before measuring reference reflectance spectra a calibration to absolute radiance of the system has been undertaken. This has been a critical step because samples heat up during measurements due to the design of the spectrometer using two heat sources for sample illumination. Thus the heat fraction has to be removed using a newly developed heat removal approach based on the radiance data and will be explained later.

In a first step the system was tested for its linearity in spectral response. For this 12 blackbody spectra from 10 to 65 °C in 5 °C increments have been measured while the heat sources were off. The result of these measurements proved that the system has a linear dependence between system input (blackbody) and system output (values at sensor). The following equation has been used to determine the system transfer function.

$$V = aB(T) + b \qquad (1)$$

Where V is the system output, and B(T) the blackbody at given temperature, (a) the multiplicative and (b) the additive constant.

This calibration approach is a time consuming procedure. Thus the blackbody measurements for calibration have been reduced to three measurements at 10°C, ambient temperature and at 65°C for operational use during the library measurements.

Spectral acquisition and temperature correction

Spectral acquisition has been carried out in library mode and with the sources on. Samples have been positioned on the system's robotic X/Y table and the centre of the measuring spot has been defined by a laser pointer. The measuring sequence consists of three measurements:

1. The background measurement (BAK). Acquisition of the radiation from the background environment which has to be removed from each target spectrum before the final reflectance spectrum is calculated. For that purpose a ~25° tilted aluminium mirror looking into the room is mounted on the X/Y table and is moved beneath the spectrometer. It only reflects the background radiation into the detector while the source is reflected into the room.

2. The reference target (GLD). This is a 100% diffuse reflecting gold plate which is recommended for reflectance measurements in geological applications using the thermal infrared (Nash 1986). It reflects the radiation from the source and from the background. Because the system is using a calibrated 100% diffuse reflector as reference apparent reflectance of greater than 100% for targets with smooth surfaces and cleavages may occur, e.g. shown for crystalline samples that show specular reflectance. This is a typical phenomenon for a bi-directional measurement method and can only be eliminated by measuring in directional hemispherical reflectance. The latter is not practical for an operational system measuring a moving drill core in a large core tray at significant speed.

3. The sample or target (SAM). This includes the reflected radiation of the source from the target (the core), the reflected radiation from the background and the emitted radiation from the sample.

For calculation of the reflectance spectrum the following equation has been used:

R= (SAM-BAK)/(GLD-BAK)   (2)

This set up was made under the assumption that sample, background and spectrometer are all at the same temperature and that the sample and the reference are lambertian reflectors.

Each final sample reflectance spectrum is an average of a set of 100 single FTIR scans. Before calculating the final reflectance spectrum a calibration and a background correction for each spectrum of the set has been undertaken. After this correction the set of reflectance spectra show a continuous reflectance increase of the baseline per spectrum into the longer wavelength due to sample heating. Because this increase is related to sample heating each spectrum can be described as a combination of one fraction reflectance and one fraction of emittance information. The reflective fraction doesn't include any temperature information so only the emittance part has been used to determine the temperature increase of the sample. As mentioned above assuming the sample has the same temperature as the environment and spectrometer the first spectrum shouldn't show any temperature increase. Thus the difference between a Planck approximation of the first spectrum of a set and the blackbody at the same ambient temperature is zero. Each following measured spectrum of the set shows an increasing temperature difference which is proportional to the temperature of the first spectrum. The exact temperature difference can be estimated if for a certain wavelength an emissivity value of 1 is assumed, e.g in this research a quartz sample has been used and the emissivity close to one has been recognized at the channel equivalent to 7.5 µm. Using equation 3

$$\hat{\rho} = \frac{\rho}{\rho_g} + \frac{\varepsilon B^{'}(T_b)\Delta T}{L_g - L_b} \qquad (3)$$

ΔT can be estimated. Plotting ΔT over the time (all 100 spectra of a set) shows the increase of the temperature versus time of a sample. The resulting curve can be approximated by a second order polynomial fit and can be used for correction. This correction procedure has been applied to all 100 single spectra and than the finale average reflectance spectrum has been calculated. All the following presented spectra are average spectra from the 100 calibrated, background and temperature corrected spectra per sample.

Orientation effects

Samples such as minerals, rocks or even drill core show large variations in surface condition, e.g. variations in orientation of cleavages or broken surfaces. The interaction of these surfaces, tilted at a specific angle, with respect to the bi-directional measurement geometry can result in an apparent reflectance > 100%, as mentioned before. This specular reflectance affects later quantitative feature-based spectral analyses, such as calculating absorption depth or reflectance peak heights. To understand the spectral behaviour regarding specular reflectance of the TIR-Logger a series of measurements have been carried out by rotating a K-feldspar (triclinic with two optical axes) cleavage surface that under a certain angle to the source directly reflected into the spectrometer. The rotation of the cleavage is carried out about the long axis and changed from 0° to 45° in 5° increments. The results showed that the reflectance values are ~4 times larger at an angle around 25° as compared to the horizontal (0°) orientation without significant changes in spectral features positions. Regarding future analyses of drill core data this knowledge has to be included in possible unmixing methods or models to avoid misinterpretation of mineral abundances by specular effects.

In addition to the above effects certain minerals show differences in spectral shape due to optical anisotropy effects caused by changes in orientation of the optical axis (Ruff, 1998, Lyon and Burns, 1963). Two cleavages, perpendicular to each other (side1 and side2), of the K-feldspar have been measured to test the spectral response of the TIR-Logger to optical anisotropy. Figure 1 shows the potential for differences in spectral shape of a single mineral crystal. It is obvious that shape and feature position of the spectrum of side 1 and 2 are totally different which can lead back to the crystal lattice and therefore to the optical axis. This leads to the next question: how homogeneous is the spectral shape of one single cleavage surface if it is be rotated in azimuth direction? Therefore a second experiment was carried out to check optical anisotropy effects by rotating the cleavage about its normal from 0 to 180° in 22.5° increments. Figure 1 displays the spectra of both surfaces from 0° to 90° azimuth angle. The spectra from 90 to 180° are not displayed because it reversely repeats the spectral shapes which can be related to the symmetry of the crystal lattice. The spectra of side 2 clearly show a continuous shift
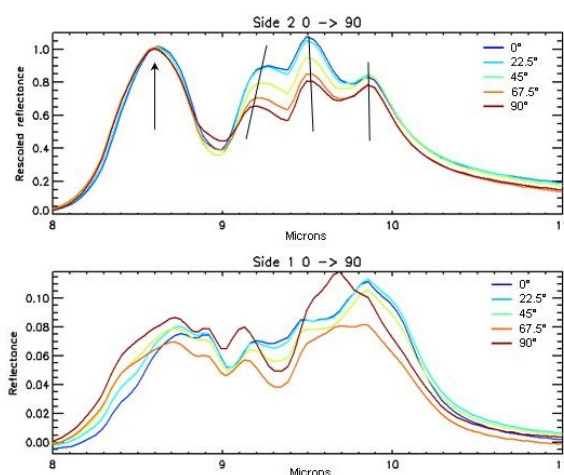

Figure 1: Spectra of two cleavage surfaces of a K-feldspar crystal measured at different azimuth angles.

in feature position (peaks and troughs) from the longer to the shorter wavelengths except the peak at ~9.5 µm. There a slight shift to the longer wavelengths occurs. The largest shift is about 163 nm from 9.854 to 9.691 µm at side 1. For all other features the position shift is around ~70 nm. Usually shifts in wavelength position are related to substitution of cations in the crystal lattice e.g. exchanges of K and Na in orthoclase or Na and Ca in plagioclase feldspars (Ruff, 1998; Hamilton et al., 2000; Christensen et al., 2000). This means that a single spectral behaviour, in this case the change of features in wavelength position, can be caused by two different processes. And that implies, for spectral core logging, that interpretation of e.g. chemical variation within feldspars has to be carefully analysed and orientation effects have to be considered, before estimations of mineral abundances and/or derivations of chemical variation of specific cations can be understood.

Results

Considering the above, 83 mineral specimens representing framework silicates (quartz, feldspars), sheet silicates (micas, etc.) and ortho-silicates (olivine) have been measured so far and the process is still ongoing. Figure 2 shows the high spectral variability of one single monomineralic sample which can be explained by orientation effects. In this case six different surfaces of a massive pure albite specimen, without any preferred cleavage surfaces, have been measured. The spectral shape indicates, especially at the longer wavelength range (12 – 14 µm), that the sample is a pure albite specimen. The large variations in spectral shape between 8 to 9.5 µm are related to optical anisotropy effects whereas the differences in
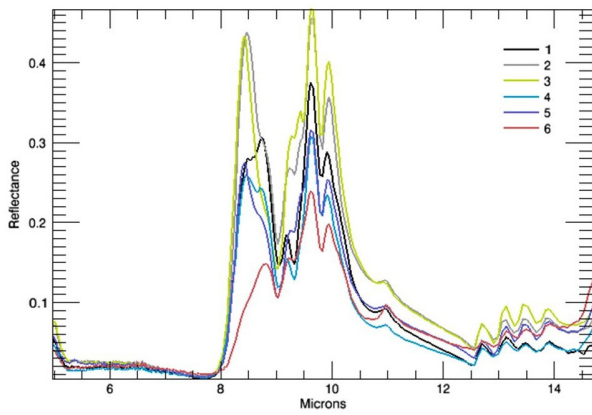
Figure 2: Spectral variation of a single albite specimen.

the reflectance magnitude can be related to surface orientation with respect to the spectrometer. However all the spectra are clearly representing the mineral albite.

A comparison of mineral spectra measured with the TIR-Logger with mineral spectra of an existing spectral reference library shows good agreement. Figure 3 presents quartz and epidote spectra from TIR-Logger (black) and from the Arizona State University (ASU) spectral library (blue)
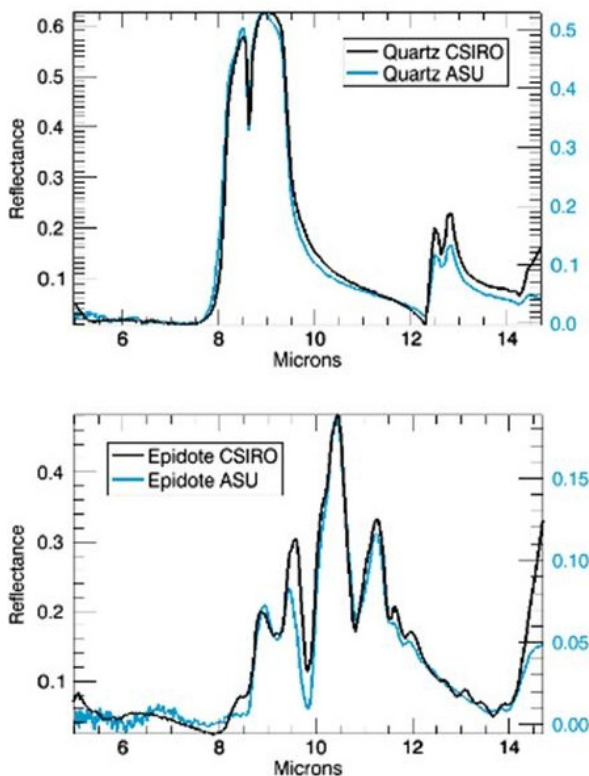

Figure 3: Comparison of quartz and epidote spectra measured with the TIR-Logger (black) and from the spectral library of the Arizona State University (blue).

(Christensen et al., 2000). The plots are scaled for a better comparison. The spectra from the ASU library have been measured in emittance and have been transformed into reflectance using Kirchhoff's law. Both examples have good overall agreement in spectral shape and feature position. Only the reflectance magnitude is different which can be explained by the different methods of spectral acquisition. A less detailed comparison of further minerals is given in Figure 4. These mineral spectra are consistent in respect of spectral shape and wavelength position too. The spectra are plotted with an offset for a better clarity.

Figure 5 presents first results of rock spectra measured with the TIR-Logger in library mode. A rock spectrum can also be described as a weighted mixed spectrum of the minerals which compose the rock. Thus each main mineral shows its specific spectral feature within the rock spectrum. For example, the Quartz-Monzodiorite shows
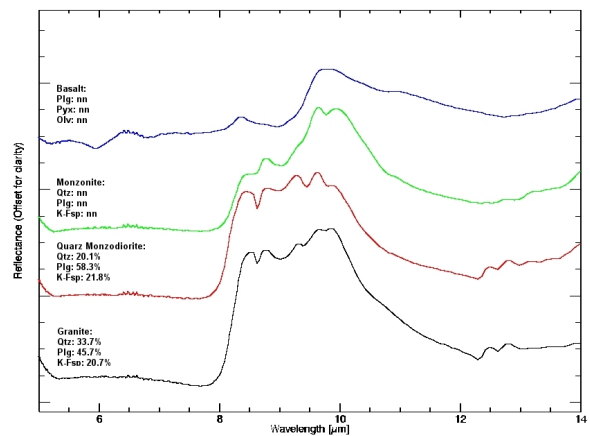

Figure 5: Rock spectra measured with the TIR-Logger

very clear quartz features at 8.625 µm, 12.5 and 12.7 µm and feldspar at 9.6 and 9.8 µm for the plagioclase. The feature at 9.3 µm may be explained by a mixture of white mica and feldspar. This result of rock spectra demonstrates the high potential for quantitative or at least qualitative analysis of the TIR-Logger data regarding the mineral compositions of rocks.

Conclusion and future work

This study has shown that the TIR-Logger provides very fast thermal infrared reflectance spectra of very good quality and reproducibility. Furthermore the comparison of single mineral TIR-Logger spectra with spectra of existing libraries has shown a good agreement. Over 300 spectra from 83 specimens have been measured so far and all samples are included in the CSIRO library da-
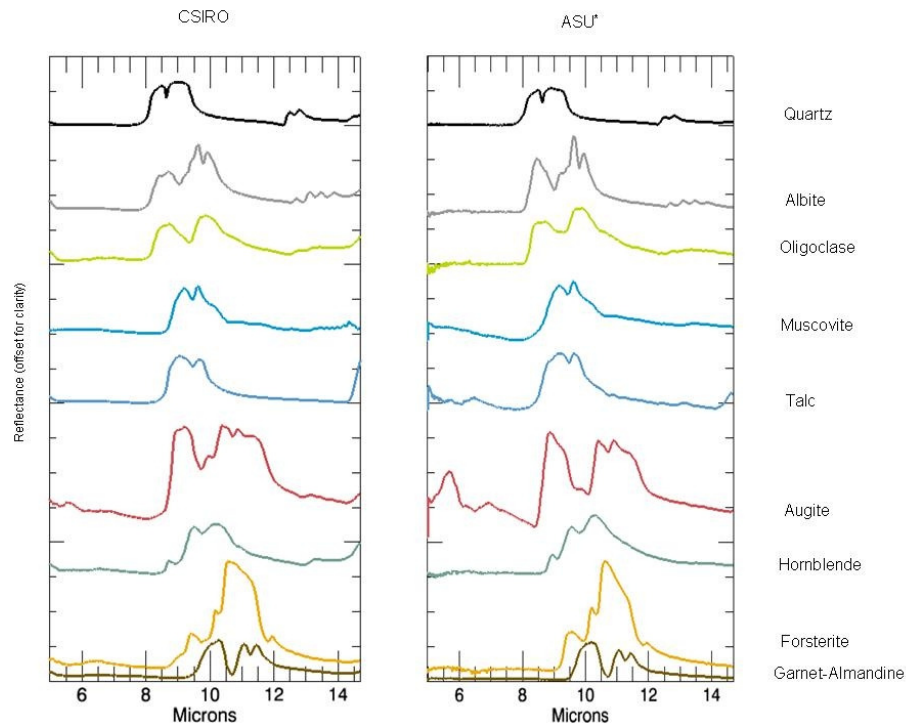
Figure 4: Spectra of common minerals measured with the TIR-Logger in comparison with mineral spectra from the Arizona State University spectral library.

tabase. Chemical analyses and mineralogical validation of particulate specimens are underway. Further specimens provided from the Australian Museum in Sydney and the Victorian Museum in Melbourne are expected to cover the whole range of rock-forming minerals.

For the future work more investigations have to be carried out to determine how many spatial/angular measurements are necessary to adequately describe a single mineral. In addition much further research on the optical anisotropy effects is necessary to obtain better knowledge about drill core samples which can contain a wide variety of crystal orientations, as well as specimens cut at different angles to the optical axis. The results of such analyses hopefully will provide valuable new information to develop new models and/or methods for quantitative spectral unmixing approaches to deal with orientation effects.

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