VISIBLE/INFRARED SPECTROSCOPY (VIRS) AS A RESEARCH TOOL IN ECONOMIC GEOLOGY: BACKGROUND AND PILOT STUDIES FROM NEWFOUNDLAND AND LABRADOR

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ABSTRACT

Visible/Infrared Reflectance Spectroscopy (VIRS) measures absorption in the 350 nm to 2500 nm region of the electromagnetic spectrum, where many minerals have distinct responses that allow their identification, even within mixed parageneses. The VIRS method characterizes a range of hydrothermal and supergene alteration minerals, and also some primary igneous and metamorphic minerals. Data acquisition is simple and rapid, but interpretation is more complex, requiring a large database of reference spectra. Automated computer programs can simplify and expedite this process, but human analysis and reasoning are also required, and VIRS data are most useful where combined with other data, notably petrography and geochemistry.

Several pilot studies, summarized here, illustrate the versatility of the VIRS method. Studies of alteration, associated with epithermal gold mineralization, easily recognized key indicator minerals such as pyrophyllite, alunite, dickite and topaz; such information may be useful in mapping zoned alteration systems, and vectoring toward the most favourable areas. A study of footwall alteration in a VMS deposit did not support previous visual identifications of pyrophyllite, but gave ambiguous results with respect to kaolinite. Modelling showed that subordinate kaolinite could be masked by interference from more abundant white mica (sericite). The VIRS data from a mesothermal vein-type gold deposit indicate subtle alteration signatures, on a scale of several metres, around auriferous veins, even though visual evidence for such effects is muted. The mineralogical causes for this effect are as yet unresolved, but this does not prevent its use as a proximity indicator in exploration. Studies of porphyry-style Mo-Cu deposits, associated with sheeted veins, document the progressive overprinting of regional chloritedominated propylitic alteration by focused potassic to phyllic alteration associated with the mineralization. A later stage of advanced argillic alteration, typified by kaolinite, was also documented in one deposit. A reconnaissance investigation of rareearth element (REE) mineralization in Labrador suggests potential for the VIRS method in studies of host rocks and mineralization. The VIRS data can distinguish Na–Fe-rich chain silicates characteristic of peralkaline igneous rocks from common pyroxenes and amphiboles, facilitating identification of potential host suites. The REE also generate unusual absorption features in the visible and near infrared, which directly indicate specific REE ions. Although there are few reference spectra for complex REE-bearing minerals, the VIRS data recognize mineralized samples, and may help to identify samples collected on the basis of other criteria, for geochemical assays. Finally, VIRS analysis of samples from central Labrador now provides the first reference spectra for the REE-enriched mineral eudialyte.

INTRODUCTION

PROJECT OVERVIEW

In 2008, the Geological Survey of Newfoundland and Labrador (GSNL) joined a small, but growing group of government agencies using portable reflectance spectrometers in applied geoscience. These instruments use the absorption of visible and infrared electromagnetic radiation to characterize mineral assemblages, and have wide applications in exploration. They also have uses in mine production, environmental monitoring, geoarcheology and many applications outside geoscience. We have now completed several pilot studies to gain practical experience and develop protocols, and now anticipate that spectroscopy will be a standard component of many research projects. The technique is particularly useful in the study of hydrothermal alteration, for which mineral identifications are notoriously difficult. This review provides background on the principles of the method, and uses results from pilot studies to illustrate potential applications. It provides supplementary material for other publications that present or interpret such data (*e.g.*, Hinchey, *this volume*; Sandeman and Rafuse, *this volume*). There are few accounts documenting such applications, mostly due to confidentiality issues. Thompson et al. (1999) provide a short overview, and an article by Hauff (2008) details applications to specific styles of alteration. This article is, in part, an expansion of a previous short paper summarizing the work (Kerr et al., 2009a). The papers compiled by King et al. (2004) include more extensive discussion of the principles and theory behind these methods. Several focused treatments document compositional shifts in minerals that can provide vectors to mineralization (e.g., Hermann et al., 2001; Jones et al., 2005; van Ruitenbeek et al., 2005), or applications to specific uses, such as the identification of kimberlite indicator minerals (e.g., Hauff and Percival, 2006). In this review, we use the simple acronym VIRS (visible/infrared reflectance spectroscopy) for the technique; the acronyms SWIR (short-wave infrared) and NIR (near infrared) are also to denote regions of the electromagnetic spectrum.

THE IMPORTANCE OF ALTERATION

Understanding alteration mineral assemblages is crucial in the study of hydrothermal ore deposits. Hydrothermal alteration vastly increases target size, and most alteration systems are spatially and temporally zoned, with overprinting relationships. Knowledge of such patterns, and the ability to recognize them, add up to a potentially powerful vectoring tool. Alteration also tracks the physicochemical variations of mineralizing fluids, which relate to their sources and evolution. Finally, alteration assemblages are important criteria for classification of all hydrothermal deposit types. Hydrothermal alteration zones contain complex mixtures of primary mineral assemblages and new minerals formed through interaction of the primary assemblage and fluids. Alteration mineral assemblages are commonly fine grained, and may even lack crystallinity, especially in low-temperature environments. Optical identification of minerals is difficult, even with powerful microscopes, and many alteration minerals simply lack diagnostic optical properties. The study of hydrothermal alteration is fraught with subjective interpretations, misidentified minerals and misunderstood paragenetic relationships. In some environments, such as volcanogenic massive sulphides (VMS), even the distinction between regional low-grade metamorphic assemblages and focused hydrothermal alteration zones is difficult, because the same minerals occur in both (e.g., Hinchey, this volume).

Quantitative techniques such as whole-rock geochemistry, X-ray diffraction (XRD) and laser ablation-inductively-coupled-mass spectrometry (LA-ICP-MS) provide valuable information on minerals that can be linked back to petrographic or field data. However, such methods are timeconsuming, labour-intensive, variably destructive and cannot be used on a real-time basis in the field. As any explorationist will attest, results from a given step in a program can immediately influence the next step in the search for ore. Portable VIRS instruments fill this role in exploration, and can also provide valuable research data on alteration and other topics.

EVOLUTION OF VIRS INSTRUMENTS

The VIRS methods were originally developed for space programs to study the Earth and other planets via remote sensing. The incident energy source came from solar radiation, and this approach also guided the first portable spectrometers, used for ground-truthing remote sensing data. The next step was the addition of internal light sources, which allowed operation in a much wider range of environments. The portable infrared mineral analyzer (PIMA), introduced in the mid-1980s, used a light-emitting panel, against which the sample was placed. The PIMA emphasized the NIR and SWIR regions, which are key for many alteration minerals. The PIMA also quickly led to the acquisition of infrared absorption spectra from a wide range of geological environments, which now provide important reference and standard material used in the interpretation of results. A recent refinement was the development of external 'light-probes' connected by fibre optic cables, which allow specific areas of samples to be better targeted. The GSNL Terraspec Pro, introduced by Analytical Spectral Devices Incorporated (ASD) in 2004, is of this type, but the lightprobe is interchangeable with an illuminated panel device, dubbed the 'muglight'. Hardware innovations in the last decade were matched by advances in computer software, such that data acquisition is increasingly faster. Automated mineral identification programs also speed up the process of data interpretation, but their outputs must still be verified, assessed and interpreted by researchers. We employ the proprietary software and libraries provided by Spectral International Inc. (SII) with the instrument, United States Geological Survey (USGS) spectral libraries, and also a specialized third-party program called 'The Spectral Geologist' (TSG), developed by AusSpec International (www.ausspec.com) This program provides sophisticated interpretation, data processing and display functions geared to exploration and geoscience applications.

PRINCIPLES AND APPLICATION OF VIRS METHODS

INFRARED ABSORPTION

The VIRS method depends on interactions between electromagnetic radiation and matter; the colour of common minerals illustrates this principle, as it is caused, in part, by absorption of specific wavelengths in the visible spectrum. Although colour is rarely diagnostic, many common miner-



Wavelength

Figure 1. The electromagnetic spectrum, showing the regions of interest in the context of visible/infrared reflectance spectroscopy, namely the visible region (390 to 750 nm), the near infrared (NIR; 750 to 1300 nm) and the short-wave infrared (SWIR, 1300 to 2500 nm). Modified after Hauff (2005) and other standard texts.

als have consistent, distinctive and sometimes unique absorption responses to infrared radiation.

The VIRS method employs electromagnetic radiation with wavelengths between 350 nm and 2500 nm (0.35 to 2.5 µm; Figure 1), representing visible light (390-750 nm), near-infrared (NIR; 600 to 1300 nm) and short-wave infrared (SWIR; 1300 to 2500 nm). Absorption features typical of the visible light region include those that generate colour variation in minerals and gems, and many of these are linked to specific transition metals. Rare-earth elements (REE) also cause distinctive absorption responses in the visible and NIR regions. Infrared absorption is caused by several effects, but the most important is the transfer of electromagnetic energy into chemical bond vibration, and absorption features may be related to specific molecular structures. Chemical bonds involving OH, N, CO₃, Cl, F, SO₄ and various cations (notably Al, Fe and Mg) generate specific absorption features, and spectra for minerals can, in part, be predicted from their crystal chemistry. Spectra may also record other features, such as composition, degree of crystallinity, volatile contents, and crystallographic orientation. The use of reference and standard spectra is as important as theoretical predictions, because minerals are naturally variable substances. A specific absorption feature may not be unique to a given mineral, but a specific combination of features commonly is diagnostic. Not all minerals are active in the infrared, and common rock-forming anhydrous silicates such as quartz and feldspars do not generally give useful spectra. The absorption spectra from natural samples better highlight the more complex and variably hydrated silicate minerals, and the non-silicates, all of which are of interest in economic geology. Natural samples are rarely monomineralic, and absorption spectra may include responses from two or more minerals. The influence of a given mineral on such results may not correlate directly to its abundance, as reflectance coefficients vary. The interpretation of spectra that record mixed mineral assemblages has inherent complications, as interference effects are possible. Such mixtures can be simulated from end-member spectra to aid in interpretation of results, but the resolution of composite mineral assemblages remains one of the challenges to VIRS. Nevertheless, the spectral signatures of such natural mixtures are empirically useful, even if all the individual minerals cannot be resolved.

SPECTROMETER DESIGN AND OPERATION

The Terraspec Pro instrument has essentially 3 components; the spectrometer module, the control computer, and



Figure 2. *A)* Schematic illustration of the ASD Terraspec *Pro instrument and accessories, after technical information provided by ASD, and Hauff (2005). B) The Terraspec Pro instrument. C) The acquisition of data from a hand sample using the light probe accessory.*

the light probe (Figure 2). The light source is designed to emit equally across the spectral region of interest, and the area analyzed by the probe is about 2 cm in diameter; the 'muglight' has an illumination window of the same diameter. The 1.2-m fibre optic cable (the most fragile component of the system) brings the reflected light to the spectrometer module, where three internal spectrometers use diffraction gratings and large photosensitive arrays to decode the signal in the visible/NIR and two SWIR regions, respectively. Prior to its first usage, and at regular intervals during its usage, the instrument is calibrated using a specialized ceramic disk that reflects uniformly across the spectrum. An individual measurement takes from 20 seconds to 1 minute; darker samples may yield better data with a longer collection period. A significant challenge is detailed record-keeping to retain the context of all individual measurements. We find it useful to first take digital photographs of samples, and indicate locations tested directly. Measurements can in some cases be averaged to reduce the total amount of data, but such treatment must be approached with caution, as the individual spectra may have subtle but important differences. Smoother surfaces (such as cut drillcore) seem to provide less total reflectance than slightly rougher broken surfaces, and darker samples may yield low-amplitude signals. However, such responses still contain absorption features, which in some cases can be 'brought out' by scale normalization (*see* later discussion).

INTERPRETATION OF SPECTRAL DATA

The output format for VIRS data consists of a line graph showing the total reflectance (measured from 0 to 1, where 1 is 100 percent of incident light) against wavelength, which is indicated in nm or µm. The instrument has a resolution of about 2 nm. Pyrophyllite from the Manuels deposit near St. John's, used as one of several internal standards, is shown in Figure 3A, measured at different times. The individual spectra from this sample would normally plot on top of one another, but the Y-axis has an arbitrary scale, so they are 'stacked' to illustrate the patterns, which are the feature of interest. Many other representations of spectra in this report use the same convention. Absorption features appear as 'negative anomalies', and their shapes also convey information, as in 'doublets' where absorption occurs at two closely adjacent wavelengths. Doublet features are characteristic patterns for several important minerals (e.g., kaolinite). The exact positions of absorption features may vary by a few nm from mineral to mineral, but such differences are within the resolution of the instrument.

It may be useful to average data from several measurements of a given sample, particularly if the overall reflectance varies, but only if their pattern is identical. Spectra from an altered granitoid rock (from the Moly Brook deposit, near Grey River) illustrate this principle, and the average is indeed representative (Figure 3B). However, subtle features in individual spectra might indicate a less abundant and sporadically distributed mineral, and this information could be lost in averaging. Nevertheless, when a dataset is well understood, averaging may simplify its representation. Normalization of the reflectance scale may also be useful in comparing measured spectra to standards, as shown by Figure 3C, representing a dark mineral in veins that cut an altered granite at the Moly Brook deposit. The original lowamplitude spectrum does contain absorption features, but these are much easier to see if data are normalized to the same reflectance range as the standards: the mineral is shown to be hornblende, not tourmaline. Data normalization is automatic within programs that attempt computerized identification, and can also be accomplished from numerical data using spreadsheet programs. It can also be accomplished using graphics programs, because it equates to simple vertical stretching of the spectrum. However, care must be taken to avoid any distortion of the horizontal scale in using such graphical methods, as the wavelength positions of absorption features are critical in interpretation.



Mineral identification depends upon comparisons against a database of reference spectra. The TSG program is very good for grouping large numbers of results into a smaller number of 'patterns' that then can be investigated individually in more detail. More detailed work can be completed using the software and associated reference libraries created by SII that allow specific absorption features to be searched automatically or manually. This approach may **Figure 3.** Examples of spectra from VIRS measurements, and illustrations of some processing and display issues. A) Repeated measurements of pyrophyllite from the Manuels Mine near St. John's, showing the consistency of measurements over time, and the locations of the absorption features characteristic of the mineral. B) An example of the averaging of individual spectra that have a common pattern to reduce the amount of data for display; see text for discussion of the hazards of this procedure. C) An example of how converting measurements and standards to a common (normalized) vertical scale can 'bring out' specific absorption features to the naked eye, and aid in visual comparisons. Examples (B) and (C) both come from altered granites at the Moly Brook Mo–Cu deposit, southern Newfoundland.

facilitate identification of less abundant minerals. Mixtures of minerals can sometimes 'impersonate' unlikely species to various degrees, and spurious identifications of highly unlikely minerals are not unknown. The TSG program has features that easily permit analysis of spectral variations in a spatial context, *e.g.*, illustrating changes with depth from measurements of drillcore. Software automation has definite advantages, but results cannot always be taken at face value, and in some cases interpretations need to be checked through visual analysis of individual spectra. The VIRS investigations are most effective when combined with independent constraints from petrographic and geochemical data. Knowledge of mineral associations is equally valuable, as the identification of one mineral may suggest others that could be present.

ABSORPTION SIGNATURES OF COMMON AND UNCOMMON MINERALS

Figure 4 illustrates the spectra for some common minerals, and some uncommon but interesting minerals, such as zunyite (Al₁₃Si₅O₂₀(OH,F)₁₈Cl). The latter is an example of a unique spectrum having features that are not shared by other minerals. Absorption in the visible spectrum is useful in identifying ferromagnesian minerals containing transition metals (e.g., chlorites, pyroxenes, garnets) and also for REE-bearing minerals. This can have important exploration uses, e.g., the rapid identification of G10 garnets indicative of diamondiferous kimberlites (Hauff and Percival, 2006; Hauff, 2008). Infrared absorption tends to be more wavelength-specific, and the spectra of minerals from given groups (e.g., amphiboles or micas) have features in common. A distinct response from OH bonds at ~1400 nm characterizes all hydrous minerals, but its precise position and geometry varies, so the spectra of individual members are distinct at a detailed level (Figure 4). A prominent feature at



Figure 4. *Examples of spectra from some common and uncommon minerals. All examples are reference spectra from the Spectral International Inc. (SII) libraries within the SPECMIN software programs.*

~2200 nm is caused by the Al-OH bond; its shape and position similarly carry mineralogical or compositional information, as used by Hinchey (*this volume*) to document shifts in white mica assemblages. Note that some minerals (*e.g.*, dickite) show distinctive 'paired' features (doublets) whereas others have only a single response. Hauff (2005) provides exhaustive information on specific minerals and specific infrared absorption features.

The end-members of natural solid solution series have distinct absorption spectra, and systematic changes may define intermediate compositions. Figure 5A shows differences between common K- and Na-bearing alunites (alkali aluminum sulphates) and the rarer ammonium (NH₄-bearing) variety known as buddingtonite. Alunite compositions may be important indicators of gold potential in epithermal systems. The same principle applies to other alteration minerals, *e.g.*, shifts in chlorite spectra define the influence of Mg, Fe and Mn end-members (Figure 5B). In white micas (commonly labelled sericite), the location of the ~2200 nm Al-OH feature carries compositional information, which may be a proximity or vectoring tool for exploration in VMS systems (*e.g.*, Hermann *et al.*, 2001; van Ruitenbeek *et al.*, 2005; Hinchey, *this volume*).

DISCUSSION OF SELECTED PILOT STUDIES

Some pilot studies discussed here were undertaken simply to test the ability of the instrument to identify minerals in known examples, but others aimed to investigate mineralization and alteration of unknown character. They are presented to illustrate instrument capability, potential complications, and the value of integration of spectral data with other information. The locations of the areas discussed in this section are shown in Figure 6.

UNUSUAL ALTERATION MINERALS AT BOBBYS POND, CENTRAL NEWFOUNDLAND

The VIRS method is used widely in the search for epithermal-style gold deposits. These deposits form at shallow levels in the Earth's crust (<1 km depth) from low-temperature fluids, and associated alteration minerals include phyllosilicates, sulphates, clay minerals and zeolites (*e.g.*, Hedenquist *et al.*, 2000; Taylor, 2007). Epithermal alteration systems are typically zoned, and Au, Ag and base metals also have distinct distributions with respect to this alteration zonation. The VIRS method is a powerful tool for identify-



Figure 5. Examples of changes in VIRS absorption patterns. A) Alunite spectra, including Na-, K-, Ca- and NH_4 -rich varieties. B) Chlorite spectra, including Mg-, Fe- Mn-rich varieties and mixtures of these end members. All examples are reference spectra from the Spectral International Inc. (SII) libraries within the SPECMIN software programs. See Hinchey (this volume) for further discussion of compositional variation in white micas. Note that these diagrams show only the short-wave infrared (SWIR) region (1300–2500 nm).



Figure 6. Locations of the areas involved in pilot VIRS studies discussed in this report.

ing many of these alteration minerals, with the notable exception of the low-temperature feldspar adularia, which does not respond.

Epithermal-style gold mineralization occurs in the Avalon Zone (e.g., O'Brien et al., 1998), and locally in central Newfoundland (Squires, 2005; Kerr, 2006). An unusual pervasive alteration zone located near Bobby's Pond, in the Victoria Lake supergroup (Figure 6), is one of only two sulphur showings listed in the Mineral Occurrence Database System (MODS; 12A/10/S001). Previous investigations (Kean and Evans, 1986) recognized massive quartz, alunite, pyrophyllite and sulphur, typical of high-sulphidation epithermal environments in which the removal of metals by low-pH fluids leaves highly aluminous alteration assemblages. Sulphur is the most obvious component, but is subordinate to the other minerals. The alteration zone is further discussed by Hinchey (2008), and its exact significance and timing with respect to nearby VMS mineralization remain unclear. The zone is barren, and likely a 'lithocap' facies (cf., Taylor, 2007), but may indicate potential for gold mineralization at depth.

Pyrophyllite and alunite are easily identified from distinctive spectral responses (Figure 7A, B). Alunite is particularly distinctive of high-sulphidation epithermal systems, and the 1400 to 1500 nm region of the SWIR provides compositional information on K-Na-NH4 end-member proportions (Figure 5). On this basis, alunite at Bobby's Pond is likely sodium-rich, rather than potassium-rich (Figure 7C). This compositional inference was substantiated by XRD data (J. Hinchey, unpublished data). The proportions of potassic versus sodic end-members in alunite are considered to record the relative roles of magmatic and meteoric fluids in mineralizing hydrothermal fluids, although opinion is divided on the significance of such variation as an indicator of economic potential (e.g., Arribas et al., 1995). Some spectra from Bobby's Pond also revealed absorption features at ~1405-1408 nm and ~2086-2088 nm. These are unusual, and diagnostic of topaz (Al₂SiO₄(F,OH)₂). Topaz is difficult to identify visually or petrographically, as it is easily confused with quartz, which is abundant. Its presence at Bobby's Pond with other aluminosilicates is geologically reasonable, and it is described from 'high sulphidation' epithermal alteration elsewhere (Taylor, 2007; Hauff, 2008). Topaz must be sporadically distributed at low abundances, so it is not easy to verify VIRS data using lithogeochemistry. Stochiometrically, the F content of topaz is about 11 wt %, but this can be lower depending on F-OH substitution. Bulk abundances of topaz below 1% would translate into only a few hundred ppm F in typical geochemical analyses of larger samples, which is consistent with the data from Bobby's Pond.



Figure 7. Spectra from Bobby's Pond sulphur showing, representing epithermal-style Al-rich alteration of felsic (?) protolith compositions. A) Samples compared to pyrophyllite reference spectra. B) Samples compared to alunite reference spectra; note the subtle features attributed to small amounts of topaz. C) Comparison of Bobby's Pond alunite spectra with K-rich and Na-rich end-member reference spectra.

Aside from the topaz recognition, our VIRS pilot study at Bobby's Pond did not yield radical new information, but it illustrates an important point. It is important to acquire multiple spectra even on single samples, because important, less abundant minerals may not show up in all measurements. Furthermore, it illustrates the dangers in averaging data without close inspection of individual spectra; the isolated topaz response would easily be lost if combined with other data from topaz-free areas.

HIGH-SULPHIDATION EPITHERMAL GOLD MIN-ERALIZATION, WESTERN AVALON ZONE

Gold mineralization in the Avalon Zone and correlative Neoproterozoic terranes in Newfoundland is considered to be of mostly epithermal character, and the Hope Brook deposit is interpreted as a deformed epithermal deposit (Dubé *et al.*, 1995; O'Brien *et al.*, 1998). The recognition of distinctive alteration facies is important in establishing potential at a given showing and choosing the next step in exploration. However, the minerals involved are hard to identify, and some epithermal-style mineralization lacks sulphides, making it hard to detect. The use of VIRS in grassroots exploration is illustrated by a pilot study of two relatively new prospecting discoveries in the western Avalon zone (Calvins Landing and Rattle Brook showings; Figure 6).

The Calvins Landing showing is located near Glovertown, and is hosted by the late Neoproterozoic metavolcanic and pyroclastic rocks of the Love Cove Group. These host rocks have experienced Paleozoic deformation and lowgrade metamorphism, the intensity of which increases toward the Dover Fault, located some ~1.5 km to the west of the showing. The mineralized zone contains specular hematite, but only traces of sulphide minerals, but strong alteration across widths of some 30 m is obvious; grab samples contained up to 4 ppm Au (Silver Spruce Resources, Press Release, June 16, 2008). The VIRS data from samples reveal pyrophyllite and alunite, as seen at Bobbys Pond (see above). Although many spectra are mixtures of the two minerals, they can be resolved individually (Figure 8A). Mixed spectra were, however, not totally explicable by pyrophyllite and alunite, and further work revealed dickite, a kaolinitegroup clay mineral. Dickite has a distinctive pattern characterized by 'doublet' absorption features at ~1380 nm and ~2200 nm (Figure 8B). Quartz-alunite-pyrophyllite-dickite

Figure 8. Spectra from the Calvins Landing and Rattle Brook gold showings in the western Avalon Zone. A) Pyrophyllite and alunite, from Calvins Landing. B) The distinctive spectra of the kaolinite-group mineral dickite at Calvins Landing. C) Assorted spectra from the Rattle Brook area, showing alunite, dickite and pyrophyllite.



assemblages are characteristic of gold-bearing high-sulphidation epithermal systems (*e.g.*, Hedenquist *et al.*, 2000; Hauff, 2008), and dickite can be an indirect indicator for gold content. The alunite spectra from Calvins Landing suggest a more potassic composition for this mineral compared to Bobby's Pond. At the Rattle Brook gold showing on the central Burin Peninsula (Figure 6), gold is hosted by broadly equivalent late Neoproterozoic metavolcanic rocks of the Marystown Group. Surface mapping and sampling of an extensive zone of alteration and mineralization provided encouraging results. The VIRS data from Rattle Brook provided similar spectra diagnostic of pyrophyllite, alunite, and dickite (Figure 8C).

Recognition of distinctive alteration assemblages was instrumental in further exploration work at both sites, and the Calvins Landing showing was eventually optioned to Silver Spruce Resources. The definition of intensely altered dickite-rich zones was used to target later sampling and prospecting. In the case of Rattle Brook, analysis of samples from areas of extensive outcrop provides data that allows spatial variation in alteration facies to be mapped. The VIRS data will clearly be useful in a more systematic examination of gold mineralization on the Burin Peninsula, which is anticipated for the summer of 2011.

FOOTWALL ALTERATION ASSEMBLAGES IN A VMS DEPOSIT, CENTRAL NEWFOUNDLAND

Like all hydrothermal deposits, volcanogenic massive sulphide (VMS) systems have discrete alteration facies that vary both in space and time (e.g., Franklin et al., 2005; Galley et al., 2007). Intense alteration forms a restricted, focused zone sitting immediately beneath the mineralization, and there may also be significant hangingwall alteration, especially where replacement processes are involved (e.g., Doyle and Allen, 2003). Mineral assemblages in footwall alteration zones depends on the protolith composition of host rocks; chlorite (± epidote, amphibole) dominates in mafic sequences, whereas sericite overwhelms in felsic rocks. Sericite is actually a mixture of fine-grained, waterrich muscovite-group phyllosilicates, of which there are several superficially identical varieties (e.g., hydromuscovite, illite, phengite, paragonite and margarite). Contrasts in alteration may define footwall and hangingwall sequences, and pinpoint favourable stratigraphic horizons on a regional scale. The challenge of deciphering these patterns is ideally suited to the application of VIRS methods.

The Victoria Lake supergroup of central Newfoundland contains many VMS deposits, including the Duck Pond mine; details of these are reviewed by Hinchey (2007, 2008) Hinchey and McNicoll (2009), and McNicoll *et al.* (*in press*). The VIRS data were acquired from several examples,

with direct use of the spectrometer in core-storage facilities, and this pilot study refers to the Daniels Pond deposit. Hinchey (*this volume*) provides further information on VIRS studies of Daniels Pond, notably with respect to the use of shifts in the wavelength position of the Al-OH absorption feature in sericite as a potential vectoring tool in both footwall and hangingwall stratigraphy.

Daniels Pond consists of Zn (\pm Cu, Pb, Ag) massive sulphides hosted within mostly felsic volcanic and pyroclastic rocks, with a total resource of some 1.2 million tonnes (Hinchey, 2008, *this volume*). Previous exploration work suggested that intensely altered footwall rocks contain mineral assemblages atypical of felsic VMS systems. Pyrophyllite and various clay minerals were reported on the basis of visual identification and softness (*e.g.*, Dadson, 2002; *see* also Hinchey, 2008). These minerals are also characteristic of many epithermal-type systems (*see* above) and Hinchey (2008) suggested a transitional VMS-epithermal affinity for this and other nearby deposits.

Drillcore samples from Daniels Pond were submitted for XRD analysis at Memorial University. The results (J. Hinchey, unpublished data; H. Gillespie, Memorial University, personal communication, 2008) did not reveal pyrophyllite, but suggested that white mica (illite) was abundant. Visually similar altered rocks from the footwall at the nearby Bobbys Pond VMS deposit (not to be confused with the sulphur showing) were shown to contain a variety of kaolinite (halloysite) by XRD, but this mineral did not appear in the Daniels Pond XRD results (J. Hinchey, unpublished data). Spectra from footwall alteration samples at Daniels Pond (Figure 9A) all have a prominent OH and water-related absorption feature at ~1400 nm, but the characteristic 'doublet' of kaolinite, and the ~2160 nm feature of pyrophyllite are absent. The closest match to the Daniels Pond spectra are from minerals generally called 'white micas' (e.g., muscovite, hydromuscovite, illite, paragonite), which are the most common alteration species in felsic VMS systems. The VIRS data confirm the absence of pyrophyllite indicated by XRD, but the presence of kaolinite is still suspected based on the closely similar properties of alteration at Daniels Pond and Bobby's Pond. Intuitively, an interference effect was suspected - the highly reflective sericite (white mica) could overwhelm responses from other minerals. This idea was tested by simulation of two-component illite-kaolinite mixtures using the SII software, assuming that reflectance coefficients are equivalent. The results (Figure 10) are telling; in situations where the illite/kaolinite ratio is >1, the diagnostic absorption features of the latter are not easily seen.

The results provide an illustration of complications that could arise from interference and masking by more abun-



Figure 9. Spectra from the footwall alteration zone at the Daniels Pond VMS deposit. A) Spectra dominated by 'white mica' signatures, but lacking the distinctive features of either pyrophyllite or kaolinite. B) Illustration of the strong similarity between Daniels Pond spectra and those of white mica, in this case muscovite. C) Comparison with other white mica minerals, including the Li-rich variety lepidolite.



Figure 10. Simulated spectra for mixtures of kaolinite and illite in increments of 10% from 100% kaolinite to 100% illite. Note that the kaolinite features are progressively obscured once the illite/kaolinite ratio exceeds unity. Reference spectra and mixing calculation from the SPECMIN software programs. Note that this figure shows only the short wave infrared (SWIR) region (1300 to 2500 nm), rather than the wider wavelength interval illustrated in Figure 9.

dant white micas or sericite, and a more general illustration of the way in which mixed mineral assemblages need to be approached in interpretation. The very strong white mica response causes problems in some respects, but these spectra may also have valuable information. As discussed by Hinchey (*this volume*) systematic shifts in the position of the Al-OH absorption feature, indicative of Na₂O:K₂O variations, provide a possible vector to the ore horizon at this deposit, which could ultimately prove more useful than the presence or absence of kaolinite-group minerals.

VEIN-RELATED ALTERATION HALOES IN A SUL-PHIDE-POOR MESOTHERMAL GOLD DEPOSIT

Gold mineralization is notoriously cryptic, especially where sulphides are not widely developed. Vein-hosted mesothermal or orogenic gold deposits provide challenges for detailed exploration, due to variations in vein attitudes, lack of continuity and poor geophysical responses. There are many anecdotes of drillholes missing mineralized veins by mere metres. The Golden Promise (Jaclyn) prospect is located southwest of Badger, in an area not previously known for gold (Figure 6), and contains coarse free gold, but little sulphide. Mineralized veins are hosted by low-grade turbiditic sedimentary rocks now considered to represent the uppermost section of the Victoria Lake supergroup (Squires, 2005; Sandeman et al., 2010). A small resource of about 0.9 Mt at 3 ppm Au has so far been defined (Pilgrim and Giroux, 2008), and the deposit has been compared to other turbiditehosted gold deposits in Nova Scotia and Australia (Sandeman et al., 2010). Visible alteration of the host rocks is limited, although a peculiar 'spotted' texture is visible in some areas. The characteristic iron-carbonate alteration seen in many other gold prospects in central Newfoundland is less common around the Jaclyn veins, possibly owing to the coarse-grained siliciclastic host rocks.

The VIRS data obtained from the sedimentary host rocks at Golden Promise mostly lack distinct absorption features in the infrared, and the peak at the short-wavelength end of the visible spectrum simply indicates their generally dark colour (Figure 11). Little can be gleaned from these patterns; the rocks are likely mostly fine-grained quartz and lesser feldspar. However, spectra collected around some individual auriferous quartz veinlets reveal subtle 'haloes', despite few clues from colour or texture, aside from faint lightening. The spectra are not yet fully interpreted in a mineralogical context, although carbonates, sericite, chlorite \pm epidote are the most likely responsive minerals. Similar patterns are evident on a larger scale around the wider gold-mineralized intervals; in drillhole GP-07-86 there is a systematic change in VIRS response above and below the inter-

val containing mineralized veins. Such observations could be very important if they reveal that an apparently barren drillhole is closely adjacent to subparallel mineralized veins, and the VIRS data could also guide assaying; further discussion is provided by Sandeman *et al.* (2010). This pilot study provides an example of empirical use of VIRS data; although the mineralogical causes of spectral variations are not fully resolved, the latter still may have utility in exploring this deposit.

ALTERATION SIGNATURES IN PORPHYRY Mo-Cu DEPOSITS IN SOUTH-CENTRAL NEWFOUND-LAND

Molybdenum mineralization is widespread in Newfoundland, and there are two potential large-tonnage deposits in south-central Newfoundland, near Grey River and Granite Lake (Figure 6). The Moly Brook and Moly Hill deposits both consist of sheeted veins, networks and stockworks of mineralized quartz veins. The host rocks to veins at Moly Brook are weakly foliated, compositionally variable, K-feldspar megacrystic quartz diorite, granodiorite and granite of Silurian age, older than the mineralization itself (A. Kerr and V. McNicoll, unpublished data; Lynch et al., 2010). The host rock at Granite Lake is a muscovite-bearing leucogranite that contains disseminated molybdenite, and it is inferred to be similar in age to the mineralized veins. Kerr et al. (2009b) describe two superimposed alteration styles at Moly Brook, *i.e.*, a regional 'dark' alteration of the host rocks, typically associated with disseminated pyrite, and a more localized alteration associated with zones of intense veining, where feldspars are reddened and muscovite appears. The dark alteration is less evident at Granite Lake, where the host rocks are more leucocratic. However, there is locally intense alteration to soft, friable, pale yellow to white or buff material interpreted to be rich in clay minerals (Tuach, 1996).

The VIRS data from Moly Brook can be classified into several groups on the basis of their general characteristics and increasing proximity to mineralization (Figure 12; Groups 1 to 5). Treated as empirical measurements, these spectra show a clear, unidirectional progression. Distal environments (Groups 1 and 2) have spectra that are rather featureless in the visible and NIR regions, but have complex absorption features in the SWIR. In Groups 3 and 4, where there is reddening of feldspars and some mica growth, the patterns become simpler and the important OH-related

Figure 11. (opposite page) VIRS data collected from drillhole GP-07-86 at the Golden Promise (Jaclyn Vein) prospect in central Newfoundland, showing the unresponsive nature of distal host rocks and the the presence of cryptic alteration haloes in the interval surrounding gold-bearing quartz veins. Modified from Sandeman et al. (2010).





Figure 12. *Multiple spectra from drillhole MB-08-13 at the Moly Brook Mo–Cu deposit in southern Newfoundland, showing the progressive change in response from least altered rocks (1) to 'dark alteration' (2), altered rocks with scattered veins (3) granites with potassic alteration and intense veining (4) and the marginal zones of mineralized veins (5).* See text for discussion.

absorption feature at \sim 1420 nm to 1440 nm deepens. The patterns become simpler with increasing proximity to, and density of, mineralized veins, implying a convergence to a simple alteration assemblage, represented by Group 5. Such empirical observations provide a usable vector toward mineralization that can be added to (and perhaps quantify) visual observations.

Figure 13 shows individual spectra in more detail, with relevant reference spectra. Those from rocks with little alteration or only dark alteration with disseminated pyrite (Figure 13A) have features in the SWIR consistent with Fe-rich chlorite-group minerals, but secondary amphiboles and epidote are also possible contributors. Spectra from samples adjacent to mineralized veins or in intervals of intense veining correspond almost perfectly to 'white micas', notably hydromuscovite, illite and related minerals (Figure 13B, C). Such signatures record intense potassic and phyllic alteration associated with mineralization. The other groups of samples are intermediate between these distal and proximal end-members. The VIRS data are broadly consistent with initial petrographic observations on the same sample database, although the fine grain size of secondary mineral assemblages presents an obstacle to such work. The next obvious step in interpretation would be to link the VIRS signatures to lithogeochemical data, such that real-time spectral measurements could be used as proxies for key geochemical indicators in logging core. The VIRS results from Moly Brook are consistent with alteration zonation patterns described from porphyry systems (e.g., Seedorf et al., 2005; Sinclair, 2007). The 'dark alteration' represents the propylitic facies corresponding to the regional footprint of large magmatic-hydrothermal systems. In this case, the heterogeneous, variably mafic character of the host granodiorite generates chlorite-dominated assemblages. White-mica-dominated alteration more closely associated with mineralization records focused 'phyllic' alteration in the core of the zoned system.

Spectra from mineralized drillholes at the Moly Hill deposit, near Granite Lake, resemble those obtained from samples showing strong phyllic alteration at Moly Brook,



Figure 13. Spectra from the Moly Brook deposit in comparison to reference spectra of relevant minerals. A) Regional 'propylitic' alteration, likely dominated by Fe-rich chlorite and epidote. B) Propylitic alteration with superimposed phyllic alteration, showing the growth of features characteristic of muscovite. C) Proximal zones dominated by phyllic alteration, showing the strong correspondence to muscovite reference spectra.

but the distinction of regional propylitic alteration was more difficult. Chlorite-dominated signatures were only obtained from melanocratic granodiorites interpreted to be enclaves of an older intrusive unit. Intense clay mineral alteration at Granite Lake was confirmed by VIRS data (Figure 14) that reveal presence of kaolinite, dickite and other species. This alteration facies likely represents late advanced argillic alteration, as it overprints other alteration facies. Advanced argillic alteration is transitional in many respects to the highalumina alteration associated with high-sulphidation epithermal systems (see earlier discussion) and its presence may suggest potential for such mineralization in the Granite Lake area.

THE POTENTIAL OF VIRS TECHNIQUES IN STUD-**IES OF REE MINERALIZATION IN LABRADOR**

Resurgent interest in exploration for REE and associated metals (Zr, Y, Nb, Be, Hf) awakened our interest in possible applications for VIRS techniques. This field diverges from the most VIRS applications, as such deposits are formed largely through magmatic processes, and hydrothermal alteration is less obvious; associated fluids are dominated instead by CO₂ and halogens (e.g., Richardson and Birkett, 1996). There are relatively few reference spectra from the complex and highly variable minerals that contain REE in available libraries. A pilot study was completed in 2010 using material from recent field work (see Kerr, this volume); although results are preliminary, they suggest some intriguing avenues for further investigation. Information discussed below comes from several areas in Labrador, where REE are associated with peralkaline plutonic and volcanic suites of generally Mesoproterozoic age (Figure 6). These deposits are summarized in recent reviews (Rafuse and Kerr, in press; Kerr, this volume) and also in previous articles (e.g., Miller, 1986, 1988). The most significant deposit is at Strange Lake, considered to be an important resource of REE and other metals, and the site of new exploration discoveries in adjacent Québec (e.g., Miller, 1986; Richardson and Birkett, 1996; Kerr, this volume).



Figure 14. Spectra from the Moly Brook deposit in the Granite Lake area, showing the characteristic features of advanced argillic alteration (kaolinite, dickite) in addition to the prevalent white mica alteration.

The REE, Y, Zr and Nb mineralization in Labrador is associated with peralkaline igneous rocks, as is common worldwide. Peralkalinity is defined in chemical terms as an excess of molecular K₂O and Na₂O over Al₂O₃, and it is not a visible characteristic. However, peralkaline rocks do contain unusual Na–Fe-rich minerals, notably aegirine (a pyroxene), and the amphiboles arfvedsonite and reibeckite. These superficially resemble more familiar chain silicates such as augite, diopside and hornblende, but their VIRS responses are distinct from those of their common counterparts, notably in the SWIR (Figure 15). The differences between common amphiboles and sodic varieties are subtle, and

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relate to the positions of specific absorption features (Figure 15C) whereas the differences for the pyroxenes are obvious. However, it should be noted that there are only a few reference spectra available for these minerals. Spectra from larger mafic grains in host granitic rocks at Strange Lake, and pegmatite-vein-like REE prospects in the Letitia Lake area, demonstrate that these diagnostic silicate minerals are easily resolved (Figure 15B, C). The VIRS investigations may thus provide a rapid and simple method of recognizing per-alkaline igneous rocks, especially in conjunction with other data such as radiometry.

The VIRS techniques should also have value in direct studies of REE-rich mineralization and exploration. The presence of REE in materials generates characteristic and unusual visible and NIR absorption, in regions of the spectrum that are normally 'quiet' for natural minerals. These effects are linked to the unfilled lower electron shells characteristic of the lanthanide elements, rather than bond vibrations, and they indicate specific REE ions, rather than mineral structures (Clark, 2004). Spectra for selected REE oxides (Figure 16A) illustrate this attribute; although these oxides do not form natural compounds, minerals containing these REE will respond similarly. Thus, VIRS methods, and remote sensing in general, have significant potential in REE exploration (e.g., Kilby and Riley, 2010). Examples of reference spectra for some REE-bearing minerals (Figure 16B) show these distinctive and complex patterns in the visible and NIR regions, and suggest that the presence of REE should be detectable, even if exact mineral identification is not possible.

Mineralized samples from Labrador (Figure 16C) also show absorption responses typical of the REE, with the most obvious corresponding to the relatively abundant light REE Nd. However, mineral identification is problematic, as spectra may record more than one mineral, and REE-bearing minerals have wildly variable compositions. The Pamela showing in the Ytterby 2 area is thought to contain allanite (a REE- and Th-rich variety of epidote) on the basis of field identification, but only one reference spectra is available (Figure 16B). Pegmatitic and aplitic samples from a bulk sample trench at the Strange Lake deposit also have obvious REE-related responses, but there are no reference spectra for unusual minerals (elpidite, gadolinite, gittinsite and stillunnamed Ca-Y-silicates) described from the deposit (Miller, 1986, 1999). There is thus potential to document and publish absorption spectra for these and other unusual minerals in Labrador deposits, ideally in conjunction with electron microprobe and/or LA-ICP-MS data. However, there is a more obvious pragmatic role for VIRS studies, because the method will detect the presence of REE mineralization in at least some samples, even if the mineralogical context cannot be resolved. This provides a method to screen samples col-



Figure 15. *A)* Reference spectra from the Na–Fe pyroxene aegirine compared to common augite and diopside. Measurements from mineralized vein-like zones in the Letitia Lake area (159, 165) match aegirine well. B) Reference spectra from the Na–Fe amphibole arfvedsonite compared to common hornblende, and samples from Labrador. Samples 089 and 090 represent the host peralkaline granite at Strange Lake, and samples 153 and 155 are from the Letitia Lake area. C) Enlargement of part of the SWIR region depicted in (B) showing the subtle differences in the position of specific absorption features.

lected according to some other criterion (*e.g.*, anomalous radioactivity) for possible REE enrichment. Although there is a common association between REE mineralization and U–Th enrichment, it is not a direct relationship, and there are REE-bearing minerals that lack these easily detectable side effects.

The mineral eudialyte (Na4(Ca, REE)2(Fe, Mn, Y, REE)ZrSi₈O₂₂(OH, Cl)₂) is an example of a REE-bearing mineral in this category. Eudialyte typically occurs in undersaturated peralkaline rocks such as syenites, and is now attracting much attention as a possible economic source of REE, because it can be enriched in valuable heavy REE (e.g., Wu et al., 2010). It is best known at Ilimaussag in south Greenland, but it also occurs in the Red Wine Intrusive Suite of central Labrador (Figure 6; Curtis and Currie, 1981), where eudialyte-rich zones are exploration targets (see Kerr, this volume, and press releases from Search Minerals). Eudialyte has some diagnostic physical features, notably a bright pink or red colour, but it also resembles some types of garnet, as implied by its colloquial nickname almandine spar. Our final contribution is to present what we believe to be the first reference visible/infrared spectra for eudialyte, representing several locations visited during 2010. The spectra (Figure 16D) are very distinctive, and show responses characteristic of the REE in the visible and NIR regions.

DISCUSSION AND CONCLUSIONS

This article has two roles, *i.e.*, to give some simplified background on VIRS methods for nonspecialists, and illustrate some potential applications in economic geology research, as well as in exploration. The six examples chosen are just a few of the many possibilities, all of which represent geoscientific research in the broadest sense; applications of the VIRS method are equally possible in other branches of Earth Science unconnected to the minerals industry. Despite this broad potential, current usage of VIRS analysis remains firmly rooted in the resource exploration



Figure 16. *A)* Spectra for selected REE oxides, showing the characteristic absorption patterns developed in the visible and near-infrared regions, which are specific to these REE cations. B) Reference spectra from several REE-bearing minerals, showing the complexity of these patterns in specific examples; data from the USGS spectral library. C) Spectra from mineralized samples in Labrador, showing the presence of REE minerals through distinctive responses. Samples 089B and 103B are pegmatites from Strange Lake, Sample 120B is a pegmatite from the Ytterby 2 area, and samples 156 and 163 are from the Letitia Lake area. D) The first published reference spectra for the REE-enriched mineral eudialyte, from the Red Wine Intrusive Suite of central Labrador, representing several different localities. Note the strong similarity amongst all measurements.

and materials science sectors, and consequently many results remain proprietary. In this discussion, it is perhaps useful to consider what would be needed to change this focus.

More than anything else, there is a need for a published, peer-reviewed framework that establishes some guidelines and standards for the collection, interpretation and representation of VIRS data. This article attempts to add to this foundation, but far more is needed, because nothing promotes new methods better than the demonstration of useful results. There is also a need for the development of standard materials that can provide quality assurance, quality control and also aid in the comparison of data derived from different instruments and groups. The use of standards and duplicates is standard for all other analytical techniques used in research, and VIRS should not differ in this respect. Although we use some internal standards (such as Manuels pyrophyllite) to monitor for instrument drift and catch potential problems, this does not really assure that the data we acquire can be rigorously compared with those acquired elsewhere.

The reference spectral libraries that are vital for mineral indentification and spectral interpretation currently have mixed status. Some sources, such as those provided by the USGS, are public domain data that are freely exchangeable, but others represent copyrighted information that is tied to individual instruments, and not so easily distributed. There are also minor but extremely irritating differences in data formats from various sources, which complicate their use in standard software, and impede information exchange. For example, software routines for simulating mixed mineral assemblages that cannot easily be exported for representation in other programs. The development of accessible searchable reference libraries, in standardized formats, would be a valuable development, especially if these could reside in a single integrated website. Ideally, those who use VIRS methods should be able to post spectra for minerals or rocks, with descriptive information, and access similar results acquired elsewhere. The development of spectral databases for specific regions or mineral associations (e.g., VMS deposits in eastern Canada, or Cordilleran Mo-W deposits, or altered ultramafic rocks) would also be a useful step. The currently available reference spectra mostly represent individual minerals, which is understandable, as these are the ultimate building blocks for the measured data, but libraries ultimately need to be extended to rocks, as these are what we have to deal with in most cases. There is value in having empirical data from variably altered rocks of various protolith types, even if the complete mineralogical context of results cannot always be immediately deciphered.

The interpretation of spectral data that reflect mixed mineral assemblages remains one of the biggest challenges in using VIRS data in fine-grained or severely altered rocks, and it is the cause of most ambiguity in results. The integration of VIRS results with other observational and analytical data will, in many cases, remove or minimize such ambiguity, but the ultimate solution lies in reducing the size of the area that is actually analyzed. In our own use of the Terraspec instrument over 2 years, we have often wished that the aperture of the light probe could be reduced by a factor of 4, so that individual mineral grains could be targeted more effectively. It is possible to mask a sample using aluminum foil with a small hole, but this is time-consuming and tedious. Similarly, powdered samples can also be analyzed, using a small petri dish with a white background, but the same drawback applies. We have recently suggested to ASD that perhaps an attachment could be developed to fit over the light probe to focus analysis, or that illumination could be delivered via a separate fibreoptic cable as a smaller bright spot, but these all present technological challenges. The greatest obstacle is that reducing the incident energy inevitably reduces the amplitude of the reflected signal, which impacts accuracy and precision of spectra. This might not be a serious problem for strong absorption features, but some more subtle responses could be lost.

Irrespective of such developments, there is a need to further refine the treatment and interpretation of mixed mineral assemblages. There are possible empirical approaches, in which mixtures of key minerals are prepared and then analyzed to provide reference spectra for known proportions. It is rumoured that studies of this type have been completed by mining companies to assist in specific exploration problems, but (if so) they have certainly not been published. However, this is not the only approach; in this century, when the speed and accuracy of computers seems to increase exponentially, there must surely be multivariate analysis or inverse-modelling techniques that can take interpretation beyond the relatively crude two-component simulations offered by existing software programs.

Progress toward these objectives and resolution of these problems require active collaboration between public organizations and the private companies that use VIRS data, and the manufacturers of such instruments, coupled with greater involvement by academic researchers. Government geoscience agencies have a strong emphasis toward applied research, strong links with both the corporate and academic sectors, and a fundamental mandate to provide public geoscience information. As such, organizations such as GSNL are ideally poised to lead such an effort and, given resources to work with, we hope to contribute to such an effort.

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