Mapping Feldspars from Above

a Thermal Infrared and Partial Least Squares-based Approach

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—
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MAPPING FELDSPARS FROM ABOVE
—
A THERMAL INFRARED AND PARTIAL LEAST SQUARES-BASED APPROACH

D I S S E R T A T I O N

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on account of the decision of the graduation committee,
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Summary

This thesis outlines an approach to quantitatively map feldspar mineral abundance as well as plagioclase composition from remotely sensed data. Thermal IR spectroscopy is combined with a statistical technique, Partial Least Squares Regression, to produce unbiased, quantitative results.

The abundance and composition of feldspars are important measures in classifying, for example, igneous rocks or metasomatic conditions during rock alteration events. Traditional laboratory techniques used to determine feldspars are time consuming, often costly and only applicable to a finite number of point observations on samples collected in the field. Thermal IR spectroscopy is able to detect spectral features related to fundamental vibrational frequencies in the Si-O framework of silicate minerals. The use of thermal IR spectroscopy from an airborne imaging platform has the ability to overcome the limitation of finite field sampling points. It provides a synoptic view of an area and allows for mapping spatial distribution patterns of feldspars and other rock-forming minerals. Since rocks consist of mineral mixtures of several silicate minerals, their thermal IR spectra contain overlapping features of all minerals in the mixtures. This can make mineral identification difficult and quantification impossible without a statistical approach. In this thesis, partial least squares regression is used for that purpose. The advantage of this method is that it does not require the presence of a large spectral database of pure endmember spectra, which is challenging to acquire.

This thesis presents results from laboratory as well as airborne spectroscopic analysis. In the laboratory domain, mineral modes from thin section study were used to build a quantitative partial least squares model between thermal IR spectra and alkali feldspar, plagioclase and quartz modes (in areal %), and composition of plagioclase (in mol% An). Results based on the laboratory spectra show that partial least squares-modeled alkali feldspar modes were within ±5.1% and plagioclase within ±8.5% estimated absolute error of those determined by thin section. Plagioclase compositions showed variations of ±7.8 mol% An compared to thin section results. These error margins are slightly smaller or similar to those reported in literature for spectral mixture analysis, but without having to supply a spectral endmember database.

In the airborne domain, hyperspectral thermal IR images of the SE-
Summary

BASS sensor were acquired over a test area in the Yerington batholith, Nevada. Preliminary tests with simulated SEBASS data indicated that the sensor’s spectral resolution and noise levels were sufficient to map feldspar abundances and plagioclase compositions to within 0.4% absolute of the predictions based on the original laboratory spectra. Spectral distortions, such as spectral tilt and reduced spectral contrast, proved to have detrimental influence on the prediction results and required correction. A new pre-processing chain for SEBASS data was developed, including the newly proposed mean and standard deviation normalization to correct tilt and restore spectral contrast in the airborne data. Predictive partial least squares regression models were applied to the airborne data resulting in the first ever quantitative airborne maps of plagioclase composition as well as alkali feldspar, plagioclase and quartz abundances. The resulting maps showed coherent patterns across multiple flightlines. The major patterns coincide with lithologies and alteration zones of the test area from literature. In an absolute sense, the typical values (5, 50 and 95 percentile) in the airborne data compare well with those known from field samples.

The added value of this research for the airborne domain clearly lies in the quantitative, but unbiased, approach that was followed. An additional, but not less important, benefit of this research is the new developed methodology to correct airborne spectra in such a way that they are comparable to laboratory spectra. This has as main advantage that now quantitative predictive models based on laboratory spectra can be directly applied to airborne hyperspectral imagery. Overall, this thesis has provided the remote sensing community with significant advances in the processing of airborne thermal imagery but also with the first ever airborne-based quantitative plagioclase composition map.
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<tr>
<td>AERO</td>
<td>The Aerospace Corporation</td>
</tr>
<tr>
<td>ASTER</td>
<td>advanced space thermal emission and reflection radiometer</td>
</tr>
<tr>
<td>DEM</td>
<td>digital elevation model</td>
</tr>
<tr>
<td>DHR</td>
<td>directional-hemispherical reflection</td>
</tr>
<tr>
<td>EMPA</td>
<td>electron microprobe analysis</td>
</tr>
<tr>
<td>ENorm</td>
<td>emissivity normalization (a type of T(\epsilon))</td>
</tr>
<tr>
<td>FOV</td>
<td>field of view</td>
</tr>
<tr>
<td>FPA</td>
<td>focal plane array</td>
</tr>
<tr>
<td>FWHM</td>
<td>full-width at half maximum</td>
</tr>
<tr>
<td>GPS</td>
<td>global positioning system</td>
</tr>
<tr>
<td>HyTES</td>
<td>hyperspectral thermal emission spectrometer</td>
</tr>
<tr>
<td>IFOV</td>
<td>instantaneous field of view</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>ISAC</td>
<td>in-scene atmospheric compensation</td>
</tr>
<tr>
<td>LWIR</td>
<td>long-wave infrared (8–14 (\mu)m)</td>
</tr>
<tr>
<td>MAGI</td>
<td>mineral and gas identifier</td>
</tr>
<tr>
<td>MASD</td>
<td>mean and standard deviation (normalization)</td>
</tr>
<tr>
<td>MASTER</td>
<td>modis and aster airb. simulator</td>
</tr>
<tr>
<td>MNF</td>
<td>minimum noise fraction</td>
</tr>
<tr>
<td>MODIS</td>
<td>moderate-resolution imaging spectroradiometer</td>
</tr>
<tr>
<td>MWIR</td>
<td>mid-wave infrared (3–5 (\mu)m)</td>
</tr>
<tr>
<td>NE(\Delta)T</td>
<td>noise equivalent difference in temperature</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared (0.7–1.0 (\mu)m)</td>
</tr>
<tr>
<td>PCA</td>
<td>principal component analysis</td>
</tr>
<tr>
<td>PLSR</td>
<td>partial least squares regression</td>
</tr>
<tr>
<td>RMSE(/P)</td>
<td>root mean squared error (/prediction)</td>
</tr>
</tbody>
</table>
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<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>SEBASS</td>
<td>spatially-enhanced broadband array spectrograph system</td>
</tr>
<tr>
<td>SMA</td>
<td>spectral mixture analysis (=unmixing)</td>
</tr>
<tr>
<td>SNR</td>
<td>signal-to-noise-ratio</td>
</tr>
<tr>
<td>SWIR</td>
<td>short-wave infrared (1.0–2.5 ( \mu m ))</td>
</tr>
<tr>
<td>TASI</td>
<td>thermal airborne spectrographic imager</td>
</tr>
<tr>
<td>TcS</td>
<td>temperature-emissivity-separation</td>
</tr>
<tr>
<td>TES</td>
<td>thermal emission spectrometer</td>
</tr>
<tr>
<td>THEMIS</td>
<td>thermal emission imaging system</td>
</tr>
<tr>
<td>TIMS</td>
<td>thermal infrared multispectral scanner</td>
</tr>
<tr>
<td>TIR</td>
<td>thermal infrared (2.5–14 ( \mu m ))</td>
</tr>
<tr>
<td>VIS</td>
<td>visible range (0.4–0.7 ( \mu m ))</td>
</tr>
<tr>
<td>WN</td>
<td>wavenumbers [cm(^{-1})]</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray Fluorescence</td>
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## Mineral abbreviations

<table>
<thead>
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<th>Ab</th>
<th>albite</th>
<th>Hbl</th>
<th>hornblende</th>
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<tbody>
<tr>
<td>Act</td>
<td>actinolite</td>
<td>Hm</td>
<td>hematite</td>
</tr>
<tr>
<td>Afsp</td>
<td>alkali feldspar</td>
<td>Ilm</td>
<td>ilmenite</td>
</tr>
<tr>
<td>An</td>
<td>anorthite</td>
<td>Jar</td>
<td>jarosite</td>
</tr>
<tr>
<td>Ana</td>
<td>analcime</td>
<td>Mgt</td>
<td>magnetite</td>
</tr>
<tr>
<td>And</td>
<td>andesine</td>
<td>Mo</td>
<td>molybdenite</td>
</tr>
<tr>
<td>An(_{xx})</td>
<td>Plg with xxmol% An</td>
<td>Ms</td>
<td>muscovite</td>
</tr>
<tr>
<td>Ap</td>
<td>apatite</td>
<td>Olg</td>
<td>oligoclase</td>
</tr>
<tr>
<td>Aug</td>
<td>augite</td>
<td>Or</td>
<td>orthoclase</td>
</tr>
<tr>
<td>Bn</td>
<td>bornite</td>
<td>Plg</td>
<td>plagioclase</td>
</tr>
<tr>
<td>Bt</td>
<td>biotite</td>
<td>Plgcomp</td>
<td>Plg composition</td>
</tr>
<tr>
<td>Cc</td>
<td>calcite</td>
<td>Py</td>
<td>pyrite</td>
</tr>
<tr>
<td>Chl</td>
<td>chlorite</td>
<td>Qtz</td>
<td>quartz</td>
</tr>
<tr>
<td>Chr</td>
<td>chrysocolla</td>
<td>Rt</td>
<td>rutil</td>
</tr>
<tr>
<td>Cp</td>
<td>chalcopyrite</td>
<td>Ser</td>
<td>sericite</td>
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<tr>
<td>Dio</td>
<td>diopside</td>
<td>Sph</td>
<td>sphene</td>
</tr>
<tr>
<td>Ep</td>
<td>epidotide</td>
<td>Tm</td>
<td>tourmaline</td>
</tr>
<tr>
<td>Gnt</td>
<td>garnet</td>
<td>Verm</td>
<td>vermiculite</td>
</tr>
<tr>
<td>Goe</td>
<td>goethite</td>
<td></td>
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Introduction

1.1 Problem statement

Minerals of the feldspar group are the most common on earth. Their abundance and their variations in composition and mineral structure make them the most important tool in the classification of igneous rocks (Deer et al., 1992). They do, however, also occur in most metamorphic rocks and to a certain degree in detrital sedimentary rocks (e.g., arkose and conglomerates; Klein & Hurlbut, 1999). In rocks where alkali feldspar and plagioclase form a co-existing mineral assemblage, the distribution of sodium over the two phases can be used as a geothermometer to estimate formation temperatures (Deer et al., 2001). If feldspar compositions can be mapped, this geothermometer can help reconstruct the thermal history of an area. In addition, feldspars are used for mapping the surface compositions of other planetary objects as well, such as Moon, Mars and asteroids (Milam et al., 2007; Christensen et al., 2004; Nash & Salisbury, 1991).

Furthermore, feldspars are economically important in two ways: either as industrial minerals or as indicators for metasomatic conditions that can be used as a vector-to-ore for mineral deposits. Microcline, as an example, is a principal constituent of pegmatite from which it is extracted as an industrial mineral and used extensively in the glass, ceramic and porcelain industry (Klein & Hurlbut, 1999). The variation in albite content is an important indicator for exploration purposes in several deposit models such as porphyry copper systems (Dilles & Einaudi, 1992), iron oxides copper-gold as well as in archaean gold systems (Marschik & Fontbote, 2001; Robert, 2001) while albitization of potash feldspar and plagioclase has also been linked to uranium mineralization (Porto da Silveira et al., 1991). Some less common feldspar minerals have been used successfully for exploration purposes as well. Buddingtonite (an ammonia feldspar) has been associated with base-metal and precious metal mineral deposits in hot-spring environments (Krohn, 1989) while adularia (a potassium feldspar) typically occurs in low temperature, 'alpine' type veins that can contain low-sulfidation, epithermal gold deposits (Queralt et al., 1996).
1. Introduction

![Ternary feldspar system](image)

**Figure 1.1** Ternary feldspar system with orthoclase ($\text{KAlSi}_3\text{O}_8$), albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) as endmembers. Solid solution between orthoclase and albite are the so-called alkali feldspars and between albite and anorthite plagioclases. Mixtures with compositions between orthoclase and anorthite are not stable below the solidus and will cause co-existing phases of one alkali feldspar and one plagioclase instead. Modified after Deer et al. (1992)

1.1.1 Feldspar classification

Feldspars are part of the tectosilicates group where $\text{SiO}_4$ and $\text{AlO}_4$ tetrahedra form an infinite 3-dimensional framework (Klein & Hurlbut, 1999). The resulting interstices in the structure are filled with univalent or bivalent cations, such as $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$ (but others such as $\text{Ba}^{2+}$, $\text{NH}_4^+$ are also possible). If a univalent cation is built into the structure, a single Si atom is replaced by Al per formula unit. For a bivalent cation, two Si are replaced by Al in order to maintain charge balance. To classify feldspars properly one needs to know a) their mineral chemistry as well as b) their structural state (Klein & Hurlbut, 1999).

Most feldspars can be chemically classified as mixtures of a ternary system with orthoclase ($\text{KAlSi}_3\text{O}_8$), albite ($\text{NaAlSi}_3\text{O}_8$) and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) as endmembers (Figure 1.1). Solid solution mixtures are mainly possible between orthoclase and albite endmembers (the so-called alkali feldspars) as well as between albite and anorthite (the so-called plagioclases). Mixtures with compositions between orthoclase and anorthite are not stable below the solidus and will cause coexisting phases of one alkali feldspar and one plagioclase instead (Deer et al., 2001).

Apart from their chemistry, feldspars can also be classified into different polymorphs by their structural state, which refers to the distribution of Al and Si over the tetrahedron sites within the crystal structure (Klein & Hurlbut, 1999). High structural state is typical for feldspars formed at high temperatures. They were cooled down rapidly and retained the monoclinic structural state that is more stable at high temperatures. This causes the Al and Si atoms to be distributed randomly over all tetrahedral sites in the crystal lattice. A typical example of a disordered,
1.1. Problem statement

High-feldspar is volcanic sanidine. Low feldspars, on the other hand, crystallized at low temperatures or cooled down slowly enough from higher temperatures to adapt to the triclinic structural state that is more stable at these lower temperatures. In the low state, Si and Al atoms have arranged themselves in a non-random fashion. They show preferences to certain tetrahedral positions in the crystal structure; they are said to be ordered. A typical maximum order example is a metamorphic microcline.

1.1.2 Thermal infrared spectroscopy

To use feldspars for classifying rock compositions or metasomatic conditions during rock alteration events, we need analytical methods to identify and classify feldspars. Traditional laboratory methods, such as optical microscopy, X-ray diffraction (XRD), electron microprobe analysis (EMPA) or transmission infrared spectroscopy, have successfully been developed and used for these purposes since the middle of the last century. These methods are, however, time consuming, often costly and only applicable to a finite number of point observations on samples collected in the field. We cannot use these techniques for mapping variations of feldspar composition over a large area nor to highlight spatially continuous patterns.

The use of TIR imaging spectroscopy has the ability to overcome these shortcomings. It provides a synoptic view of an area and allows for mapping spatial distribution patterns of the rock-forming mineralogy. In literature, only a few studies have attempted to map feldspars from airborne data. Ramsey et al. (1999) used spectral mixture analysis (i.e., unmixing) on TIMS data to map compositions of sand dunes dominated by quartz, orthoclase and oligoclase. Vaughan et al. (2003) attempted to differentiate microcline from albite in airborne SEBASS data but had difficulties when quartz was present in the mixtures. Vaughan et al. (2005) did some forward modeling of spectral mineral mixtures (including feldspars) until the mixed spectrum matched airborne SEBASS spectra but results with feldspars showed discrepancies with XRD data. Riley et al. (2007) classified SEBASS imagery in four plagioclase classes and orthoclase (alkali feldspar) using a feature fitting algorithm. The authors did not attempt a quantitative approach to map mineral abundances. Cudahy et al. (2001b) analyzed SEBASS data and found qualitative indications of three different plagioclase compositions. These authors further mapped relative differences in plagioclase composition based on a band ratio of two individual wavelength bands in the airborne data.

To date, no attempts have been made to quantitatively map feldspar abundances and plagioclase compositions from airborne remote sensing data. The main reason appears to be the very limited availability of high spectral resolution, high signal-to-noise-ratio data, which in the past were limited to images from the SEBASS sensor. With several new airborne instruments under development or recently deployed (Table 2.2), it is an opportune time to assess how far remote sensing imagery can be useful in characterizing feldspar chemistry and mineralogy.
1. Introduction

1.2 Research objectives

The general objective of the study presented in this thesis is to determine whether airborne hyperspectral thermal infrared imagery can be used to identify major feldspar mineral groups and quantitatively map their abundances as well as the chemical compositions of the plagioclase group. To achieve this goal, the following specific objectives were defined:

- to develop a thermal infrared laboratory measurement procedure that results in repeatable and accurate spectral measurements of the sample material
- to develop a quantitative link between TIR laboratory spectra and mineral information from traditional analytic methods
- to apply this quantitative link to airborne hyperspectral TIR data and
- to evaluate the resulting mineral maps for accuracy and added value as compared to ground-based methods

1.3 Test area

The Ann-Mason area of the Yerington batholith in Nevada was chosen as a test area for the algorithms (Figure 1.2). The area contains a porphyry copper system in its northern part and skarn alteration close to its contact with sedimentary units in the south. Both alteration systems are characterized by mineral reactions that change feldspar abundance as well as plagioclase composition in the rocks in 3-dimensional patterns. Additionally, post-alteration faulting with block rotation exposes a 6 km vertical profile (including alteration zones of different paleo-depth) at today’s surface (Dilles & Einaudi, 1992), making the area highly suitable for testing feldspar abundance and composition mapping. Detailed information on original lithologies and alteration patterns in the Ann-Mason area are available in existing literature (e.g., Dilles et al., 2000b; Einaudi, 2000; Dilles & Einaudi, 1992; Dilles, 1987, 1984; Proffett & Dilles, 1984; Proffett, 1977) which allow comparison of ground-based techniques to remote sensing results. Low vegetation cover and good outcrop situation in the Ann-Mason block further facilitate the use of remote sensing data.

1.3.1 Geologic setting

In this section the general geologic setting and the lithologic units of the test area are described. The lithologic descriptions are summarized after Dilles et al. (2000b), Dilles & Einaudi (1992) and Proffett & Dilles (1984). A generalized geologic map of the area is shown in Figure 1.3.
Figure 1.2 Overview map of Ann-Mason test area and its spatial relation to other fault blocks with porphyry systems (Blue Hill and MacArthur) in the Yerington batholith. ASTER near infrared false color composite shows irrigated fields in red, tailings and evaporites in cyan to white and water-filled mine pit in black.
1. Introduction

Figure 1.3 Generalized geologic map of test area, simplified after Proffett & Dilles (1984). Gray box indicates extent of the area covered by airborne SEBASS mosaic over Ann-Mason (Flightlines 22-29.)
1.3. Test area

1.3.1.1 Pre-batholith

The general lithologies that existed in the Yerington area before the intrusions of the Yerington batholith, consist of Triassic volcanics, unconformably overlain by a marine sedimentary-volcaniclastic sequence of variable compositions.

McConnell Canyon. The middle to late Triassic McConnell Canyon volcanics are the oldest outcropping rocks in the area. The 1300-m-thick sequence consists of andesitic flows at the bottom and more felsic rocks (containing small quartz and feldspar phenocrysts) at the top.

Clastic and evaporitic sediments. This unit combines various late Triassic to middle Jurassic sedimentary rocks of a volcanic-arc origin. It contains carbonates, evaporitic, volcanoclastic and argillaceous sedimentary rocks. The carbonates of this sequence host the skarn deposits at the southern margin of the Ann-Mason area.

Quartzite. This well-sorted, eolian quartzite forms the top of the pre-alteration sequence. It consists of a medium-grained sandstone with minor feldspar. The base of the unit can be arkosic (i.e., less sorted and higher feldspar content). Since this unit has a high quartz (and partially feldspar) content, it should be clearly visible in remote sensing data. Hence, it is not merged with other pre-alteration sediments in the generalized geologic map, and kept as a separate lithologic unit.

1.3.1.2 Syn-batholith

In the middle Jurassic, a major magmatic arc developed as a consequence to subduction tectonics to the west. It produced volcanic eruptions followed by emplacement of three major phases of plutonic rocks and porphyry dike swarms. Of the three major intrusions, each was progressively smaller in volume and more silicic in composition.

Artesia Lake. The Artesia Lake volcanics are the first sign of the middle Jurassic volcanic activity. While genetically related to the later intrusions, they pre-date the main intrusive phase. The Artesia Lake volcanics consists of 1500 m of intermediate to silicic volcanic rocks. In the test area, this unit is restricted to a small crop near the extreme SW corner.

McLeod Hill. The McLeod Hill quartz monzodiorite forms the first major intrusive body in the area. The unit consists of quartz monzodiorite with hornblende and biotite, and was emplaced as a series of dike-like intrusions with steeply dipping internal contacts. The unit contains about 15% quartz and 10% alkali feldspar (Dilles, 2012), much less than the following two phases.

Bear. The Bear quartz monzonite is the second intrusive phase in the area. It intrudes mainly the McLeod Hill phase but locally also directly the Artesia Lake volcanics. The Bear unit is strongly compositionally zoned with a graphic-textured, granitic border phase along the top and side of the intrusion, changing into the more typical, homogeneous hornblende quartz monzonite towards the center of the intrusion. In the Ann-Mason
area, the Bear phase is almost exclusively represented by the granitic
border phase with 20–25% quartz and 20–25% alkali feldspar (Dilles,
2012). The Bear and McLeod Hill units together comprise 95% of the
exposed volume of the batholith. They form the precursor pluton of the
porphyry system (Sillitoe, 2010), but neither of them is directly related
to the later copper mineralization (see Section 1.3.3).

Luhr Hill. The Luhr Hill granite represents the third major intrusive
phase in the Yerington batholith. It consists of deeply emplaced, por-
phyritic hornblende-biotite granite with alkali feldspar megacrysts (often
5-10 mm in length). It contains about 20–24% quartz and 25–30% alkali
feldspar (Dilles, 2012). The Luhr Hill granite has several cupolas, one
of which is exposed in the Ann-Mason area (see map and cross section
in Figures 1.3 and 1.4). The cupola focused gases and fluids in its roof
section and caused hydraulic fracturing of the host rocks. The fracturing
promoted the emplacement of porphyry dikes, for which the cupula
acted as parental magma chamber.

Porphyries. The quartz porphyry dikes are linked to the Luhr Hill
granite intrusion. The dikes consist to 50% of an aplitic groundmass
of quartz, alkali feldspar and minor plagioclase and biotite. The other
50% are made up of phenocrysts of the same minerals, plus hornblende,
sphene and magnetite. The dikes show coarsening downwards and
they start a few hundred to a maximum of a thousand meters below
the top of the granite intrusion. Most dikes exit the Luhr Hill granite
through the top of cupolas and form dike swarms of parallel intrusions
that cut through the overlying units (Figure 1.3 and 1.4). At least three
generations of porphyry dikes have been identified in the Ann-Mason
area and at least five in the Yerington mine (a few kilometers east of the
Ann-Mason area but part of a different dike swarm). All porphyry copper
deposits in the Yerington batholith are associated with the porphyry dike
swarms (see also Section 1.3.3).

1.3.1.3 Post-batholith

Following the intrusion of the Yerington batholith, a series of subaerial
volcanic rocks are deposited that are not preserved in the Ann-Mason
area. Neither is a large batholith that occurs south of Yerington. Follow-
ing a long period of non-deposition or erosion, Tertiary ignimbrites and
lavas are the first rocks that are preserved in the test area.

Singatse volcanics. Following the batholitic intrusions with an erosional
contact are the Singatse Tertiary volcanics (Oligocene to early Miocene).
They consist of an up to 2-km-thick sequence of intermediate to felsic vol-
canic rocks. Several of the units show ignimbritic textures but tuffs and
lavas also occur. The erosional contact between the Jurassic batholith
and Tertiary Singatse volcanic rocks can be seen in the western edge of
the test area. The northern edge a low-angle normal fault separates Jur-
asic from Tertiary rocks. Here the tertiary volcanics obscure the central
part of the dike swarm and the Ann-Mason deposit (see Section 1.3.3).
Figure 1.4 Conceptual cross section through Ann-Mason system in original orientation. Alteration zones are shown in same color scheme as in Figure 1.5, but sub-classes are generalized. Abbreviations: (weak) potassic (wkK and K), sodic-calcic (Na-Ca), sodic (Na), sericite (ser), porphyry dikes (porph). Red and blue arrows indicate fluid paths of magmatic fluids and sedimentary brines, respectively. Figure modified after Dilles et al. (2000a).
1. Introduction

Figure 1.5: Map of alteration zones in test area after Dilles & Elhaad (1992). Geologic map is used as backdrop for orientation.
1.3. Test area

Extensional tectonics. During the middle Miocene age, rapid extensional tectonics created several sets of closely-spaced, east-dipping normal faults, where the younger fault sets cut off the older sets. The normal faulting contained a rotational component that pivoted the entire pre-Miocene batholithic rock sequences (including alteration zones and porphyry copper system) almost 90 degrees to the west. This created the current layout of the Ann-Mason area where the subvolcanic top of the system is lying to the west of the area and the Luhr Hill granite cupola at 7 km paleo-depth is situated to the east of the area. Figure 1.4 shows the original orientation of the porphyry copper system in a N-S cross section and with indications of paleo-depth. For the remainder of the document, the terms "deeper" or "below" will refer to the system in its original orientation, while cardinal directions will refer to relations in the current, rotated situation.

1.3.2 Hydrothermal alteration

Hydrothermal alteration in the Ann-Mason area is strongly linked to the intrusion of the third intrusive phase (Luhr Hill granite and porphyry dikes) while McLeod and Bear intrusions (phases 1 and 2) played a very subordinate role. Resulting mineral patterns of the third phase show indications of two different hydrothermal fluid sources: magmatic fluids being released by the crystallization of water-rich magma in the intrusive bodies and sedimentary brines that were released from the Triassic to Jurassic marine sediment stacks and percolated south to north through the system (Figure 1.4). Furthermore, the hydrothermal alteration activities of the Luhr Hill phase can be divided into pre-, main stage and late stage alteration as compared to the porphyry dike emplacement. Below, a general overview of the alteration phases and zones in the test area is given. This information is summarized after Dilles et al. (2000b) and Dilles & Einaudi (1992). A generalized alteration map of the area is shown in Figure 1.5, an alteration cross section in Figure 1.4 and the detailed mineral assemblages are shown in Table 1.1.

1.3.2.1 Pre-main stage

Endoskarn. The endoskarn is characterized by hydrothermal garnet (grossular to andradite), calcic plagioclase and/or clinopyroxene (diopside). Garnet-bearing endoskarn (assemblage ES-1) occurs in small patches in the McLeod Hill qtz monzodiorite within 200 m of the contact with carbonate rocks of the Triassic-Jurassic sediments. ES-1 contains mainly garnet and plagioclase of An$_{50-68}$. Diopside endoskarn (ES-2) is more widespread and appears up to 1000 m from the contact at 3 to >6 km paleo-depth. Diopside endoskarn forms bleached rocks with mafic minerals being altered to diopside and sphene, and feldspars being altered to intermediate plagioclase of An$_{21-36}$. 

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1. Introduction

1.3.2.2 Main stage

The main stage alteration is dominated by a small, central area of potassic alteration that follows the porphyry dike swarm, and more extensive area of sodic-clastic altered rocks surrounding it. Propylitic alteration is weaker but influences the upper 60% of the original system down to a paleo-depth of 4 km.

**Potassic.** Potassic alteration in Ann-Mason is characterized by the replacement of hornblende with hydrothermal ("shreddy") biotite. Small amounts of hydrothermal K-feldspar were reported in drill cores but have not yet been observed on the surface. The potassic alteration is spatially associated with the axis of the porphyry dike swarm and the apex of the Luhr Hill granite cupola. Weak potassic alteration occurs in a larger part of the Luhr Hill cupola. Beyond these two areas, potassic alteration occurs very sparsely. Most of the potassically altered areas in Ann-Mason are covered by Tertiary Singatse volcanics and are only known from drill cores. Hence, they are not visible in Figure 1.5. Figure 1.4 shows the position of potassic alteration in the conceptual cross section through the system.

**Sodic-calcic.** The main stage sodic-calcic altered rocks show a bleached appearance. Several sub-zones were identified based on their mineral assemblages, of which S-2 is by far the most common and best developed. Alkali feldspar is typically replaced with intermediate plagioclase (An$_{20-26}$) or epidote, and quartz. Mafic minerals are replaced with actinolite. Geographically, sodic-calcic alteration occurs above the apex of the Luhr Hill cupola, surrounding a central zone of potassic alteration. The sodic-calcic zone furthermore extends laterally along the deep margins of the Luhr Hill cupola and close to the dike swarm about 2 km above the roof of the cupola.

**Propylitic.** Propylitic alteration is characterized by partial replacement of hornblende with actinolite, biotite with chlorite and plagioclase with albite, epidote and sericite. Alkali feldspar is stable in the propylitic alteration zone. The propylitic assemblage (PA) is not shown in Figures 1.5 and 1.4 for clarity reasons, but propylitic alteration is widespread through the area affecting all lithologies from the tertiary erosion surface to a paleo-depth of 4 km.

1.3.2.3 Late stage

Late stage hydrothermal alteration consists of an earlier (and related) chloritic and sodic alteration and a later sericite alteration with tourmaline breccias. Together, the late stage alteration zones form a funnel-shaped volume that expands upwards from the ore zone (potassic alteration).

**Sodic.** The large extent of sodic alteration in the Ann-Mason area is rather atypical for porphyry copper systems. The sodic zone occupies the central part of the funnel-shaped, late stage alteration volume and is characterized by bleached rocks void of mafic minerals. The most common assemblage is the albite-sericite assemblage (A-2) which is per-
Table 1.1  Hydrothermal alteration assemblages in Ann-Mason area (after Dilles & Einaudi (1992)).

<table>
<thead>
<tr>
<th>Alteration type</th>
<th>Symbol</th>
<th>New (added) and recrystallized minerals&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Relict minerals&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-main stage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endoskarn</td>
<td>ES-1</td>
<td>Grandite and labradorite (An&lt;sub&gt;50-68&lt;/sub&gt;) ± Dio ± Rt</td>
<td>Olg/And + Sph + Hbl + Afsp</td>
</tr>
<tr>
<td></td>
<td>ES-2</td>
<td>Olg/And(An&lt;sub&gt;2-36&lt;/sub&gt;)&lt;sup&gt;c&lt;/sup&gt; ± Dio ± Hbl + Sph ± Qtz + ±Ep</td>
<td>Olg/And + Sph + Hbl + Afsp</td>
</tr>
<tr>
<td>Main stage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodic-calcic</td>
<td>S-1</td>
<td>Olg/And&lt;sup&gt;d&lt;/sup&gt; + Sph + Qtz ± Rt</td>
<td>Olg/And + Sph</td>
</tr>
<tr>
<td></td>
<td>S-2</td>
<td>Olg/(Ab)&lt;sup&gt;e&lt;/sup&gt; ± Act + Qtz + Sph + Ep ± Py</td>
<td>Olg + Sph</td>
</tr>
<tr>
<td></td>
<td>S-5</td>
<td>Olg/(Ab)&lt;sup&gt;e&lt;/sup&gt; ± Qtz + Sph ± Ep ± Act(±Chl)</td>
<td>Olg/And + Hbl + Sph ± Afsp</td>
</tr>
<tr>
<td></td>
<td>S-6</td>
<td>Olg/Ab&lt;sup&gt;d&lt;/sup&gt; ± Qtz + Sph + Ep + Act</td>
<td>Olg + Sph</td>
</tr>
<tr>
<td></td>
<td>S-7</td>
<td>Olg/Ab&lt;sup&gt;d&lt;/sup&gt; ± Qtz + Sph + Ep + Act</td>
<td>Olg + Afsp + Sph</td>
</tr>
<tr>
<td>Weak sodic-calcic</td>
<td>SW</td>
<td>Ep + Sph ±(Olg)/Ab ± Qtz ± Act ± Bt ± Ser ± Py (±Chl ± Rt)</td>
<td>Olg + Afsp+ Hbl + Sph (±Mgt)</td>
</tr>
<tr>
<td>Potassic</td>
<td>K</td>
<td>Afsp + Ab&lt;sup&gt;d&lt;/sup&gt; ± Bt + Qtz + Cp ± Bn ± Mo + Rt + Chl&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Olg + Afsp + Bt</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>Bt ± Ep ± Qtz + Ab&lt;sup&gt;d&lt;/sup&gt; ± CP ± Bn or Py ± Rt ± Ser&lt;sup&gt;c&lt;/sup&gt; ± Cc ± Chl&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Bt ± Olg ± Afsp + Mgt ± Sph (±Ilm)</td>
</tr>
<tr>
<td></td>
<td>WB</td>
<td>Bt ± Ep ± Cp ± Qtz</td>
<td>Olg + Afsp+ Hbl + Mgt + Sph</td>
</tr>
<tr>
<td>Propylitic</td>
<td>PA</td>
<td>Act ± Bt + Chl + Ab&lt;sup&gt;d&lt;/sup&gt; ± Ep + Hm + Ser ± Cc + Rt ± Py ± Tm (± Cp)</td>
<td>Olg/And + Afsp + Hbl + Bt + Mgt + Sph</td>
</tr>
<tr>
<td>Late stage</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloritic</td>
<td>C</td>
<td>Chl ± Rt ± Qtz</td>
<td>Ab ± Afsp ± 2nd Bt ± Bt + Mgt ± Ep + Rt (± Cp)</td>
</tr>
<tr>
<td></td>
<td>CB</td>
<td>Chl ± Hm ± Py ± Ser ± Cc ± Ab&lt;sup&gt;d&lt;/sup&gt; ± Ep (±Cp ± Verm)</td>
<td>Ab ± Afsp ± 2nd Bt ± Bt + Mgt ± Ep + Rt (± Cp)</td>
</tr>
<tr>
<td></td>
<td>PC</td>
<td>Chl ± Ab&lt;sup&gt;d&lt;/sup&gt; ± Hm ± Rt ± Ep ± Py ± Ser ± Cc (±Cp ± Verm)</td>
<td>Afsp + Mgt ± Olg</td>
</tr>
<tr>
<td>Sodic (albitic)</td>
<td>A-1</td>
<td>Olg/Ab&lt;sup&gt;e&lt;/sup&gt; ± Chl ± Verm ± Rt ± Sph ± Py ± Qtz</td>
<td>Olg ± 2nd Bt ± Bt + Rt ± Cp (± Mo)</td>
</tr>
<tr>
<td></td>
<td>A-2</td>
<td>Ab ± Chl ± Ser + Rt + Py (±Tm ± Verm)</td>
<td>(± CP)</td>
</tr>
<tr>
<td></td>
<td>Atm</td>
<td>Ab + Tm ± Rt + Py ± Chl ± Ser</td>
<td>± Afsp (±CP)</td>
</tr>
<tr>
<td>Sericitic</td>
<td>SQ</td>
<td>Ser + Qtz + Py + Rt (±Cp ± Tm)</td>
<td>(± CP)</td>
</tr>
<tr>
<td></td>
<td>TBx</td>
<td>Tm + Qtz + Py + Rt ± Ser (±Cp)</td>
<td>(± CP)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Minerals in parentheses occur in trace amounts; others listed in order of abundance
<sup>b</sup> Quartz, apatite and zircon are present as relict minerals in all assemblages
<sup>c</sup> Specifies compositional range present in assemblage; a sample may contain a large range of An content
<sup>d</sup> Albite forms pseudomorphs after primary igneous plagioclase
<sup>e</sup> Mineral is commonly present, but textures suggest that it partially or entirely postdates formation of assemblage and is therefore largely retrograde
1. Introduction

Vasively developed inside the porphyry dikes. Alkali feldspar is replaced by albite \( (An_{1-2}) \) and quartz, plagioclase by albite and sercite, and mafic minerals are altered to chlorite and sercite. The sodic alteration extends into and overprints the top part of the potassic alteration.

**Chloritic.** The chlorite alteration can be temporally and genetically tied to the sodic alteration, which it flanks like a narrow sheath. Opposite to the sodic alteration, chloritic alteration is mainly developed in the McLeod Hill and Bear units, and not in the porphyry dikes. In the deeper parts (assemblage CB), hydrothermal biotite (from potassic alteration) is chloritized and plagioclase is partially altered to albite and sercite. Alkali feldspars are stable. In shallower areas without preceding potassic alteration (assemblage PC), the mineral reactions are similar but instead of hydrothermal biotite, magmatic biotite and hornblende are replaced by chlorite. Chloritic alteration is not shown in Figure 1.4 for clarity reasons.

**Sericitic.** Sericite alteration and related tourmaline breccias are the most recent alteration phases and occur in the upper parts of the Ann-Mason system. At the tertiary erosion surface, they cover 50% of the area. Sericite alteration occurs along steeply dipping (in original orientation) fracture zones, mainly within the sodic alteration but also several kilometers away from the central axis of the dike swarm. In sericitic alteration, igneous rocks are replaced by sercite and quartz. In one type of sericite alteration, the original rock texture and quartz content of the rocks are preserved, while all other minerals are mainly replaced by sercite. The second type of sericite alteration occurs mainly in central parts of fracture zones: original textures are obliterated, and the rocks are dominated by recrystallized quartz with only a minor sercite component. Tourmaline breccias are spatially related but cover less extensive areas than sercite alteration. The matrix consist of quartz, tourmaline and pyrite, and the clasts of sercite or sodic altered magmatic rocks.

### 1.3.3 Mineralization

This section on mineralization in the Ann-Mason area is based on Dilles & Einaudi (1992) and pers. comm with J. Dilles 2009.

The Ann-Mason deposit is a hypogene (i.e., original, non-weathering-related) sulfide body with at least 495 tons of ore, averaging 0.4 wt% Cu and >0.01 wt% Mo. Copper mineralization is directly linked to the third intrusive phase: the Luhr Hill granite cupola and its accompanying porphyry dikes. The Ann-Mason deposit developed in the dike swarm above the cupola at paleo-depths of 2.5 km and roughly coincides with the upper part of the potassic alteration zone (partly overprinted by late sodic alteration). Currently, both the deposit and most of the potassic zone are not cropping out at the surface since they are covered with Tertiary Singatse volcanics across a low-angle normal fault. Extensive exploratory drilling has shown that the ore body starts a few hundred meters below the surface and extends more than 2000 m in depth. The
1.4. Structure of the thesis

Sulfide minerals that constitute the ore body are mainly chalcopyrite (CuFeS$_2$), bornite (Cu$_5$FeS$_4$), pyrite (FeS$_2$) and some chalcosite (Cu$_2$S).

Apart from potassic alteration, other zones also show a relationship with ore grade: the western part of the Ann-Mason area shows $>5$ vol% of sulfides related to late stage sericite alteration. Unfortunately, copper-free pyrite is the dominating sulfide mineral, making this mineralization economically less interesting. Sodic, as well as sodic-calcic alteration typically removed ore grade, and those mineral zones are now showing low sulfide content and bleached appearances.

1.4 Structure of the thesis

This thesis consists of a total of seven chapters. Apart from the introduction and synthesis, the five remaining core-chapters have either been published in peer-reviewed journals or are in preparation.

Chapter 2 reviews previously published infrared studies on feldspar minerals. Successes as well as limitations of different approaches are highlighted and existing work scrutinized in terms of their applicability to remote sensing techniques. The chapter defines the present state-of-the-art in feldspar infrared work for remote sensing applications and guides the research directions of the following chapters.

Chapter 3 describes a new spectrometer setup and measurement procedure intended to spectrally characterize typical earth science samples. This instrument is then used to measure high quality TIR spectra in the laboratory on samples from a test area which are used as input to the following chapters.

Chapter 4 introduces a PLSR-based model to predict feldspar modes and plagioclase compositions from laboratory TIR spectra. The results from this chapter help to assess this statistical technique under laboratory conditions before applying it to airborne imagery in the next parts of this thesis.

Chapter 5 investigates whether hyperspectral, airborne TIR data from the SEBASS sensor is theoretically able to detect feldspar minerals and quantitatively predict modes and compositions in igneous rocks. For that purpose the laboratory spectra are down-sampled and noise is added to mimic typical airborne conditions and the distorted spectra are used in a PLSR predictive model.

Chapter 6 applies the PLSR models developed in earlier chapters to actual airborne SEBASS data over a test area. The resulting patterns are compared to existing lithologic and alteration maps of the test area.

Chapter 7 provides a summary of the results of the previous Chapters 2 to 6 and discusses the outcomes and their implications for the mapping of feldspars from airborne remote sensing data.
Thermal infrared spectroscopy of feldspars — a review\textsuperscript{1}

2.1 Introduction

Chapter 1 has shown that feldspars are scientifically and economically important and that their frequent occurrence makes them ideal for classifying, among others, igneous and hydrothermally altered rocks. It was also established that in order to use feldspars for rock classification analytical methods are needed to identify and classify feldspars.

In this chapter, traditional analytical methods are briefly treated. Consecutively, previously published infrared studies on feldspar minerals are examined. Successes as well as limitations of different approaches are highlighted and existing work are scrutinized in terms of their applicability to remote sensing techniques. In the end, the present state-of-the-art in feldspar infrared work for remote sensing applications are defined, existing gaps identified and research directions recommended.

2.2 Analytical methods

2.2.1 Traditional methods

Traditionally, feldspar composition and structure have been investigated using methods such as optical microscopy, electron microprobe analysis (EMPA), cathodoluminescence and X-ray diffraction (XRD) analysis.

Optical microscopy gives information, amongst others, on refractive index, birefringence, cleavage, extinction angle, coarser exsolution structures and twinning patterns, which are indirect evidence for the underlying mineralogy of the sample. These data are very time consuming to gather and a well trained operator is required. Another limitation exists in fine-grained samples (such as the matrix in volcanic rocks) where

\textsuperscript{1}This chapter is based on the following review paper: Hecker, C., van der Meijde, M. and van der Meer, F.D. (2010) Thermal infrared spectroscopy on feldspars: successes, limitations and their implications for remote sensing. \textit{Earth \cdot Science Reviews}, 103(1–2), 60–70.
optical microscopy only provides information on the larger phenocrysts rather than the average composition of the entire sample.

EMPA works with an electron beam that can be focused on microscopically small areas (ideally <1 µm). The electron beam creates X-rays with distinct energy levels which are diagnostic for the composition of the target area (Klein & Hurlbut, 1999). EMPA allows for point measurements, transects or grids over individual mineral grains. It is especially suitable to analyze microscopic exsolution and zonation patterns as well as for very fine-grained volcanic matrices. Sample preparation includes making polished thin sections which is costly and time consuming.

Cathodoluminescence in feldspars can be used to qualitatively show differences in trace element composition, highlight structural defects and can be used to illustrate chemical growth zonations (Deer et al., 2001; Smith & Brown, 1988).

Powder X-ray diffraction (XRD) is a technique where collimated X-rays are reflected off a powdered mineral sample (Klein & Hurlbut, 1999). Constructive interference creates reflectance peaks, whose position depends on the spacing of layers in the crystal structure. Several peak positions together define a particular mineral and mineral mixtures can be analyzed as well, as long as overlapping peaks can be deconvolved. With the help of extensive libraries XRD can be used to determine feldspar composition and mineral structure. XRD is less valuable for samples with strong intergrowth, since all orientational information is lost and peak overlaps and broadening lead to inadequate results (Smith & Brown, 1988). In the next section infrared techniques will be treated in detail and investigated in how far some of the traditional analytical methods can be replaced by infrared spectroscopy.

<table>
<thead>
<tr>
<th>Application Field</th>
<th>VIS (13000 - 4000 cm⁻¹)</th>
<th>NIR (10000 - 4000 cm⁻¹)</th>
<th>MIR (400 - 100 cm⁻¹)</th>
<th>FIR (400 - 100 cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopy</td>
<td>VIS</td>
<td>NIR</td>
<td>MIR</td>
<td>FIR</td>
</tr>
<tr>
<td>Astronomy</td>
<td>VIS</td>
<td>NIR</td>
<td>MIR</td>
<td>FIR</td>
</tr>
<tr>
<td>Remote Sensing</td>
<td>VIS</td>
<td>NIR</td>
<td>SWIR</td>
<td>TIR</td>
</tr>
</tbody>
</table>

**Figure 2.1** Subdivision of the infrared region according to different application fields: spectroscopy (Stuart, 2004), astronomy (Infrared Processing and Analysis Center, 2012) and remote sensing (Gupta, 2003; van der Meer & de Jong, 2001; Hackwell et al., 1996).
2.2. Analytical methods

2.2.2 Infrared spectroscopy

2.2.2.1 IR spectroscopy overview

Several schemes exist to subdivide the infrared (IR) part of the electromagnetic spectrum into sub-regions (Figure 2.1). Which scheme is used depends largely on the application field and the instrumentation used. Since most of the spectroscopic work done on feldspars has been recorded on laboratory Fourier-transform infrared (FTIR) spectrometers, the spectroscopic subdivision by Stuart (2004) is applied to the laboratory studies for the remainder of this document. Since the term *thermal infrared* is generally used by the remote sensing community, this term is given preference when remote sensing applications are discussed. Wavelengths are generally listed in units of micrometers. Where reference is made to specific wavelengths in wavenumbers (i.e., reciprocal centimeters) the equivalent micrometers are listed as well for consistency in reading. Furthermore, the term *remote sensing* as used in this document describes the measurements of reflected or emitted energy by an airborne or spaceborne sensor, usually (although not necessarily) recording these values in 2-dimensional images. Even though sample and sensor are not in physical contact during laboratory IR spectroscopy measurements, they are not included as part of the remote sensing techniques here.

2.2.2.2 IR spectroscopic setups

Several specific IR spectroscopy setups exist. Even though they are closely related, they differ distinctly in sample preparation and in the measurement geometry of the instrument (Figure 2.2). Sample material can either be oriented single crystals, randomly oriented powder samples (including powder pressed to pellets) or rock fragments. In the case of single crystals, the orientation of the crystallographic axes has a distinct influence on the resulting spectra, while these effects are (mostly) averaged out in the remaining preparation methods. Depending on the experimental setup we can measure the amount of transmitted, reflected or emitted energy. Below the major measurement geometries are briefly explained. Figure 2.3 illustrates albite spectra measured with different measurement geometries. A detailed review of IR experiment setups for geologic samples can be found in King et al. (2004).

Transmission mode. The transmittance of a sample is the percentage of the radiance that penetrates through the sample at a given wavelength such that

\[ \text{Transmittance}(\lambda) = \frac{B_{\text{trans}}(\lambda)}{B_0(\lambda)} \]  

where \( B_{\text{trans}} \) is the radiance transmitted through the sample material and \( B_0 \) is the original radiance impinging on the sample. All major studies of mineral spectra prior to 1975 have used transmittance spectra (Salisbury et al., 1991). Transmittance studies require very little material, give
2. TIR spectroscopy of feldspars — a review

Figure 2.2 Sketches of different measurement geometries in laboratory MIR spectroscopy setups: transmission, diffuse reflectance (DRIFTS), directional-hemispherical reflection (DHR) and emission (from left to right). Arrows indicate directions of electromagnetic energy.

optimal information on absorbance of the material, are easily interpreted and quantified and work best on finely ground powders (King et al., 2004). The resulting spectra are only dependent on the sample’s absorption coefficient and have high signal to noise ratio.

Diffuse reflectance mode. This method is sometimes referred to as DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy; Griffiths & De Haseth, 2007) or bi-conical reflection. It measures the percentage of energy that is reflected from the sample such that

\[
\text{Reflectance}(\lambda) = \frac{B_{\text{refl}}(\lambda)}{B_0(\lambda)}
\]

where \(B_{\text{refl}}\) is the radiance reflected from the sample material and \(B_0\) is the original radiance impinging on the sample. This method is especially suitable for powdered samples. Two elliptical mirrors focus incoming energy onto the sample and collect the reflected energy onto the detector. The method includes some sample preparation (grinding/sieving) and has a high signal to noise levels. Since bi-conical diffuse reflectance values do not vary linearly with sample concentrations, a further data processing step is necessary before a quantitative analysis (King et al., 2004).

Directional-hemispherical reflectance (DHR). DHR measurements are also reflectance measurements like DRIFTS (see above) but are achieved with an integrating sphere. A collimated beam of light is directed onto the sample and the reflected energy is measured. The integrating sphere measures not only the specular (mirror-like) component of the reflected energy but also collects the energy of all diffuse rays that leave the sample under different angles. By applying Kirchhoff’s law

\[
\text{Emissivity} = 1 - \text{Reflectance}
\]

emissivity spectra are calculated from DHR data (Hapke, 1993; Nicodemus, 1965). Earlier research has confirmed that for all practical terrestrial situations, DHR data of minerals and rocks can indeed be used to determine their emissivity spectra (Korb et al., 1999; Salisbury et al., 1994).
2.2. Analytical methods

![Graph showing comparison between albite spectra measured with different measurement geometries.](image)

**Figure 2.3** Comparison between albite spectra measured with different measurement geometries. Transmittance measurement shows narrow features and high spectral contrast. DRIFTS and emission measurements show similar features but differences in their detailed shape and absolute values. All three examples on “Amelia albite” from the JHU and ASU spectral libraries. Note: transmission spectrum uses different y-scale. DRIFTS reflectance values were recalculated to emissivity for easier comparison.

Emission mode. Emission IR spectroscopy measures the energy emitted from the sample itself such that

\[
\text{Emissivity}(\lambda, T) = \frac{B_{\text{em, sample}}(\lambda, T)}{B_{\text{em, BB}}(\lambda, T)} \tag{2.4}
\]

where \(B_{\text{em, sample}}\) is the radiance emitted by the sample at temperature \(T\) and \(B_{\text{em, BB}}\) is the radiance emitted by a perfectly radiating object (called blackbody) at the same temperature \(T\). To distinguish the sample signal from the energy emitted by the instrument and nearby objects such as walls, the samples are usually heated to about 70–100 °C and calibrated using a blackbody target (Ruff et al., 1997). Emission mode IR can be challenging in the laboratory because of the relatively low radiance of the samples relative to the detector and down-welling radiance. Additionally, care has to be taken to make sure samples retain a constant temperature throughout the measurement (King et al., 2004). Data acquired with this laboratory setup are most directly comparable to remote sensing data, which are usually acquired in emission mode as well. Emission measurements are popular with research groups active in quantitative, planetary remote sensing, since the method does not rely on the validity of Kirchhoff’s law (such as DHR measurements) which may be not applicable in all planetary situations (Salisbury et al., 1994).
Spectroscopic visible and near infrared (NIR) analyses on feldspar samples can contain spectral information even though the fundamental vibrational frequencies of an aluminum silicate framework (such as in feldspars) must occur in the MIR around 10 $\mu$m in the so-called reststrahlen region (Hunt, 1977). Overtones and combination tones (multiples of and additions) of fundamental silicate frequencies could occur in the visible and NIR, but are too weak to be detected. Hence, spectral features recorded on feldspars in the visible and NIR reveal information on impurities and special cations in the structure rather than the silicate framework itself. Previous work has shown that substitute or exsolved (ferrous and ferric) iron in feldspars can be one cause of features in the visible and NIR (Nash & Salisbury, 1991; Adams & Goullaud, 1978; Hunt et al., 1973). In the case of plagioclase, the wide absorption feature caused by Fe$^{2+}$ shifts with the plagioclase composition between 1.1 and 1.3 $\mu$m and could even be used as an indicator of plagioclase composition (Adams & Goullaud, 1978). Unfortunately, the feature is masked by atmospheric water vapor (in terrestrial applications) and pyroxene (in mixtures in planetary applications) which hampers its usability in remote sensing studies. Another source of visible/NIR features in apparently fresh feldspars can be a starting alteration to hydroxyl groups-bearing clays such as kaolinite (Hunt et al., 1973). In the case of the rare buddingtonite feldspar ($\text{NH}_4\text{AlSi}_3\text{O}_8 \cdot 5\text{H}_2\text{O}$) the NIR features caused by ammonium ion have been used to identify the minerals in remote sensing data and link it to gold-bearing alteration systems (Felzer et al., 1994). Most other feldspars are spectrally non-distinct in the NIR.

Even though numerous studies on MIR spectroscopy of feldspars exist, their results often cannot be directly related to remote sensing applications. One of the limitations is the choice of laboratory measurement technique (e.g., in transmission mode) with no or only limited relevance to emission mode measurements employed by most remote sensors in the MIR. Another restriction is induced by the earth’s atmosphere: remote sensing of the earth’s surface from airborne or spaceborne platforms can only be performed in atmospheric windows, a range of wavelengths in which the atmosphere is relatively transparent. General reviews on the laboratory techniques are given by Farmer (1974), Estep-Barnes (1977), Lehmann (1983), Smith & Brown (1988) and Deer et al. (2001), and will not be repeated here. Below, mid-infrared studies that revealed results relevant to remote sensing will be shortly reviewed.

**Chemical composition.** Transmission studies were the first to show that MIR spectroscopy can be used to distinguish between feldspars of different composition. Changes in cation weight, bond strength and slight deformation in crystal structure can shift the wavelength of spectral features or split up one feature into two. This causes distinct spectral
2.2. Analytical methods

Figure 2.4  Example spectra of the alkali feldspar group. Clear differences in the reststrahlen features (8–10 µm), in the number of small but distinct features in the 12.5–13.5 µm range (arrows) and a slight shift of the 17 µm feature. Perkhite is spectrally a mixture of the microcline and albite endmembers. Spectra from the ASU spectral library. Perkhite and microcline spectra are offset to lower emissivity values for clarity.

differences in the transmission spectra of plagioclase and alkali feldspars in the 9–25 µm (1100–400 cm$^{-1}$) range (Iishi et al., 1971). Amongst the alkali feldspars, microcline can be differentiated from albite in the 12.5–14.3 µm (800–700 cm$^{-1}$) range since the two minerals show two and four small spectral features in that range, respectively (Zhang et al., 1997; Salje et al., 1989). It can furthermore be observed that the 17.2 µm (580 cm$^{-1}$) absorption band in microcline gradually shifts towards 16.9 µm (590 cm$^{-1}$) in albite. Both of these effects are also visible in emission spectra (Figure 2.4). Nash & Salisbury (1991) determined that plagioclase compositions could be revealed from the MIR spectra of the Reststrahlen feature region (8–12 µm; Figure 2.5 shows these differences on a set of plagioclase spectra from ASU). Other authors focus on the position of a spectral feature which shifts from 15.4 µm in albite to 16.2 µm in anorthite (Thompson & Wadsworth, 1957). A recent study analyzed the plagioclase composition and abundance in the mixed spectra of drill cores and focused on two particular wavelengths (Cudahy et al., 2009). The study revealed a relationship between ratios of the 9.66 and 9.92 peak heights and plagioclase composition determined from XRD 111 and 131 d-spacing values. It appears that for sodium-rich plagioclase the ratio is a high value, which gradually decreases with increasing calcium component. Several authors studied the so called Christiansen feature (CF) rather than individual sharp bands in the MIR. The CF is a distinct reflectance minimum that occurs just short of the major molecular vibration band (Salisbury et al., 1991). At that wavelength the reflectance is close to 0, the refractive index is close to 1 and scattering as well as
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Figure 2.5 Example spectra of the plagioclase group. Clear differences in the reststrahlen bands (8–11 μm) with An showing a distinct feature at 10.5–10.6 μm which is missing in Ab. Intermediate plagioclase spectra are approximately equivalent to isochemical, mechanical mixtures of Ab and An endmember spectra. Feature at 15.3 (Ab) shifts to longer wavelength with increase in An component. Spectra from the ASU spectral library. All spectra except An are offset to lower emissivity values for clarity.

absorption are at a minimum. Existing work on monomineralic samples has shown that the CF frequency of especially plagioclase but also alkali feldspars varies with their composition and mineralogy, from 7.5 to 8.1 μm and 7.7 to 7.8, respectively (Nash & Salisbury, 1991; Conel, 1969).

Structural state. As mentioned above, different structural states are represented in the feldspar lattice by different levels of disorder in the Si/Al distribution. A previous study on transmission infrared spectra showed that high and low albite had similar spectral trends but differed in the fine structure (Iiishi et al., 1971); low structural state has deeper narrower features while in high structural state individual features may not even be resolved (Figure 2.6). The same differences could be observed for sanidine (high state) and maximum microcline (low state). In more recent studies hard-mode infrared spectroscopy (HMIS) was used on feldspars (Zhang et al., 1997; Salje et al., 1989). These authors managed to quantitatively link changes in HMIS absorbance spectra to the Si/Al ordering within alkali feldspars. They demonstrated that ordering of Si/Al is related to sharpening of peaks as well as some small shifting. The influence of the structural state on infrared spectra can easily be explained. Due to differences in their atomic weight, bond strength and bond length in the lattice structure, Al and Si bonds vibrate at different frequencies and, with it, bring about slightly shifted spectral
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IR features. If Si and Al are situated on different, distinct tetrahedron sites (ordered or low state), the IR spectrum shows sharp, individual features. In disordered or high state, Si/Al are randomly distributed over all tetrahedral sites, the related (yet slightly shifted) features overlap each other and cause wider, shallower and less defined spectral features.

Particle Size. In the 1960s a study noted that the grain size in particulate samples influenced the absolute emissivity values as well as the contrast in the spectra (Lyon, 1965). The study demonstrated, however, that differences in grain size did not change the position of the emissivity minima (at resolution of 6 cm\(^{-1}\)). A later study did find, however, that if particle size approached micrometer scale, the spectral behavior of the material did change and new features did appear in the spectrum (Conel, 1969). These additional reflectance peaks at fine grain sizes were termed transparency peaks by Salisbury et al. (1991) and are shown in Figure 2.7. The authors explained them by a process of volume scattering where energy passes through the interior of very fine particles, rather than being reflected off the top of the mineral grain. In order to avoid any problems with transparency features, particulate samples can be kept coarse enough. As a rule of thumb, volume scattering is sufficiently controlled to not display transparency features if particle sizes are kept above 10 times the wavelength of interest (about 100 µm for MIR studies) (King et al., 2004).

Quantitative mineralogy in mixtures. In quantitative infrared spectro-
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Figure 2.7 Comparison between spectrum of coarse-grained and fine-grained sample of an identical albite. Loss in spectral contrast and development of transparency features (arrows) with decreasing particle size are evident. Measurements taken with a DRIFTS setup at JHU and are part of the ASTER spectral library. Reflectance values were recalculated to emissivity for easier comparison between plots.

Scanning electron microscopy of mixtures, one tries to determine the composition of the sample by comparing the mixed spectrum to the spectra of pure classes. As early as 1965 a study indicated that rock spectra could be mixtures of the spectra of the minerals they contain (Lyon, 1965). Gillespie (1992b) mentioned that thermal infrared image pixels can be modeled as mixtures of their endmembers. These results were confirmed by a more recent study on artificial mixtures of particulate rock-forming minerals (Thomson & Salisbury, 1993). Their results indicated that mid-infrared mixtures can be modeled as a linear combination of the minerals the mixture contains. Research by Ramsey & Christensen (1998) showed that linear unmixing of particulate mineral mixtures work down to 63 μm particle size and if reference libraries for smaller particles are available, reasonable unmixing results can be achieved down to 10 μm. In powders with grain sizes finer than 10 μm, volume scattering becomes so dominant, that linear unmixing models fail and that radiative transfer models have to be applied to quantify the components in the mixture (Ramsey & Christensen, 1998; Hapke, 1993). Situations with very fine powders do, however, rarely occur in terrestrial systems and may be more problematic in planetary situations (Ramsey & Christensen, 1998). Feely & Christensen (1999) applied the linear unmixing to terrestrial rock samples that were measured under laboratory conditions. When comparing their results to "traditional" petrographic analysis, they found detection limits for most minerals, including feldspars, of about 5% of the sample surface. More recent studies looked specifically at plagioclase...
samples (Milam et al., 2007, 2004). The authors established that the plagioclase composition could be determined with a (1σ) accuracy of ±4% on artificial samples containing only plagioclase as well as on samples containing other silicate in the mixture. When comparing IR spectra of real rock samples with microprobe average compositions, they report slightly lower agreements in plagioclase composition to within +10/–6%, which they attributed to small sampling errors in the microprobe analysis.

Reference spectral libraries. In order to unmix rock and soil spectra into their mineral components, standardized spectral measurements of a set of pure endmember components are needed; so called reference libraries or spectral libraries. With the advent of airborne and spaceborne thermal infrared missions, such as TIMS, MASTER, SEBASS, ASTER, MODIS, TES, THEMIS, spectral libraries were needed to understand, interpret and model the remote sensing data. Several organizations have published mid-infrared spectral libraries which include spectra of various feldspar minerals. Amongst them are the Johns Hopkins Spectral Library (Salisbury et al., 1991), the Arizona State University library (Christensen et al., 2000), the spectral library of the United States Geologic Survey (Clark et al., 2007) as well as the Jet Propulsion Laboratory’s ASTER spectral library (a compilation of JHU data and JPL’s own dataset; Baldridge et al., 2009).

The data contained in the spectral libraries have been recorded with different instruments and measurement geometries and with different measurement procedures. This inevitably causes discrepancies in wavelength accuracy and absolute reflectance values. Most laboratories use the distinct quartz feature around 8.62 µm to check their wavelength calibration. This should keep the wavelength discrepancies between labs to a minimum for the reststrahlen feature region of silicate minerals (8–12 µm) which is mainly used for feldspar identification. The absolute reflectance values are more difficult to control and depend a lot on sample preparation, sample grain sizes and measurement geometry. While all datasets are suitable for qualitative comparison between each other and to remote sensing data, only data recorded with comparable geometries and similar grain size fractions can be used in a quantitative way (Salisbury et al., 1991).

2.3 Discussion

As the review above indicates, fundamental laboratory IR studies on minerals do exist, several of them at least including information on the feldspar group. Not all laboratory IR techniques can be extended into a remote sensing application. Depending on the measurement technique or physical conditions used during laboratory analysis, results may be usable in a quantitative way, in a qualitative way as an indication or not at all. Table 2.1 summarizes the findings of existing studies that attempted to analyze feldspar characteristics. Empty fields in the table
2. TIR spectroscopy of feldspars — a review

indicate that no published research was encountered in that area during the review work. As part of the summary, the success level was rated of each measurement technique-feldspar characteristic-combination. The following discussion is based on Table 2.1 and complemented with an assessment on which laboratory results may be applicable to remote sensing studies.

Measuring feldspars with different IR experimental setups produces results that are similar at first glance but noticeably vary when looked at in detail. An example is given in Figure 2.3 that shows albite spectra measured in transmission, DRIFTS and emission mode. Absolute values and exact peak positions differ. Certain trends do, however, occur across measurement methods; as an example sodic plagioclase spectra show distinct features between 12.5–13.5 \( \mu \text{m} \) (Figure 2.3). The exact wavelengths of the features again depends on the method used.

In transmission mode features are generally narrow, show more details and occur at shorter wavelengths than their reflective equivalent (Hunt & Salisbury, 1969). This makes transmission measurement particularly useful when determining structural state of feldspars since the sharpness and spectral contrast of the features is an important indication for Al/Si-ordering in the structure. With spectra of reflective and emissive IR methods showing less spectral details and wider features, quantitatively determining structural state should be difficult and has not been attempted. Nevertheless, one study demonstrated spectral differences in emission spectra in a qualitative way (Ruff, 1998).

Determining mineral chemistry of plagioclase and alkali feldspars with infrared spectra can either be based on a wavelength position of a spectral feature, the general shape of a combination of features or the depth of one or several features (Table 2.1). The dependence on very sharp features in the spectra is far less than for determining structural state. Hence, chemical compositions have been successfully determined with all IR measurement techniques. However, some of the spectral indices listed in Table 2.1 have their limitations. The CF frequency mainly works in pure feldspar samples, since the CF range of alkali feldspars overlaps with that of plagioclase as well as other mineral groups. In rock samples, CF merely allows differentiation into major rock classes rather than determination of feldspar compositions. Another disadvantage of IR technique in general is the co-linearity of the individual feldspar spectra. This entails that a mixture of microcline and albite look spectrally identical to perthite. Similarly a mixture of intermediately ordered microcline, and oligoclase is spectrally analogous to anorthoclase (Ruff, 1998). As a consequence it is impossible with these IR techniques to determine whether we have a mixture of two feldspar endmembers or a single, intermediately composed feldspar in the sample. Furthermore samples often show several generations of plagioclase or zoned igneous plagioclase compositions. In both cases IR techniques cannot resolve the different groups and return results of an average composition in the sample (Milam et al., 2007).

Quantitative mineralogy has been applied mainly to transmittance
2.3. Discussion

and emission data. In transmission spectra, concentrations are linked to spectral transmittance through the Beer-Lambert law (King et al., 2004) and in emission mode linear deconvolution into spectral endmembers has been applied successfully by several authors (see Table 2.1 for examples). Diffuse reflectance measurements are far less commonly used for determining quantitative sample compositions. This is likely related to the mathematical complications involved when linking DRIFTS spectra to concentrations in the sample. Spectra either have to be treated with a Kubelka-Munk transform, or Hapke theory has to be applied to predict the scattering within the sample (King et al., 2004).

An important prerequisite for quantitatively deconvolving mixed spectra is the availability of a spectral library with suitable endmembers. As long as particle sizes and IR measurement setup are identical for the spectral library and the sample measurement, deconvolution of feldspar and other silicate minerals generates excellent results. In exceptional cases spectral libraries from diffuse reflectance measurements can also be used to analyze emission spectra, but not until they were empirically adjusted to match expected emission spectra (Feely & Christensen, 1999).

As mentioned earlier, IR spectroscopy techniques cannot resolve different generations or chemical zonations of feldspars in the sample. Measured IR spectra are purely a representation of the average mineralogy that is currently present in the sample. Whether a certain mineral was stable in the sample or was metastable but incompletely replaced, cannot be determined. This is a clear disadvantage of IR techniques as compared to thin section analysis or EMPA, where stable mineral assemblages in the sample can be determined and overprinting relationships can be detected. A possible solution to this problem could be infrared microscopy. It combines the spatial information of a microscope with the spectral information of infrared spectroscopy (Griffiths & De Haseth, 2007). Measurements are done in transmission or reflectance mode and spectroscopic IR images of thin sections or polished slabs can be produced. IR microscopy could be used to understand and quantify the effects of feldspar overprinting, zonations, exsolution and twinning on bulk infrared spectra.
Table 2.1: Linking feldspar characteristics to features and successes in five typical MIR measurement setups. Example references are given for each statement. Relative success estimates range from ++ to –; a question mark indicates that no attempt has been made to investigate a given combination of characteristic and measurement setup, or no such literature was found in the review process. Abbreviations used: microcline (Mi), orthoclase (Or), sanidine (Sa), albite (Ab), anorthite (An), alkali feldspars (Afsp), plagioclase (Plag), Christiansen feature (CF).

<table>
<thead>
<tr>
<th>Mineral Chemistry</th>
<th>Transmission measurements</th>
<th>DRIFT measurements</th>
<th>DHR measurements</th>
<th>Emission measurements</th>
<th>Airborne emission measurements</th>
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<tr>
<td>Afsp</td>
<td>++ Clear spectral differences between Mi, Sa and Ab&lt;sup&gt;a&lt;/sup&gt;</td>
<td>++ Spectral library of various Afsp compositions show distinct differences&lt;sup&gt;f&lt;/sup&gt;</td>
<td>++ Spectral library of various Afsp compositions show distinct differences&lt;sup&gt;f&lt;/sup&gt;</td>
<td>++ Spectral library of various Afsp compositions show distinct differences&lt;sup&gt;f&lt;/sup&gt;</td>
<td>- Differentiation between Mi and Ab in airborne data is difficult if quartz is dominant in mixture&lt;sup&gt;p&lt;/sup&gt;</td>
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<td></td>
<td>++ Feature shifts from 590 cm&lt;sup&gt;-1&lt;/sup&gt; (Ab; 16.95 µm) to 579 cm&lt;sup&gt;-1&lt;/sup&gt; (Or; 17.27 µm)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>++ Range between 12.5-14.0 µm show 4 (Ab) and 2 features&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Mi and Ab show similar spectra but with slightly different wavelengths and relative depths of features in reststrahlen bands&lt;sup&gt;i&lt;/sup&gt;</td>
<td>++ Spectral library of various Afsp compositions show distinct differences&lt;sup&gt;f&lt;/sup&gt;</td>
<td>+/- Mapping variations in plagioclase composition by ratios of 9.9/9.6 µm emissivity lows; coherent patterns but no quantitative assessment of results yet&lt;sup&gt;l&lt;/sup&gt;</td>
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<td></td>
<td>700-800 cm&lt;sup&gt;-1&lt;/sup&gt; (12.5-14.3 µm) show 2 (Or) and 4 features (Ab). Intermediate compositions behave like mechanical mixtures of endmembers&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>+ Intermediate plagioclase spectra approx. equivalent to isochemical, mechanical mixtures of Ab and An end-member spectra&lt;sup&gt;e&lt;/sup&gt;</td>
<td>++ Distinct feature of Ca-plag at 950 cm&lt;sup&gt;-1&lt;/sup&gt;(10.5 µm) getting more pronounced towards An&lt;sup&gt;j&lt;/sup&gt;</td>
<td>+/- CF system. shifts from 7.50 (Ab) to 7.81 µm (Mi) in pure Afsp samples&lt;sup&gt;k&lt;/sup&gt;</td>
<td>- Differentiation of 2 generations plag not possible. Spectra represent average&lt;sup&gt;h&lt;/sup&gt;</td>
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<td></td>
<td>+/- Feature shifts from 15.4 (Ab) to 16.2 (An)&lt;sup&gt;i&lt;/sup&gt;</td>
<td>++ Spectral library of various plag compositions show distinct differences&lt;sup&gt;f&lt;/sup&gt;</td>
<td>++ Spectral library of various plag compositions show distinct differences&lt;sup&gt;f&lt;/sup&gt;</td>
<td>++ Distinct feature of Ca-plag at 950 cm&lt;sup&gt;-1&lt;/sup&gt;(10.5 µm) getting more pronounced towards An&lt;sup&gt;j&lt;/sup&gt;</td>
<td>- Differentiation between Ab and An can be difficult and shows discrepancies with XRD in ground samples&lt;sup&gt;r&lt;/sup&gt;</td>
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<tr>
<td></td>
<td>Intermediate plagoclase spectra approx. equivalent to isochemical, mechanical mixtures of Ab and An end-member spectra&lt;sup&gt;e&lt;/sup&gt;</td>
<td>+/- CF shifts systematically from 7.66 (Ab) to 8.03 (An) in pure fsp samples&lt;sup&gt;g&lt;/sup&gt;</td>
<td>+/- CF system. shifts from 7.50 (Ab) to 8.04 µm (An) in pure plag samples&lt;sup&gt;k&lt;/sup&gt;</td>
<td>++ Plag composition determ. by deconvolution of rock spectra into fractions of pure Ab, An and intermediate plag spectra. Accuracy ± 4&lt;sup&gt;l&lt;/sup&gt;</td>
<td>- Differentiation between 2 generations plag not possible. Spectra represent average&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
<tr>
<td>Plag</td>
<td>+/– CF system. shifts from 7.50 (Ab) to 8.04 µm (An) in pure plag samples&lt;sup&gt;k&lt;/sup&gt;</td>
<td>++ Distinct feature of Ca-plag at 950 cm&lt;sup&gt;-1&lt;/sup&gt;(10.5 µm) getting more pronounced towards An&lt;sup&gt;j&lt;/sup&gt;</td>
<td>+/- CF system. shifts from 7.50 (Ab) to 7.81 µm (Mi) in pure Afsp samples&lt;sup&gt;k&lt;/sup&gt;</td>
<td>- Differentiation between Ab and An can be difficult and shows discrepancies with XRD in ground samples&lt;sup&gt;r&lt;/sup&gt;</td>
<td>- Differentiation of 2 generations plag not possible. Spectra represent average&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
<tr>
<td>Structural state</td>
<td>Transmission measurements</td>
<td>DRIFT measurements</td>
<td>DHR measurements</td>
<td>Emission measurements</td>
<td>Airborne emission measurements</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------------------</td>
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<td>----------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td><strong>Afsp</strong></td>
<td>++ Absorption features in Afsp become narrower and deeper with increasing order&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td><strong>Plag</strong></td>
<td>++ Absorption features in Ab become narrower and deeper with increasing order&lt;sup&gt;a&lt;/sup&gt;</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td><strong>Quant. miner.</strong></td>
<td>Intermediate compositions behave like mechanical mixtures of endmembers&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td><strong>Quant. miner.</strong></td>
<td>Intermediate plagioclase spectra approx. equivalent to isochemical, mechanical mixtures of Ab and An endmember spectra&lt;sup&gt;e&lt;/sup&gt;</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

---
<sup>a</sup> Iishi et al. (1971)  
<sup>b</sup> Zhang et al. (1997)  
<sup>c</sup> Salje et al. (1989)  
<sup>d</sup> Thompson & Wadsworth (1986)  
<sup>e</sup> Smith & Brown (1988)  
<sup>f</sup> Salje et al. (1989)  
<sup>g</sup> Thompson & Wadsworth (1986)  
<sup>h</sup> Ruff (1998)  
<sup>i</sup> Thomson & Salisbury (1993)  
<sup>j</sup> Ruff (1998)  
<sup>k</sup> Conel (1969)  
<sup>l</sup> Milam et al. (2004)  
<sup>m</sup> Milam et al. (2007)  
<sup>n</sup> Ramsey & Christensen (1996)  
<sup>o</sup> Feely & Christensen (1999)  
<sup>p</sup> Vaughan et al. (2003)  
<sup>q</sup> Cudahy et al. (2001d)  
<sup>r</sup> Vaughan et al. (2005)
2.3.1 Application to airborne imagery

With the exception of the active MIRACO2-LAS sensor (Cudahy et al., 1999) all operational airborne and spaceborne thermal infrared (TIR) remote sensors detect the energy emitted by the target area itself. Laboratory emission measurements mimic the remote sensing data more closely than any other laboratory technique, which can reportedly be an advantage in situation where minerals show a preferred orientation (e.g., mica on foliation surfaces) or when thin coatings are present (e.g., desert varnish; King et al., 2004). However, several studies have shown that directional-hemispherical reflectance measurements on minerals are equivalent to emission measurements in most terrestrial situations (Korb et al., 1999; Salisbury et al., 1994). Hence, any laboratory study using emission mode or DHR measurements can be used to analyze TIR remote sensing imagery in a quantitative way, such as spectral unmixing into mineral endmembers, while transmission and diffuse reflectance studies can only be used qualitatively for interpretations of remote sensing (Salisbury et al., 1991).

Currently, research in thermal remote sensing of feldspars (and silicates in general) is driven by planetary science (e.g., Michalski & Fergason, 2009; Byrnes et al., 2007; Milam et al., 2007; Christensen et al., 1998). The main goal is the extension of the fundamental research in the laboratory to the conditions and mixed targets and map mineral occurrences across the surface on Moon, Mars and other planetary objects in our solar system.

A small number of studies have applied laboratory feldspar results to terrestrial test cases (e.g., Vaughan et al., 2005, 2003; Cudahy et al., 2001d; Ramsey et al., 1999) and many challenges remain untackled. Thomson & Salisbury (1993), for example, wondered about the limiting factors that affect our ability to unmix thermal imagery in a terrestrial environment. They further questioned the maximum number of mineral components that can be unmixed and about the influence of coatings, such as desert varnish, on the results. Vaughan et al. (2003) mentioned that even if differentiating feldspar minerals in airborne thermal imagery is theoretically possible with a given sensor, unmixing the feldspar endmember may not work if their diagnostic features occur on the slope of a much more dominant spectral feature of, for example, quartz. In a later study (Vaughan et al., 2005) they again used airborne TIR remote sensing images for mineral mapping through linear mixing of endmembers. They showed in their results that feldspars occurred in XRD results while they could not or only incompletely be detected in the airborne data and vice versa. They attribute the discrepancies to scale differences between XRD point sample location and pixel integrated spectra in hypserspectral thermal image data. Whether their explanation is valid or not, is difficult to say, but it shows the need for further experiments. Their explanation could be tested by applying a dense grid of ground measurements over an area the size of several image pixels. The grid would show the distribution and relative abundance of minerals
2.3. Discussion

within an individual image pixel and give a better link between ground and remote sensing data. An alternative explanation of their results could be found in the fact that the authors did not apply a linear unmixing algorithm (as is commonly done). Instead they created linear mixtures from pure mineral spectra themselves, and compared the outcome to their mixtures. It is often the case that more (legitimate) minerals can be automatically unmixed out of a rock spectrum than those that are visible to the human observer in the first place. Hence, feldspars in small concentrations could have been missed in their spectra. Cudahy et al. (2001d) established a link between XRD peak positions to spectral indices in thermal infrared spectra. When applying their results to airborne hyperspectral thermal data, they created a plagioclase chemistry map that showed coherent patterns which were virtually seamless across flightlines. Upon closer inspection, the plagioclase compositions in the airborne data do not seem to directly compare with compositions in field samples. No clear reason has been found (yet) to explain this discrepancy and further studies are required to establish a strong link between feldspar compositions in EMPA, thin sections and XRD on one side and thermal infrared imagery on the other hand.

2.3.2 Existing and upcoming sensors

The recent lack of interest in terrestrial applications can be attributed to two main causes a) a relatively restrictive terrestrial atmosphere that limits thermal remote sensing to roughly 3–5 $\mu$m and 8–14 $\mu$m and b) the scarcity of high spectral resolution sensors in the thermal infrared. Luckily, the reststrahlen bands of the feldspar silicate framework fall within the terrestrial atmospheric windows but other vibrational fundamentals, beyond the 14 $\mu$m region, cannot be used on earth. Ozone, with a strong absorption around 9 $\mu$m, further limits the applicability spaceborne studies of feldspars, since most feldspars have part of their diagnostic features around that wavelength (Ramsey, 2004).

In terms of sensor availability large improvements are expected within the next couple of years. For many years the SEBASS instrument (Hackwell et al., 1996) was the only high spectral resolution thermal instrument available, but data availability for civil applications was very limited. Currently, SEBASS data are flown and available commercially (pers. communication D. Riley, The Aerospace Corporation). Several other airborne thermal imaging systems have recently been deployed or are close to completion (compare Table 2.2). All of them measure emission in the reststrahlen window, usually between 8 and 12 $\mu$m. This means that any characteristics of feldspars outside of that range (e.g., alkali feldspar triplet at 16.6 $\mu$m) cannot be used in airborne applications. The wider range of SEBASS (extends to 13.5 $\mu$m) could allow for detection of typical, yet small, spectral features in alkali feldspar in the 12.5–13.5 range. These higher wavelength bands do, however, display a large amount of difficult to correct atmospheric influences and may not be effective in detecting small mineral features (Vaughan et al., 2003).
2. TIR spectroscopy of feldspars — a review

The number of bands the airborne systems record varies a lot between the different systems. The number of bands recorded appears to have only a limited influence on detecting and characterizing feldspars in thermal imagery as long as the number of minerals in the mixture stays well below the number of bands recorded (Milam et al., 2007). Noise level in thermal imagery data, however, can be of much more crucial importance. Richter et al. (2005) determined that noise equivalent difference in temperature (NEΔT) of around 0.1 K still gave good retrieval of mineral spectra for the proposed ARES sensor. Table 2.2 shows that SEBASS and the proposed HyTES combine high spectral resolution (number of bands) with NEΔT levels at or below 0.1 K and show the highest potential for successfully characterizing feldspars in airborne thermal infrared remote sensing imagery.

With several airborne, hyperspectral thermal IR sensors available or close to completion, standardized processing techniques and spectral indices need to be developed in order to produce commercially interesting feldspar products, such as number of feldspar species, plagioclase and alkali feldspar composition, their structural state and a relative or semi-quantitative abundance value within the rocks.

2.4 Conclusions

From the papers reviewed here the following conclusions can be drawn on IR spectroscopy of feldspars and its implications for remote sensing studies:

1. Much fundamental research in the IR spectral behavior of feldspar has been done. The majority of studies were based on transmission measurements and the applicability to emission remote sensing has to be tested first.

2. Linear unmixing (or deconvolution) of laboratory rock spectra into pure mineral components works well in the MIR. For feldspars a 5% minimum fraction has to be present in the rock to still be detectable. Plagioclase composition can be determined to within about ±4 mol% An (1σ). Modeled plagioclase modes are within ±11% of petrographically determined modes. Unmixing accuracies have yet to be determined for alkali feldspar.

3. Unmixing of thermal airborne imagery of terrestrial rocks has only been attempted in a few cases and with mixed results. Minimum fractions, expectable compositional accuracies, maximum plausible number of endmembers, influence of weathering and coatings require further investigation.

4. Chemical zonation or different generations of feldspars cannot be detected with IR spectroscopy. The IR spectra reveal the current average plagioclase and average alkali feldspar composition in the sample.
<table>
<thead>
<tr>
<th>Sensor name</th>
<th>Coordinating organization</th>
<th>Spectral range</th>
<th>Nr. of bands</th>
<th>Spectral resolution</th>
<th>NEAT / signal-to-noise ratio</th>
<th>Availability</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEBASS</td>
<td>Aerospace Corporation, USA</td>
<td>7.5–13.5 µm</td>
<td>128</td>
<td>10 nm (at 10 µm)</td>
<td>NEAT: 0.05 K / SNR: 3100:1 (300 K; 10 µm)</td>
<td>1995–</td>
<td>Kirkland et al. (2002); Hackwell et al. (1996)</td>
</tr>
<tr>
<td>AHI</td>
<td>University of Hawai'i, USA</td>
<td>7.5–11.5 µm</td>
<td>256</td>
<td>125 nm</td>
<td>NEAT: ca. 0.19 K / SNR: 1000:1 (303.15 K; at 10 µm)</td>
<td>1998–</td>
<td>Vagni (2007); Lucey et al. (2001)</td>
</tr>
<tr>
<td>TASI-600</td>
<td>ITRES, Canada</td>
<td>8.0–11.5 µm</td>
<td>64</td>
<td>125 nm</td>
<td>?</td>
<td>2006–</td>
<td>ITRES Research Limited (2012); Shimoni (2009)</td>
</tr>
<tr>
<td>AISA Owl</td>
<td>SPECIM, Finland</td>
<td>8.0–12.0 µm</td>
<td>84</td>
<td>100 nm</td>
<td>NEAT: 0.12 K / SNR: 580:1 (300 K; 10 µm)</td>
<td>Early 2010</td>
<td>Spectral Imaging Ltd. (2012a); Holma et al. (2009); Shimoni (2009)</td>
</tr>
<tr>
<td>MAKO</td>
<td>Aerospace Corporation, USA</td>
<td>7.8–13.4 µm</td>
<td>128</td>
<td>40 nm (at 10 µm)</td>
<td>NEAT: 0.1 K (10 µm)</td>
<td>2011–</td>
<td>Hall et al. (2011a); Tratt &amp; Hall (2011)</td>
</tr>
<tr>
<td>MAGI</td>
<td>Aerospace Corporation, USA</td>
<td>7.0–12.7 µm</td>
<td>32</td>
<td>≈190 nm (?)</td>
<td>NEAT: 0.1 K</td>
<td>2012–</td>
<td>Hall et al. (2011b, 2008)</td>
</tr>
<tr>
<td>HyTES</td>
<td>JPL, USA</td>
<td>7.5–12.0 µm</td>
<td>256</td>
<td>35 nm</td>
<td>NEAT: 0.1 K / SNR: 620:1 (300 K; 10 µm; binning=2)</td>
<td>Late 2012</td>
<td>Hook et al. (2009)</td>
</tr>
<tr>
<td>SIELETERS</td>
<td>ONERA, France</td>
<td>8.0–11.5 µm</td>
<td>n/a</td>
<td>&lt;230 nm (at 10 µm)</td>
<td>NEAT: &lt;0.2 K / SNR: &gt;310:1 (300 K; 10 µm)</td>
<td>?</td>
<td>Shimoni (2009); Thetas et al. (2009)</td>
</tr>
<tr>
<td>ARES</td>
<td>DLR, Germany</td>
<td>8.1–12.1 µm</td>
<td>30</td>
<td>280 nm</td>
<td>NEAT: 0.1 K (9.0–10.0 µm)</td>
<td>?a</td>
<td>DLR ARES Website (2009); Richter et al. (2005); Wilson &amp; Cocks (2003)</td>
</tr>
</tbody>
</table>

Table 2.2 Sensor characteristics of existing and future TIR sensors with potential in remote sensing of feldspars (Modified after Hecker et al. (2010)).

*aProject discontinued; pers. comm. M. Bachmann, DLR
2. TIR spectroscopy of feldspars — a review

5. Differentiating *high* from *low* structural state feldspar is possible with IR transmission spectroscopy and has been illustrated qualitatively in other IR lab techniques. If structural state can be extracted quantitatively from DHR or emission spectra and whether it can be detected with remote sensing requires further investigation.

6. The effect of twinning and exsolution textures in feldspars on their MIR spectra has been demonstrated in transmission mode. Further research is required to determine whether these differences can be detected in reflectance and emission mode as well and whether or not it can be distinguished in remote sensing imagery. IR microscopy could be able to bridge the gap between microscopic studies and IR bulk interpretations.

7. Standardized processing techniques and spectral feldspar indices for thermal infrared imagery need to be developed. Commercially interesting products include number of feldspar species, plagioclase and alkali feldspar composition, their structural state and a relative or semi-quantitative abundance value within the rocks.
3.1 Introduction

The review of existing literature in Chapter 2 has shown that not all thermal infrared spectra are appropriate for quantitative comparison to hyperspectral airborne TIR imagery. Only spectra acquired with directional-hemispherical or emissive instruments are suitable in that sense. In order to support the analysis of hyperspectral TIR data and to expand the spectroscopic facilities of the Faculty ITC into the thermal infrared range, a directional-hemispherical laboratory spectrometer was procured, customized and tested. In this chapter, the spectrometer setup is described and the standard measurement procedure explained. The instrument is then used in Chapter 4 to measure high quality laboratory TIR spectra on samples from the Ann-Mason test area.

3.1.1 Background

In the remote sensing community, laboratory vibrational spectroscopy is used for two purposes: firstly, as a testbed to see if a certain application works in the laboratory before upscaling to airborne or spaceborne data (e.g., Luleva et al., 2011; Michalski et al., 2004; Milam et al., 2004; Hamilton & Christensen, 2000), and secondly to calibrate and ground truth remotely-sensed data on samples taken from the study area (among others Kodikara et al., 2012; van der Werff et al., 2008; Vaughan et al., 2005). To meet these objectives, laboratory instruments and techniques have to be used that produce results that are quantitatively comparable to those acquired by remote sensing. The literature review in Chapter 2 shows that the majority of existing studies were based on transmission measurements. The applicability of these results to quantitative emission

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3. Laboratory spectrometer setup

remote sensing is often not possible. Instead, directional-hemispherical reflectance or emission laboratory measurements are required.

While many instruments exist for the visible, near and short-wave infrared wavelength ranges, no suitable off-the-shelf solutions are available specifically for the thermal infrared spectroscopy (DHR or emission) of rocks and soils. Procurement starts with a standard laboratory Fourier-transform infrared spectrometer which has to be modified to overcome the following shortcomings: (a) the sample holder is usually not large enough for a typical earth science sample material, (b) the measurement spot impinging on the sample is not large enough to give representative results in inhomogeneous, coarse samples, and (c) the measurement geometry is not suitable for comparison to remote sensing data.

Below, a new spectrometer setup is described, intended to measure typical samples in earth science applications. Contrary to similar existing instruments, this new design allows for full range acquisitions (near infrared to thermal infrared) on the same measurement spot, permits two types of calibration modes and has a large sample port of 30 mm for good averaging on inhomogeneous samples. The instrument modifications and the standard measurement parameters used will be explained, and the performance of the system will be evaluated.

3.2 Instrument Setup

The configuration currently employed at the Jet Propulsion Laboratory (JPL) Earth Surface Science group in Pasadena (CA, USA) was used as a starting point for the design of the new instrument setup. Similar reflectance instruments are also operated by other organizations (e.g., Geologic Survey of Japan, Johns Hopkins University); all are ultimately based on Jack Salisbury’s initial integrating sphere instrument at the US Geologic Survey (USGS) from the 1980s. However, our setup includes key differences, such as a larger integrating sphere, a double detector setup, internal sphere wall calibration and an automated calibration switching mechanism. These features are described in more detail below.

As our base instrument a Bruker Vertex70 research-grade laboratory FTIR spectrometer was chosen, with sufficient possibilities to modify and extend its capabilities. The wavelength modulation in the instrument is achieved with an interferometer based on cube-corner reflectors on a rocking arm, rather than with flat mirrors as in a traditional Michelson-type interferometer (Griffiths & De Haseth, 2007), making the system insensitive to alignment or vibrations. Internal mirrors are gold-coated to optimize energy throughput in the thermal infrared. The system is delivered with a double internal source and double beam splitter option that allows measurements over an extended spectral range (Table 3.1). The internal sample compartment permits the installation of standard accessories, such as measurements of KBr pellets in transmission mode, reflectance measurements in DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) mode or the use of an ATR (Attenuated Total
3.2. Instrument Setup

<table>
<thead>
<tr>
<th>Component</th>
<th>SWIR/TIR</th>
<th>Description</th>
<th>Cooling</th>
<th>Range [cm$^{-1}$]</th>
<th>Range [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source1</td>
<td>SWIR</td>
<td>Tungsten source (internal)</td>
<td>—</td>
<td>15,000–2,000</td>
<td>0.7–5.0</td>
</tr>
<tr>
<td>Source2</td>
<td>TIR</td>
<td>Globar source (internal)</td>
<td>—</td>
<td>7,000–600</td>
<td>1.4–16.7</td>
</tr>
<tr>
<td>Source3*</td>
<td>TIR</td>
<td>Globar source 150 W (external)</td>
<td>water cooled</td>
<td>10,000–600</td>
<td>1.0–16.7</td>
</tr>
<tr>
<td>Beamsplit.1</td>
<td>SWIR</td>
<td>Si on CaF$_2$ Splitter</td>
<td>n/a</td>
<td>15,000–1,200</td>
<td>0.7–8.3</td>
</tr>
<tr>
<td>Beamsplit.2*</td>
<td>TIR</td>
<td>Ge on KBr Splitter</td>
<td>n/a</td>
<td>7,800–370</td>
<td>1.3–27.0</td>
</tr>
<tr>
<td>Detector1</td>
<td>SWIR/TIR</td>
<td>DLaTGS detector (internal)</td>
<td>room temperature</td>
<td>10,000–370</td>
<td>1.0–27.0</td>
</tr>
<tr>
<td>Detector2</td>
<td>SWIR</td>
<td>InGaAs diode detector (on integrating sphere)</td>
<td>Peltier</td>
<td>12,800–4,000</td>
<td>0.8–2.5</td>
</tr>
<tr>
<td>Detector3*</td>
<td>TIR</td>
<td>MCT mid-band detector (on integrating sphere)</td>
<td>liquid N$_2$</td>
<td>10,000–600</td>
<td>1.0–16.7</td>
</tr>
</tbody>
</table>

* These components are used in the standard UT-ITC measurement procedure for directional-hemispherical reflectance in the thermal infrared.

Reflectance) accessory. These standard accessories can be used if a representative sample of a few grams can be produced and no quantitative linking to remote sensing data is necessary (Hecker et al., 2010; Salisbury et al., 1991).

3.2.1 Modifications

The spectrometer needed to be adjusted so that the resulting spectra could be compared to thermal infrared emission spectra from remote sensors. This requires either an emissive or a directional-hemispherical reflectance (DHR) measurement geometry with an integrating sphere (Salisbury et al., 1991). Since the former contains the extra complexity of measuring samples at a controlled and stabilized temperature, it was decided to use a design with an integrating sphere. The purpose of the sphere is to produce an angularly averaged measurement, integrating all reflection directions in the hemisphere above the sample.
3. Laboratory spectrometer setup

![Diagram of laboratory spectrometer setup]

**Figure 3.1** Overview of instrument setup with external components labeled.

### 3.2.1.1 Sphere Design

An integrating sphere of 150 mm diameter was machined from a block of aluminum. The surface was blasted with glass pearls first, then gold-coated by galvanization to a thickness of about 3 µm in order to create a highly-diffuse reflecting surface. The coating is reportedly 97% reflective and 95% diffuse for wavelengths < 25 µm (Koehl, 2006).

The sphere is connected to the spectrometer’s external ports by a connecting funnel (Figures 3.1 and 3.2). The energy coming from the interior of the spectrometer is nearly collimated (convergent at 4 degrees) and enters the sphere through an entrance port at the left equator. A folding mirror re-directs the radiation through a port at the south pole onto the sample with an incidence angle of 10 degrees from normal (Figure 3.2). The Mercury Cadmium Telluride (MCT) TIR detector is positioned at the top of the sphere in a way that the folding mirror acts as a baffle and prevents the first reflection from directly entering the detector. The Indium Gallium Arsenide (InGaAs) SWIR detector at the right equator is unbaffled but slightly set back from the sphere wall, which prevents most of the first reflected energy from entering the SWIR detector.

By using a laboratory jack below the integrating sphere, sample material can be raised to the sample port at the sphere’s south pole. As a consequence, this design (a) allows for large rock samples to be measured without weighing down the instrument-sphere connection, (b) prevents lose material from falling into the sphere without the use of throughput-reducing window material and (c) allows for measuring soils in Petri dishes. When measuring soil samples in the near-infrared a typical setup
3.2. Instrument Setup

Figure 3.2 Sketch of instrument setup and internal beam path. The gray beam path inside the sphere illustrates the comparative calibration method in which the sphere wall is used as the reference.

is to place a Petri dish with soil material on a sample port at the top of the sphere and measure through the dish. Petri dishes are opaque in the TIR and thus cannot be penetrated by TIR radiation if placed on top of the sphere.

3.2.1.2 Calibration Design

The design of the sphere allows for two different calibration procedures: the substitution and comparative methods. To calibrate by the substitution method, a reference material is first placed under the sample port and a reference measurement is taken. Then the reference is substituted by the sample and a sample measurement is taken. The reference and sample measurements are ratioed against each other to convert the spectrum to reflectance percentages.

In the comparative method the sample is placed under the sample port and becomes an integral part of the sphere wall during the reference as well as sample measurements. To perform a reference measurement the folding mirror of the sphere can be rotated such that the incoming energy is deflected onto the gold-coated sphere wall instead of the sample (Figure 3.2). The sphere wall itself is used as the reference material. After the reference measurement, the folding mirror is rotated back and the sample in the sample port is measured. The two spectra are ratioed to
convert to reflectance percentages. For long measurements the folding mirror lever was equipped with an electric motor (Figure 3.3). Through automated swapping, several reference and sample measurement cycles can be measured without moving the sample to compensate for drift in the instrument or changes in atmospheric composition.

### 3.2.1.3 External TIR Source

To boost energy throughput and signal-to-noise ratio, a high-power, water-cooled globar source was attached to the rear side of the instrument (Figures 3.1 and 3.2). Energy enters through a source entry port and is deflected into the interferometer via a movable mirror. Since the energy of the external source does not pass through the aperture wheel before entering the interferometer, the aperture always remains on maximum.

### 3.2.1.4 \( N_2 \) Purge

The humidity of the interferometer is kept low by use of desiccants inside the housing. Additionally, the system can be purged with \( N_2 \) during series of measurements. This further reduces water vapor and \( CO_2 \) inside the system, both of which can impact the measured TIR spectra. The purge gas enters the interferometer compartment and flows through the connecting funnel to the integrating sphere, where it exits through the various ports.

### 3.2.1.5 Sample Port

The sample port is 30 mm in diameter with a measurement spot of about 25 mm. For samples that are smaller than 30 mm, port reducers of the same diffuse gold coating as the sphere can be attached to the
3.3 Measurement Procedures

A standard TIR measurement procedure using the integrating sphere was developed for the spectral laboratories at the University of Twente, Faculty ITC (UT-ITC). It satisfies the requirements for typical earth science samples in terms of, for example, signal-to-noise ratio, spectral resolution and measurement time. This standard procedure is a baseline from which adjustments can be made as necessary.

3.3.1 Instrument Preparation

At least 60 minutes before the first measurements the external globar source is turned on, the MCT detector cooled with liquid nitrogen and the purge gas flow set to 100 L/h. This guarantees a stable system during the measurements. If the Dewar of an already-cold MCT detector has to be refilled in mid-campaign, a waiting period of 30 minutes is observed before resuming measurements. During campaigns spanning several days the purge gas flow is reduced to 50 L/h at night. The external globar source is kept on until the end of the campaign.

3.3.2 Sample Preparation

Rock samples need little preparation. They are kept in the instrument room overnight to equalize temperature. Samples that are overly dusty (e.g., sawed drill cores) are cleaned with demineralized water and a brush and left to air dry overnight. Particulate samples, such as soils, are poured into Petri dishes. Depending on the application, clumps may be broken up and smoothened or kept in their original state. Samples are placed on a laboratory jack where aluminum foil is used to fix them in place and hold them level. They are then raised to just below the sample port with minimal to no opening between sample and port. For rock samples a flat part of the sample is selected to ensure good contact with the sample port. For very uneven samples this may not be possible, in which case some of the incoming radiation will leak past the sample and produce spectra with reduced reflectance values.

3.3.3 Settings

In the standard setup spectra are measured from 4,000–625 cm\(^{-1}\) (2.5 to 16.0 µm) at a resolution of 4 cm\(^{-1}\). Five hundred and twelve (512) scans are co-added for both reference and sample measurement. The
3. Laboratory spectrometer setup

Table 3.2  Extended measurement settings.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td>External watercooled globar</td>
</tr>
<tr>
<td>Beam splitter</td>
<td>KBr</td>
</tr>
<tr>
<td>Beam Path</td>
<td>External sphere</td>
</tr>
<tr>
<td>Detector</td>
<td>Liquid nitrogen cooled MCT</td>
</tr>
<tr>
<td>Spectral resolution</td>
<td>4 cm(^{-1})</td>
</tr>
<tr>
<td>Spectra recording range</td>
<td>7,000–500 cm(^{-1}) (1.4–20 µm)</td>
</tr>
<tr>
<td>Spectra useful range</td>
<td>4,000–625 cm(^{-1}) (2.5–16.0 µm)</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>double-sided forward-backward</td>
</tr>
<tr>
<td>Phase correction</td>
<td>Power spectrum</td>
</tr>
<tr>
<td>Phase resolution</td>
<td>128 cm(^{-1})</td>
</tr>
<tr>
<td>Apodization</td>
<td>Happ-Genzel</td>
</tr>
<tr>
<td>Zero filling factor</td>
<td>4</td>
</tr>
<tr>
<td>Scanner velocity</td>
<td>20 kHz</td>
</tr>
<tr>
<td>Aperture</td>
<td>Open (source limited)</td>
</tr>
<tr>
<td>Low pass filter</td>
<td>20 kHz</td>
</tr>
<tr>
<td>High pass filter</td>
<td>Open</td>
</tr>
<tr>
<td>Purge</td>
<td>Nitrogen gas at 100 L/h</td>
</tr>
<tr>
<td>Acquisition delay</td>
<td>120 seconds purge delay after sample switch</td>
</tr>
</tbody>
</table>

The number of co-added scans is a compromise to keep the scan numbers identical for the highly-reflective gold standard and for the much less reflective samples. Most sample materials do not achieve a sufficiently high signal-to-noise ratio (SNR) with 512 scans so that the operator must decide how many times to repeat the sample measurement (see next paragraph). Since the gold standard is only measured once per sample, nearly half of the measurement time is saved. For more details on the settings see Table 3.2.

3.3.4 Measurement Sequence

The system is calibrated using the substitution method. A highly diffuse Labsphere Infragold\(^\text{®}\) standard is used which has a 2.5–15 µm calibration certificate traceable to the National Institutes of Standards and Technology (NIST). Even though the instrument drift is minimal, atmospheric changes in the system warrant a calibration measurement before each new sample. After placing the standard under the sampling port, the system is left to purge for two minutes, after which the reference measurement begins. The standard under the sample port is then replaced by the sample. After a two minute purge delay the sample is repeatedly measured (usually eight times without moving the sample) until an SNR acceptable for the application is reached. If an average measurement of an inhomogeneous sample is required, the sample can be moved in between repeat measurements. An entire measurement sequence (including reference measurement, eight repeat measurements of the sample and twice two minutes purge delay) lasts for about 30
3.3 Measurement Procedures

3.3.5 Background Radiation Removal

A small fraction of the incoming light is reflected back into the sphere off the edge of the sample port rather than from the sample itself. The resulting spectra show elevated reflectance values that require correction. This effect is more pronounced when a port reducer is used, since a larger fraction of the incoming energy is reflected by the port reducer. To correct for this effect a background radiation measurement is taken once a day with an empty sample port. Most of the incoming energy exits the system through the empty port. The small fraction scattered back from the edge of the sphere is recorded in a background measurement, which is used in the formula to convert the sample spectra to absolute reflectance spectra.

3.3.6 Calculation of Reflectance and Emissivity Spectra

As a standard procedure in FTIR spectroscopy, energy spectra are measured as a function of mirror movement, which is then recalculated by the manufacturer’s software to a function of wavelength through a Fourier transform. The measured energy at the detector depends on the radiance leaving the target \( B_{\text{sample}} \) or \( B_{\text{reference}} \), respectively, the background radiance \( B_{\text{background}} \) mentioned above, as well as the spectrometer’s response function \( F(\lambda) \). The measured energies \( V \) are then:

\[
V_{\text{sample}}(\lambda) = [B_{\text{sample}}(\lambda) + B_{\text{background}}(\lambda)] F(\lambda) \tag{3.1}
\]
\[
V_{\text{reference}}(\lambda) = [B_{\text{reference}}(\lambda) + B_{\text{background}}(\lambda)] F(\lambda) \tag{3.2}
\]
\[
V_{\text{open}}(\lambda) = B_{\text{background}}(\lambda) F(\lambda) \tag{3.3}
\]

for sample, reference and open sample port measurement, respectively (see Figure 3.4).

The sample reflectance spectrum \( R_{\text{sample}} \) can be defined as:

\[
R_{\text{sample}}(\lambda) = \frac{B_{\text{sample}}(\lambda) R_{\text{reference}}(\lambda)}{B_{\text{reference}}(\lambda)} \tag{3.4}
\]

where \( B_{\text{sample}} \) is the radiance reaching the detector from the sample, \( B_{\text{reference}} \) the radiance reaching the detector from the reference material (i.e., gold standard) and \( R_{\text{reference}} \) the calibrated reflectance spectrum of the gold standard.

By substituting Equations 3.1 to 3.3 into Equation 3.4 we obtain:

\[
R_{\text{sample}}(\lambda) = \frac{V_{\text{sample}}(\lambda)}{V_{\text{reference}}(\lambda)} R_{\text{reference}}(\lambda) \quad \frac{V_{\text{open}}(\lambda)}{V_{\text{open}}(\lambda)} = \frac{F(\lambda)}{F(\lambda)} \tag{3.5}
\]

where the spectrometer’s response function \( F(\lambda) \) can be isolated from the differences and drops out of the equation. The final version of the
3. Laboratory spectrometer setup

Figure 3.4 Example of raw energy spectra for a measurement sequence of a sample (here quartz sand with port reducer installed). In orange the gold standard energy spectrum ($V_{\text{reference}}$), in green the quartz sand sample ($V_{\text{sample}}$) and in red the open sample port ($V_{\text{open}}$). The blue line shows the fraction of incoming energy that is reflected by the sample port edge and port reducer ($V_{\text{open}}$) as a function of wavelength.

The equation is:

$$R_{\text{sample}}(\lambda) = \frac{V_{\text{sample}}(\lambda) - V_{\text{open}}(\lambda)}{V_{\text{reference}}(\lambda) - V_{\text{open}}(\lambda)} R_{\text{reference}}(\lambda)$$

(3.6)

where $V_{\text{sample}}$, $V_{\text{reference}}$ and $V_{\text{open}}$ are taken from measurement, and $R_{\text{reference}}$ is the existing calibrated reflectance spectrum of the standard material (e.g., Infragold®).

Depending on the application, reflectance spectra may not be the desired format for further processing. Using Kirchhoff’s Law (Nicodemus, 1965), which in its simplest form can be written as:

$$\varepsilon_{\text{sample}}(\lambda) = 1 - R_{\text{sample}}(\lambda)$$

(3.7)

emissivity spectra ($\varepsilon_{\text{sample}}$) can be calculated from reflectance spectra ($R_{\text{sample}}$) of the sample.

3.4 Standards

Standard materials are important to check system behavior relative to itself in the short and long run, and in absolute terms as compared to
other laboratories. The diffuse gold standard used in all measurements is about 97% reflective and behaves quite differently from typical earth science samples that for the most part reflect in the range of 0% to 20%.

To measure the performance of the instrument on a typical earth science sample, a quartz sand standard was acquired from CSIRO Australia (see below). Furthermore, demineralized water, with a reflectance of only a few percent, is used to check the noise levels at very low signal values. These two standard samples are used in all reproducibility tests and comparisons with other laboratories. They are measured at the beginning and/or the end of measurement campaigns to confirm system performance; these are mandatory checks after a component has been changed or re-aligned, for example, mirror alignments, replacement of laser or source globar.

3.4.1 Quartz Sand

The quartz standard is a 99.5% pure quartz sand acquired by CSIRO’s Division of Minerals and Mining from Cook Industries Pty Ltd, Australia. Its purity was tested with X-Ray Fluorescence (XRF), Induced Coupled Plasma Mass Spectrometry (ICP-MS) and Loss on Ignition (LoI) analyses. Particle size was determined by laser diffraction for the range of 20 nm to 2 mm. The sample was first dispersed in water with sodium hexametaphosphate as an additive and placed in an ultrasonic bath for 20 minutes. All particles in the quartz sand standard fall within the 100–500 µm grain size range. For the measurement, the quartz sand sample is poured into a Petri dish, the surface is flattened and lightly compressed with a spatula such that the surface is even with the rim of the dish, and a small amount of sand is sprinkled on top of the flattened surface to minimize particle orientation issues in the measured signal. The sample is placed under the sample port such that the edges of the sample port contact the sample material.

3.4.2 Water

For the water sample, a Petri dish is (over-)filled with demineralized water. This is brought up to the sample port until the water surface is in contact with the outside of the sphere. Through surface tension, water engulfs the sample port without entering the sphere.

3.5 Results

In this section spectra taken on the standard samples are shown, along with calculated system performance indicators.

3.5.1 Reproducibility

To test the reproducibility of the system, replicate measurements were taken of the same sample material. To illustrate reproducibility over a...
3. Laboratory spectrometer setup

Figure 3.5 Ten day reproducibility test. Mean spectrum (black line) of 10 quartz sand measurements taken on ten days in a two week period, and the corresponding standard deviation (light blue band). Standard deviations are in the range 0.001 to 0.007 for most wavelengths.

typical measurement campaign, the same sample material was measured on ten different days over a two week period. For each wavelength the mean and standard deviation of the ten measurements were calculated and the mean spectrum was plotted with the standard deviation as an uncertainty band around the mean.

The spectra of the quartz sand sample show good reproducibility over the two-week period, with standard deviations ranging between 0.001 to 0.007 reflectance values for most wavelengths (Figure 3.5). Wavelength ranges influenced by water vapor and CO$_2$ show a larger standard deviation of the measurements due to small variations in atmospheric conditions during measurements even with the N$_2$-purge. Towards 16 µm the standard deviation increases as this wavelength is near the limit of the useful detector range. The spectra of the demineralized water also show good reproducibility over the two weeks, with standard deviations of under 0.002 for most wavelengths (Figure 3.6).

To illustrate the long-term reproducibility between measurement campaigns, four measurements of the quartz sand standard spanning 20 months were compared. Measurements of the standard were taken at the beginning of measurement campaigns as well as after maintenance on optical components of the system, for example, port reducers installed, NeHe laser or globar source replaced, mirrors or interferometer aligned. The results show a standard deviation between 0.002 and 0.006 (Figure 3.7), hence, the long-term reproducibility is as good as the two-
3.5. Results

Figure 3.6  Ten day reproducibility test. Mean spectrum (black line) of 10 demineralized water measurements taken on ten days in a two week period, and the corresponding standard deviation (light blue band). Standard deviations are below 0.002 for most wavelengths. Note y-scale difference from Figure 3.5.

... week reproducibility. This illustrates that reference measurement and background radiance removal properly corrected the effects of aging and maintenance on optical components, and that they did not influence the measured absolute emissivity spectra beyond the measured short-term uncertainty level of the system.

3.5.2 Absolute Reflectance Values

In order to assess the absolute reflectance values measured by this instrument setup, NIST-traceable standards of various reflectance levels are needed. While these reflectance standards are readily available for NIR and SWIR, they are missing for the mid-infrared (MIR). Instead, MIR reflectance levels are commonly pegged at two extremes: zero (with the help of, for example, a light trap or an empty sample port measurement) and near-perfect reflection (using the gold standard). A linear response of the system is assumed for intermediate reflectances. To evaluate the absolute reflectance values in a comparative sense, the average spectra of our two standards were compared with results from FTIR spectrometers of other leading organizations in the field of laboratory spectroscopy on earth science samples.
3. Laboratory spectrometer setup

Figure 3.7  Long term reproducibility test. Mean spectrum (black line) of four quartz sand measurements taken over the course of twenty months, and the corresponding standard deviation (light blue band). Standard deviations are in the range 0.002 to 0.006 for most wavelengths.

3.5.2.1 Quartz Standard

Spectra of the same quartz sand standard were measured at several laboratories (Abbott, E., JPL; Crowley, J., USGS Reston; Ninomiya-san, GSJ) and compared. The instruments used at these laboratories vary in make, age, interferometer type and measurement protocol. However, they all use a directional-hemispherical integrating sphere and a resolution of 4 $\text{cm}^{-1}$. The agreement between different laboratories is highest for low reflectance values (Figure 3.8). In spectral features, where reflectance is high, the discrepancies between laboratories are larger but stay within 0.07 reflectance units of each other for most of the usable spectral range. For wavelengths longer than 14 $\mu\text{m}$ the discrepancies increases due to the end of the useful detector range for some of the systems. Wavelengths short of 3 $\mu\text{m}$ also show increased variance with a spread of about 10% which could be caused by the end of the calibration range of the calibration standards.

The UT-ITC spectrum of the quartz sand (oven dried) is in good agreement with the spectra of the other laboratories; absolute reflectance values plot mostly in between the other laboratories' measurements or within 0.025 reflectance units of the mean of the three laboratories (for the effective detector range). For very low reflectance values, the UT-ITC spectrum tends to have marginally lower values than the other three spectra.
3.5. Results

Figure 3.8 Spectra of the same quartz sand standard measured by UT-ITC (solid black: oven-dried; dashed black: air-dried), compared to JPL (red), GSJ (blue) and USGS (green).

3.5.2.2 Demineralized Water Standard

The UT-ITC demineralized water spectrum was compared to a distilled water spectrum from JHU available in the ASTER spectral library (Baldridge et al., 2009), one from the spectroscopy laboratory at USGS Reston (tap water; Ribeiro da Luz, 2011) and one from JPL (Abbott, 2011). The comparison of these spectra (Figure 3.9) show distinctly different noise levels, which are a function of the instrument setup, the variable and unknown number of scans that were co-added to produce the spectra and some unknown smoothing, and should not be used as a measure of instrument quality. Since our comparison is of absolute reflectance values, the variable noise levels do not affect its interpretation. The four absolute reflectance values are in good agreement, being within 0.007 reflectance units for most of the usable spectral range.

The UT-ITC demineralized water spectrum is in good agreement with the spectra of the other laboratories and plots in between their measurements for wavelengths < 5 µm. For longer wavelengths, the UT-ITC measurement shows a small negative bias but is within 0.004 reflectance units of the mean of the other three laboratories.
3. Laboratory spectrometer setup

![Graph](image)

Figure 3.9  Spectra of demineralized water measured by UT-ITC (black), compared to JPL (red), JHU (blue) and USGS (green).

3.6 Discussion and Recommendations

The substitution calibration method used in our standard measurement method, which was also used in the other instrument set-ups at JPL, JHU and USGS, creates small radiometric inaccuracies (Hanssen & Snail, 2006). This is because the sample is part of the sphere wall, so that the average sphere wall reflectance is lower when the sample, instead of the reference material, is in the sample port. This effect makes low reflection samples appear even darker than they are. Jacquez & Kuppenheim (1955, Eq. 3.9) quantify the substitution error for a simple integrating sphere. When their equation is applied to our system, the substitution for a sample of 40% reflectance results in an underestimation of more than 11% relative (about 0.044 absolute reflectance). One of the design features of our system is the movable folding mirror that also allows the radiometrically superior comparative calibration method, which uses the sphere wall as the calibration standard. However, by moving the mirror to measure the calibration spot on the sphere wall, the measuring geometry of the sphere is slightly altered, thus changing the average optical path length of the radiation before it enters the detector. This small difference proved to be too much, so that the resulting reflectance spectra showed strong residual influence of atmospheric gases. Therefore, the system is currently operated in the substitution calibration mode. **Recommendation:** To take full advantage of the comparative calibration mode, the sphere design should produce identical average path lengths.
3.6. Discussion and Recommendations

for the calibration and sample measurements. One way to achieve this would be a folding mirror that rotates through 180 degrees, folding the energy to the measurement port on the south pole or upwards towards the calibration spot on the north pole of the integrating sphere. The detector would have to be placed in the same plane as the incident energy most logically at the far end on the equator of the sphere. Compared to our design, this sphere would be perfectly symmetrical but would allow for only one detector placement and would also require baffles for the detector on the inside of the sphere. An alternative design for an absolute diffuse reflectometer using an integrating sphere is offered by Sheffer et al. (1990). Their design uses a lower hemisphere that is separated from the upper one at the equator and rotates on the vertical axis. If with the current design the substitution method is to be used in the future, a partial mathematical correction of the substitution error should be developed. Since some of the necessary parameters, for example sphere wall reflectance and the assumption that total energy absorption at detector ports is correct, are not known accurately for our sphere, parallel tests on an absolute diffuse reflectance system should be undertaken for calibration.

Particulate standard materials are susceptible to changes in humidity content. For an experiment with an emissive FT-IR system, the quartz sand standard was heated overnight in a forced convection oven to 70 degrees Celsius. When measured a day later with the directional-hemispherical instrument described above, the standard showed reflection peaks that were over 4% higher than in air-dried state. After several months in a closed, but not airtight, container, the reflectance values returned to normal. It appears that heating the sample removed extra humidity from the air-dried sample, thus increasing its reflectivity. Even though the sample contained no hygroscopic minerals and had been wet-sieved to remove particles smaller than 0.1 mm, it appears that the removal of the excess water was reversible, so that with time the sample re-adjusted to its earlier air-dried state. This serendipitous experiment raises the question of how far even coarser particulate standards change their reflectivity in response to the relative humidity of the laboratory environment.

Recommendation: If possible homogeneous solids should be used as standard materials as their reflectivity is less likely to change in response to changing environmental conditions. A single synthetic quartz crystal would be a possibility. However exact optical axis orientation of the standard as well as polarization effects of the spectrometer setup would have to be controlled. Instead, amorphous glass standards, such as obsidian, could be used. An alternative would be particulate samples, oven-dried and stored in a desiccator before every measurement. With dry \( N_2 \) running over the sample, even an extended measurement period of 60 minutes should not significantly change the sample moisture content.

Comparison with other laboratory revealed that at low reflectance values the UT-ITC spectra are offset to lower values. Since port reducers
3. Laboratory spectrometer setup

are frequently used in the UT-ITC laboratory to measure samples smaller than the full sample port, the processing chain to absolute reflectance values requires background radiation removal to correct for the energy that bounces back into the sphere from the edge of the sample port rather than the sample itself. The long term stability measurements (Figure 3.7) proved that background radiation removal is effective and that there is no statistical difference between measurements with and without port reducers. It is likely that at other laboratories a small fraction of the incident radiation scatters off the sample port edge as well, but since no port reducers are applied, this small effect goes unnoticed and is not corrected for. To our knowledge, none of the other laboratories routinely employs open sample port or light trap measurements to remove the background radiance. This finding is corroborated by the results in Figure 3.4 the blue line shows that the fraction of incoming energy that is reflected by the sample port edge and port reducer increases from 2% at 2.5 $\mu m$ to over 4% at 16 $\mu m$. By comparison, without port reducer these values are about 0.8% and 1.6%, respectively. However, the resulting reflectance spectra show mutually identical values at low reflectances (Figure 3.7), indicating that the background radiation removal is successful. If this wavelength-dependent effect applies to other instruments, it explains why at longer wavelengths spectra of other laboratories drift gradually to higher reflectance values as compared to UT-ITC results.

Recommendation: Other TIR spectroscopy laboratories may consider doing empty sample port/light trap measurements to check the amount of energy measured in the system without a sample present. If the directly reflected energy, that is, the energy that does not first hit the sample, exceeds several percent of the total measured energy, background radiation removal should be considered.
4.1 Introduction

In order to be able to compare laboratory TIR spectroscopy to airborne TIR imagery, customized instruments with particular measurement geometries have to be used. In Chapter 3, the ITC-UT instrument setup was described, including the measurement settings and the optimized processing chain to measure absolute directional-hemispherical reflectance values of typical earth science samples in the thermal infrared. In the following chapter, laboratory spectral measurements on rock samples are used to test in how far we can determine mineral modes of feldspars and quartz as well as plagioclase composition with the help of partial least squares regression. In this chapter, the statistical regression models are built on laboratory spectra, before they are applied to airborne imagery in the next parts of this thesis.

4.1.1 Differences to existing approaches

Optical mineralogy has been a successful and commonly used analytical method by petrologists for many decades. With the help of a petrographic microscope, thin sections of rock samples can be analyzed to reveal, among others, mineralogic composition, textures and overprinting relationships between minerals. Alternatively, infrared spectroscopy has been used in mineralogic studies (e.g., van Ruitenbeek et al., 2005; Hunt & Turner, 1953). Different analytical approaches measure the reflected, transmitted, absorbed or emitted portion of infrared radiation as a function of wavelength, which influence the information we can extract from the spectroscopic data (e.g., Hecker et al., 2010; Ramsey, 2004). Historically, reflectance measurements in the short-wave infrared

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1This chapter is based on the following paper: Hecker, C., Dilles, J.H., van der Meijde, M. and van der Meer, F.D. (2012) Thermal infrared spectroscopy and partial least squares regression to determine mineral modes of granitoid rocks. *Geochemistry, Geophysics, Geosystems (G3)*, 13(3), 1-15.
4. Laboratory TIR spectroscopy and PLSR modeling

region have received most of the attention. A number of important rock-forming silicate minerals (such as quartz and most feldspars), however, are indistinct in short-wave infrared spectra and show conspicuous spectral features only at longer wavelengths (Salisbury et al., 1991). Existing literature has shown that thermal infrared (TIR) spectra can be used successfully to identify rock-forming minerals in samples (e.g., Vaughan et al., 2005; Salisbury & D’Aria, 1992) as well as to give quantitative information on minerals in a rock sample (e.g., Milam et al., 2007; Feely & Christensen, 1999; Ramsey & Christensen, 1998; Ruff, 1998).

Most existing studies (e.g., Milam et al., 2004; Ramsey, 2004; Feely & Christensen, 1999; Ramsey et al., 1999; Thomson & Salisbury, 1993; Gillespie, 1992b) extract quantitative mineral abundance information from TIR spectra by means of a linear spectral mixture analysis (SMA). The fundamental assumption is that the measured rock spectrum is a linear combination of its components (minerals), weighted by each mineral’s areal fraction. Typically, the fractions of each possible mineral are varied until the resulting rock spectrum shows the least root mean square error as compared to the measured rock spectrum. Earlier studies have shown that the assumption of linear mixtures is essentially true in the thermal infrared wavelength region for rocks or coarse particulate samples, where surface reflection dominates and volume scattering (energy passing through the grains) is minimal (e.g., Feely & Christensen, 1999; Ramsey & Christensen, 1998; Thomson & Salisbury, 1993). To function properly and give reliable results, SMA algorithms require a database that contains spectra of all mineral components that are to be expected in the rocks to be analyzed. Missing endmembers can either result in large root mean square errors or are partially (but incorrectly) compensated by linear combinations of other minerals (Rogge et al., 2006). Especially with complex mineral groups (like feldspars and amphiboles) it can be challenging to acquire pure sample material and representative spectra for all compositional and structural variations within the group. Furthermore, an over-complete spectral database (i.e., containing spectra that do not occur in the rock spectrum to be unmixed), as well as strong correlation between endmembers can lead to an increased error of the abundance estimates similar to an incomplete database (van der Meer & Jia, 2012; Rogge et al., 2006).

In this chapter, a different approach is presented to extract mineralogic information from TIR spectra. An approach that is not based on an input library of pure mineral spectra nor tries to extract spectral endmembers from the (Bandfield et al., 2000). Instead, modal mineralogy information on a number of samples is used to build a quantitative multivariate partial least squares regression (PLSR) model that links the mineralogy of the samples to their respective TIR spectral signatures. The resulting PLSR model can be applied to another set of samples, for which only TIR spectra are available, and modal mineralogy can be estimated quickly and inexpensively from TIR spectra. The methodology has potential to a) partially replace expensive and time consuming laboratory analyses (such as thin section analysis or x-ray diffraction),
b) conduct modal determination from TIR spectra directly in the field and c) be applied to airborne data for mapping of spatial mineralogic patterns on TIR imagery. Here the methodology will be assessed on a petrographically well-defined sample dataset from Yerington, Nevada (Dilles & Einaudi, 1992; Dilles, 1984). The results will show if and how well thermal infrared reflectance spectroscopy and PLSR can estimate modal percentages of the main rock forming minerals in samples.

4.2 Methodology

4.2.1 Modal Mineralogy

Modal mineralogy from optical microscopy was chosen as the reference method to which all PLSR results will be compared. This petrographic information (see Table A.1 in Appendix A) stems from Dilles (1984) and Dilles & Einaudi (1992), and was collected on igneous samples (ranging from gabbroic and andesitic to granitic) from a porphyry copper deposit in Yerington, Nevada. Hydrothermal alteration in the area created distinct zones of potassic, sodic-calcic, quartz-sericite and tourmaline alteration. Areas close to neighboring sedimentary rocks show skarn alteration (see Section 1.3 for details). Alkali feldspar, plagioclase and quartz (Afsp, Plg, Qtz) modes were determined in percent of the thin section area (areal%) with traditional polarization microscopy (Dilles, 1984). These areal% data were not converted to typical volume% used for mineral modes sensu stricto since spectroscopy is sensitive to areal% as well. Error estimates for the modal mineralogy are similar to those typically quoted in literature, with accuracies of ±5–15% for major minerals (≥ 10% of area) and ±<5% for minor minerals (<10% of area) (Hamilton & Christensen, 2000; Feely & Christensen, 1999). In altered samples, for each mineral phase the percentage of alteration as well as the alteration product was taken into account. This ensures that the tabular modal descriptions represent the current mineral composition of the samples (after alteration) and gives the best possible basis for comparison to TIR spectra.

Plagioclase composition (Plgcomp) was determined using the a-normal method (i.e., measurement of extinction angle with 010 cleavage in grain sections normal to a-axis, Deer et al., 1992) on several grains per thin section, and confirmed with electron microprobe on selected samples, with corresponding errors approximately ±1-2 mol% and ±1 mol%, respectively. In samples with zoned plagioclase, compositions were estimated on several spots from core to rim of individual grains and the results were averaged.

4.2.2 Thermal Infrared Spectroscopy

Since coverslips ruled out spectroscopy directly on the thin sections, the corresponding offcuts from the thin section production were used in the
4. Laboratory TIR spectroscopy and PLSR modeling

TIR reflectance spectroscopy assuming that mineral modes were similar. The 105 sample blocks were prepared for the spectral measurements by grinding the measurement surface with 80-grit silicon carbide powder. This removed remnants of epoxy glue, sodium cobaltinitrite staining and saw markings from the surface to be measured. The blocks were washed with distilled water and left to air dry for a day.

The TIR directional-hemispherical reflectance spectra were recorded with the Bruker Vertex 70 FTIR spectrometer (as described in Chapter 3 and (Hecker et al., 2011)), and ITC’s standard TIR measurement procedure was used as the basis for the measurement of the offcuts. Spectra were recorded from 1330–625 cm\(^{-1}\) (7.5 to 16.0 \(\mu\)m) at a resolution of 4 cm\(^{-1}\). A Labsphere Infragold diffuse gold standard was used as a reference before each new sample. For the reference as well as sample measurement, 512 scans were co-added. Additionally, each sample was measured a total of eight times (without moving the sample) and averaged again to improve signal-to-noise ratio. Repeatability of the FTIR measurements is high for most of the spectral range with standard deviations of the eight repeat measurements per sample around 0.0015 reflectance units (roughly 0.6% of a typical reflectance value of 0.25). The standard deviation increases to 0.0080 toward the far end of the wavelength range where the limits of the detector sensitivity range are reached.

For this particular study a 20 mm port reducer with the same diffuse gold coating was mounted to the sampling port to prevent incident energy from leaking past the edges of the sample blocks. This reduces the measurement spot from about 25 mm to 20 mm diameter on the sample surface (about a third of the entire offcut’s surface area). The central part of each block was measured except for very heterogeneous samples, where the most representative part of the block was selected for measurement. For two samples, duplicate measurements were done at the beginning and the end of the measurement series (spanning several months) to test for possible drift in detector sensitivity as well as for sampling errors (i.e., slightly different measuring spot on the sample surface). The difference in the duplicates usually stays within 0.01 reflectance units, with an occasional value up to 0.02.

4.2.3 Partial Least Squares Regression

Partial least squares regression (PLSR) is a quantitative multivariate statistical tool that allows for the analysis of data with strong correlations and with noise (Wold et al., 2001). In a first step, a PLSR model is built, using a training set of samples for which the spectral information as well as the modal mineralogy is known. In the second step, the resulting PLSR model can be applied to new samples for which only spectra are available, and the modal mineralogy is modeled from the TIR spectra alone. In this thesis four PLSR models were built to predict alkali feldspar, plagioclase and quartz modes, as well as the average plagioclase composition in the samples.
4.2. Methodology

Contrary to the more general multiple linear regression model, PLSR can also handle datasets with more variables than samples. Hence, it is especially useful for spectroscopic datasets that contain reflectance values at hundreds to thousands of wavelengths. While originally developed for the field of chemometrics, PLSR has been applied to a number of spectroscopic studies in diverse application fields such as vegetation studies (e.g., Asner & Martin, 2008), soil mechanics (Yitagesu et al., 2009) and land degradation (Farifteh et al., 2007). Goetz et al. (2009) used PLSR to build a predictive mineral model from near and short-wave infrared spectra recorded on gangue material on a conveyor belt. Cudahy et al. (2001d, 2009) applied PLSR for the first time to thermal infrared spectra of rock samples and compared them to X-ray diffraction d-spacing results.

PLSR creates a regression model that uses a set of predictor variables \( X \) (in this case, the TIR spectra) to predict the occurrence and concentration of a set of response variables \( Y \) (in this case, the modal mineralogy of the samples from the thin section analysis). Similar to a principal component analysis (PCA), the high dimensional \( X \)-matrix is reduced to a few factors or latent variables by a projection to an orthogonal system of small dimensionality. The main difference being that in a PCA, the variance in \( X \) is maximized while in a PLSR the covariance between \( X \) and \( Y \) is maximized (Esbensen, 2006). This causes the first few factors to contain the spectral content that is most representative and predictive of the \( Y \) values while higher number factors contain spectral content that is either not related to the particular predicted \( Y \) or contains noise. In this thesis, the nonlinear iterative partial least squares (NIPALS) algorithm as implemented in The Unscrambler software (Camo Software, 2010) was used. For a more detailed introduction to PLSR theory and algorithms, the reader is referred to excellent existing literature (e.g., Esbensen, 2006; Wold et al., 2001; Geladi & Kowalski, 1986)

4.2.3.1 Pre-processing

A typical pre-processing chain for PLSR input data consists of data transformation, mean-centering and scaling (Wold et al., 2001). While PLSR does not have any particular prerequisites in terms of variable distribution (Chin, 1998), a symmetric histogram is preferred (Wold et al., 2001). For this particular data set, the response variables (mineral modes) were transformed with arcsine (modes of alkali feldspar and quartz as well as the composition of the plagioclase) or power transformation (plagioclase modes) to improve the symmetry of their histograms. To improve numerical stability and facilitate interpretation (Wold et al., 2001), predictor and response variables were mean-centered by subtracting the average of the individual variable (Geladi & Kowalski, 1986). Scaling of variables is important if they do not share the same value ranges. In those cases, variables with small value ranges will be under-represented in the final model. For this dataset, no scaling was applied since all variables are already expressed in percentages and cover, therefore, the same value
range. Not scaling the spectral variables has two further advantages: first, the resulting regression coefficients are directly interpretable in terms of spectral features of minerals and second, it prevents measurement noise in low reflective parts of the spectrum from influencing the model results.

4.2.3.2 Validation

During the building of the PLSR model (i.e., projection of the TIR spectra into orthogonal factors), the main spectral information that is explaining the mineral modes is compressed in the first few factors, while later factors contain mainly noise. The validation of the PLSR model has two main purposes: a) to separate the factors that contain useful information from those that are consisting mainly of noise and b) to supply a quantitative measure of the expected error in the model. This quantitative measure of the overall “goodness of fit” is represented by a root mean square error of prediction (RMSEP) that is defined as

\[ RMSEP = \sqrt{\frac{\sum_{i=1}^{n} (\hat{y}_i - y_{i,\text{ref}})^2}{n}} \]  

(4.1)

where \( \hat{y}_i \) is the modeled response variable, \( y_{i,\text{ref}} \) the true measured response variable and \( n \) is the number of samples.

RMSEP can either be calculated on an entirely separate validation dataset (not included during the model building), or by cross validation, an iterative process that withholds each time a number of samples from of the model building set. The limited number of samples (105, plus two duplicates) and the level of uncertainty in the thin section data make the use of an independent validation dataset (e.g., 1/3 of all samples not available for model building) undesirable. Instead, a segmented cross validation was used, where samples were split up into 10 segments. The samples were first ordered by the variable to be predicted and successively one-for-one distributed into the 10 segments. This technique ensures that each segment contains an equal number of samples with low, medium and high values of a particular response variable. The two duplicates were each assigned to the same group as their respective original measurement, to prevent the same sample from occurring in the model building as well as validation set.

The PLSR model is built 10 times, each time a different segment is kept out of the model building set and used for validation. RMSEP values are calculated for each segment and averaged to form the overall RMSEP of the model.

4.2.3.3 Number of Factors

The selection of the proper number of factors is imperative for a good regression model: too small and the model will not be able to account for the complexity of the mixed samples, too large and the model will over-fit
4.3. Results

As a guideline, the number of factors that creates the best prediction (i.e., smallest RMSEP) was considered optimal (Figures B.1, B.3, B.5, and B.7 in Appendix B). If the predicted error only decreased minimally when including an extra factor, it was decided to not include the extra factor, as a model with less factors is more robust when applied to new data (Esbensen, 2006). In the case of the plagioclase composition model, the RMSEP plot had a local minimum at five and a global minimum at eight factors. The model using eight factors was observably overfitting the calibration data: the loading weights started to become very unspecific and noisy, and the regression coefficients stopped showing spectral features characteristic of the mineral being modeled (for examples of loading weights and regression coefficients see the results section). In this particular case, the local minimum at five factors in the RMSEP plot was used as the cutoff.

4.2.3.4 Prediction

As the final stage in the PLSR modeling, the previously built models are used to predict sample fractions for the modeled minerals from the TIR spectroscopy. For that purpose the PLSR model’s regression coefficients are applied to thermal infrared reflectance spectra with unknown mineral modes, where the predicted variable

\[ \hat{y} = B_0 + B_1 X_1 + B_2 X_2 + \ldots + B_n X_n \]  

(4.2)

where \( \hat{y} \) is the predicted response variable (e.g., quartz modes), \( B_1 \) to \( B_n \) the regression coefficients at all wavelengths, \( X_1 \) to \( X_n \) the reflectance values at all wavelengths and \( B_0 \) the regression coefficient bias. In a final step, the inverse of the earlier data transformations are applied to revert the prediction results to compositional information in the original units of areal percentages.

4.3 Results

4.3.1 TIR Spectra

The igneous rocks studied here are typically intermediate in acidity and contain two feldspars, quartz, and sometimes amphiboles or pyroxenes that have features in the TIR rock spectra. Additionally, alteration minerals that occur frequently are sericite, secondary alkali and plagioclase feldspar, epidote and chlorite. Figure 4.1 shows examples of TIR rock spectra from this study with the most diagnostic features in the reststrahlen band (about 8–12 μm). The range of 12.5–14.0 μm contains additional features of feldspar (Figure 4.1c) and quartz (Figure 4.1d). Figure 4.1c is an example in which all TIR active minerals have been albitedized by alteration and the TIR spectrum only shows features of Na-plagioclase. Most other samples, however, are strongly mixed spectra...
Figure 4.1 Thermal infrared spectra from a selection of samples as an illustration of their spectral content. The major spectral features are labeled with the mineral that causes it. Qtz = quartz, Mcl = microcline, Na_plag = sodic plagioclase, Hbl = hornblende, Ca_plag = calcic plagioclase, Ms = muscovite.
4.3. Results

with overlapping features of several minerals in the reststrahlen band (e.g., Figures 4.1a and 4.1b) that can make mineral identification difficult and quantification impossible without multivariate modeling or mixing analysis.

4.3.2 PLSR Model Outputs

The main outputs of a PLSR model are the RMSEP plot, the loading weights and the regression coefficient spectra (Figure 4.2 and Appendix B). The use and the interpretation of each of these output datasets will be explained on the example of the alkali feldspar model. The plagioclase, quartz and plagioclase composition models are explained in detail in Appendix B.

4.3.2.1 RMSEP Plot

The RMSEP plot shows the predicted mean error (from the cross validation analysis) as a function of the number of factors used. For the alkali feldspar model, the predicted error increases again after a global minimum at six factors, as the model starts fitting noise in the data (Figure B.1). Since the gain in RMSEP between a model of five and six factors is minimal, the more robust five factor model was used.

4.3.2.2 Loading Weights

Since the predictor variables are spectral data, the resulting loading weights and regression coefficients can be plotted and interpreted as spectra as well. The loading weights of a factor show which wavelengths are important in defining that particular factor. Through spectral interpretation of the loading weights, we can understand which minerals and mineral combinations drive the particular PLSR model factor and, therefore, have a positive or negative link with the predicted variable.

A negative link denotes that inverse features of a particular mineral reduce the modeled amount in case those features are present. This is best explained in the case of the simple quartz model (Appendix B): If only factor 1 was used, samples with large albite content would have modeled quartz modes that are too high (due to overlaps in the quartz and albite reststrahlen features). The second factor is used to compensate for this effect and will reduce the quartz estimates in samples that are rich in albite, and increase the quartz estimates if samples are poor in albite. Hence, loading weights as well as regression coefficients (see below) can contain positive as well as inverse features of minerals to come up with an optimal modal estimate for the predicted mineral. For the alkali feldspar model, the loading weights of factor 1 (Figure 4.2) are strongly dominated by microcline, with reststrahlen features at 8.56, 9.24, 9.48 and 9.81 (all wavelengths are in units of $\mu$m). There are also features at 12.98, 13.37 and 15.35 that are caused by microcline. Loading weights of factor 2 show a negative link with a quartz spectrum and a positive link
4. Laboratory TIR spectroscopy and PLSR modeling

Figure 4.2 Loading weights (factors 1 to 4) and regression coefficients of the alkali feldspar model displayed as functions of wavelength. Wavelengths with regression coefficient values far from zero are influential for PLSR model.

with a couple of microcline features at 9.49 and 9.82. Loading weights of factor 3 show a negative link with a few albite features at 9.78 and 15.25, and a weak positive link with microcline features at 8.57, 8.76, 9.28, 9.47, 9.66, 12.69, 13.45. The 8.31 feature could not be assigned to a mineral. The loading weights of factor 4 are dominated by albite. The features show a negative link with albite at 8.58, 9.64, 9.81, 9.95, as well as the four features between 12.5 and 14 and the feature at 15.21. Furthermore, a broad feature at 10.78 indicates a link with more Ca-rich plagioclase, such as labradorite or bytownite. The loading weights of factor 5 (not displayed here) show clear structure but the features could not be assigned to a particular mineral spectrum.

4.3.2.3 Regression Coefficients

Regression coefficients summarize the relationship between the predictor variables and the response variable. While the loading weights show the influential wavelengths that define a particular factor, the regression coefficients show the influential wavelengths for the entire PLSR model. Wavelengths where the regression coefficients are close to zero have a
negligible influence on the prediction of a particular response variable, while large positive and large negative values indicate wavelengths that have a strong positive and negative link with the response variable in question. Applying the regression coefficients to thermal infrared spectra with unknown mineral modes results in a predicted value of that particular mineral.

The regression coefficient spectrum of the alkali feldspar model combines the information from the loading weights of factors 1 to 5. Most spectral features are linked positively to spectral features of microcline (8.62, 8.99, 9.28, 9.40, 9.47; all wavelengths in units of µm). The features at 8.21 and 8.62 are negatively linked to quartz, and features at 12.69, 13.12, 13.43 and 15.21 are negatively linked to albite. At the 10.78 wavelength, typical for Ca-rich plagioclase, the coefficients are nearly zero, thus showing that this wavelength region is not relevant in determining alkali feldspar modes. No evidence of other minerals was detected in the regression coefficients of the alkali feldspar model.

In a similar fashion, the regression coefficients of the other three models were analyzed (see Appendix B for details). The plagioclase model is guided by a combination of different albite features, as well as a Ca-plagioclase feature. Quartz and microcline features are included to a lesser degree in predicting the plagioclase amount in the sample.

The quartz model is a very simple model that contains only two factors. The regression coefficients also represent the simplicity of this model, which is driven mainly by the presence of quartz features and to a lesser degree by the absence of albite features.

The plagioclase composition model is the most complex model. The local minima in the RMSEP plot show that the projection of the predictor spectra to latent variables is not yet ideally predicting the response variable, and that the dataset possibly contains one or several outliers. Since all reasonable outliers (e.g., vague data description, uncertain mineral identification in thin section study) had been removed from the dataset earlier, no unjustifiable outlier removal, to artificially improve model performance, was implemented at this stage. As a consequence, the loading weight spectrum of the plagioclase composition model contains an accumulation of many mineral features and possibly noise. From the identifiable features, it appears that the plagioclase spectrum is mainly driven by sodic and calcic plagioclase as well as quartz content.

**4.3.3 Measured Versus Predicted**

After applying the regression coefficients to the spectral measurements and inverting the preprocessing transformation, the TIR spectrum of each sample predicts alkali feldspar, plagioclase and quartz modes, as well as a plagioclase composition. The PLSR modeling prediction results show the modeled percentage of a mineral in the TIR spectrum of the sample compared to the measured composition from the thin section analysis (Figure 4.3). Performance parameters of the various models are summarized in Table 4.1. The alkali feldspar (Afsp) model (Figure 4.3a)
4. Laboratory TIR spectroscopy and PLSR modeling

![Graphs showing PLSR modeling results for different minerals.]

**Figure 4.3** PLSR modeling results predicted (from spectroscopy) versus measured (from thin section) in areal percentages within the samples. Dashed line is regression line between measured and predicted values. Thin solid line represents the 1:1 line. Open circles indicate duplicate samples.

works well ($R^2 = 0.81$). It does contain, however, a small group of samples that contain 20–30% Afsp in the thin section measurements but only 5–15% in the PLSR model results. They do not show any common lithology or alteration patterns that could explain this discrepancy and for this reason they were kept in the model as is. The RMSEP for the Afsp model is $\pm 5.1\%$ absolute, which is equivalent to the lower end of the error estimate of the reference method.

The plagioclase model (Figure 4.3b) performs well ($R^2 = 0.80$). Samples with very low to no plagioclase show a larger spread in their model results than the rest of the samples. The RMSEP of the plagioclase prediction is $\pm 8.5\%$ absolute and can be attributed to the value range of the plagioclase percentages. The quartz model (Figure 4.3c) has an $R^2$ of 0.70. The prediction residuals show that the variance increases with increasing quartz content. This result can (at least partially) be attributed
4.3. Results

Table 4.1 Summary of PLSR modeling results per mineral.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Afsp</th>
<th>Plg</th>
<th>Qtz</th>
<th>Plgcomp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of factors used</td>
<td>5</td>
<td>4</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>RMSEP [in % abs.]</td>
<td>5.1</td>
<td>8.5</td>
<td>6.9</td>
<td>7.8</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.81</td>
<td>0.80</td>
<td>0.70</td>
<td>0.59</td>
</tr>
<tr>
<td>Slope (of regr. line)</td>
<td>0.86</td>
<td>0.82</td>
<td>0.79</td>
<td>0.61</td>
</tr>
</tbody>
</table>

$^a$ Mineral abbreviations used are as follows: Afsp = alkali feldspar; Plg = plagioclase; Qtz = quartz; Plgcomp = plagioclase composition.

to the thin section reference method, which has a growing estimated error with increases in quartz content. The RMSEP for quartz is ±6.9% absolute for the entire model. However, samples with less than about 30% quartz (in this case most igneous samples without the influence of quartz-sericite alteration) model better with a RMSEP of ±5.8% absolute.

The relationship between the measured versus predicted plagioclase compositions (Figure 4.3d) has an $R^2$ of 0.59, which is weaker than for the previous models. It is believed that the reference values from the thin section analysis overestimate the average anorthite content of plagioclase for samples with $>\text{An}_{40}$ due to the common procedure to measure core, intermediate zone and rim. The intermediate zones (and rims) dominate the area, but with most samples showing normally zoned plagioclase crystals (i.e., with calcic cores), averaging the measurements overestimates the calcic component as compared to spectroscopic results. The RMSEP of the plagioclase composition prediction has an estimated error of about ±8 mol% anorthite. There are clusters of samples that plot well off the regression line: a cluster at measured An$_{38}$ (that plots above the line) represents hornblende gabbroic rocks and other rocks with a distinct lack of Afsp. The cause for this is not understood and can also not be identified in the loading weights of the plagioclase model. A second cluster at a measured An$_{33}$ (that plots below the regression line) represents samples that have been slightly altered to chlorite, epidote ± sericite. The main spectral feature of chlorite around 9.86 $\mu$m could easily interfere with the oligoclase-feature at the same wavelength. It has to be noted, however, that no quantitative, consistent link could be made between the residuals of the plagioclase composition prediction and the amount of chlorite (or epidote/sericite for that matter) in the sample.

4.3.4 Ternary Plot

The modal mineralogy from thin section measurements and PLSR modeling on spectroscopic data are represented in a QAP (quartz-alkali feldspar-plagioclase) plot for plutonic rocks (Figure 4.4) (Le Maitre, 1989). The modal mineral percentages of the three minerals were normalized...
4. Laboratory TIR spectroscopy and PLSR modeling

Figure 4.4 Quartz-alkali feldspar-plagioclase diagram with thin section measurements (black dots) connected by a line to the corresponding composition predicted from the spectroscopic data (gray diamonds). Clusters a to e are described in the text. Triangle subdivisions are according to Le Maitre (1989). For field labels see Figure 4.5.

...to 100% before plotting. Although not strictly applicable to altered igneous rocks, both altered and unaltered rocks were plotted on the QAP diagram to compare the results of both methods. Contrary to the recommendations of Le Maitre (1989), the extreme sodic endmember of the plagioclase group (An$_{0}$–An$_{5}$) was kept with the plagioclase count rather than summing them up with the alkali feldspar modes since the sodic plagioclases form part of a continuous albite-oligoclase mixture sequence in the reference dataset. Five clusters of samples are discernible in the QAP diagram: a) the monzogranite group, b) the quartz monzodiorite group, c) the tonalite to quartz diorite group, d) the gabbros and e) a cluster in the top third of the QAP diagram containing samples rich in quartz and very poor in feldspars. Those of cluster e) have undergone quartz-sericite ($\pm$pyrite, $\pm$tourmaline) alteration, where the feldspars are mainly replaced by fine-grained sericite. The same five clusters are also visible in the PLSR predicted compositions from the spectroscopic data (Figure 4.4). Only a few predictions (under 8%) do cross into another cluster. This demonstrates that we can use the combination of TIR spectroscopy and PLSR modeling to classify rock samples in a QAP ternary diagram.
4.3. Error Estimates

In order to illustrate the order of magnitude of the QAP plot uncertainties, ternary error regions were plotted for the reference method as well as for the PLSR prediction (Figure 4.5). The error regions show how their spatial extent changes with location in the QAP plot. One random sample each was selected from clusters a, c and e. For the reference method uncertainty, the average of the quoted error estimates (±10% for major minerals and ±5% for minor minerals) were added and subtracted from the original areal percentages. These error-modified points were normalized to 100%, added to a QAP diagram and the convex hull of the resulting points was used as the ternary error region. For the uncertainties in the spectroscopic predictions, the quartz, alkali feldspar and plagioclase model RMSEPs (Table 4.1) were added and subtracted from the respective original predicted values, normalized to 100% and the convex hull of the resulting points was used as the ternary error region.

Sample y325 with roughly similar proportions of quartz, alkali feldspar and plagioclase shows a relatively small and isotropic prediction uncertainty field (Figure 4.5). Other samples (e.g., y695) have modal values along the edge of the QAP diagram or close to a corner. As negative values are not physically possible, the uncertainty fields are truncated at the edge of the triangle and become anisotropic in shape. Samples with
4. Laboratory TIR spectroscopy and PLSR modeling

Q + A + P totaling much less than 100% prior to normalization (e.g., y695 Q + A + P = 52%) show larger error fields as small errors of 6–8% result in large error regions after the normalization. Figure 4.5 shows that in all three cases the measured and predicted uncertainty fields overlap and are not significantly different from each other.

To illustrate the reproducibility of the method, the duplicate samples are highlighted by open circles in Figures 4.3 and 4.5. In all cases the PLSR predictions based on the duplicate measurements plot very close to the originals and always within a 2% absolute margin. Since the duplicate measurements were taken several months later and on a different spot on the sample, the small deviations show that error propagation through sampling error and instrument noise and drift contributes less than 2% absolute to the overall uncertainty.

4.4 Discussion

Table 4.1 and Figure 4.3 summarize some of the key parameters of the four PLSR models applied in this chapter and Appendix B provides some additional information. The loading weights and regression coefficients show that the models are driven by the most important mineral components in which we are interested. No spectral features of unexpected or accessory minerals were detected in the models, which implies that the bases for the models are robust. The quartz model is based on only two factors due to its distinct spectral features with no variations due to composition. Using only two factors also greatly reduces the risk of overfitting the data, which is important when the model is applied to another dataset or study area of interest. The alkali feldspar and plagioclase models use five and four factors, respectively. Many of the factors show similar features in the loading weights but with different relative feature depths and slight shifts in wavelengths. These factors are required to account for changes in composition and mineralogy in the alkali feldspar and plagioclase group and are not a sign of redundancy or overfitting. The crossvalidation results and the clear structure in all loading weights give confidence that these 4–5 factor models are also robust and applicable to other datasets. Since “plagioclase composition” does not have a spectral signature as such, and depends on the amount and compositions of the different plagioclase minerals in the rock, the plgcomp model is more complex and less straight forward than the other three. The RMSEP plot (Figure B.7) shows local minima, which are a sign of remaining outliers in the data. While the loading weights of the plagioclase composition model are clearly driven by spectral features of various plagioclase compositions, the regression coefficients show less structure than in other models and display some noise.

Figure 4.2 shows that the reference method and the predicted values from spectroscopy have discrepancies but the relative contributions of reference method and model toward these errors are irresolvable. Ideally, one would like to confirm the results with a reference method that has
4.4. Discussion

A smaller uncertainty and is less dependent on specialist interpretation than thin section analysis. X-ray diffraction (XRD) is generally a qualitative process that identifies minerals in the sample, but not their amounts. Quantitative XRD strives to give quantitative mineralogic information but uncertainties with thin section analysis is often cited around 10% (Amaral et al., 2006) which does not represent a significant enough reduction in reference method uncertainty as compared to the ±5–15% for major minerals in thin section analysis. X-ray fluorescence (XRF) and scanning electron microprobe in turn give quantitative chemical information on a sample or on a small spot on a sample, respectively. Both require a model (based on order of mineral crystallization from melt) to get from oxide chemistry to normative mineralogy. Many of the samples in the test area have undergone hydrothermal alteration by different fluids at different temperatures and intensities. They do not necessarily follow the normative models. Hence, the methods mentioned above would not significantly improve the uncertainties in the reference method.

Three samples (sample numbers y538, y645 and y697b) of the monzogranite cluster (figure 4.4, cluster a) show large differences between thin section and PLSR prediction. In two cases (y645 and y697b) the thin section observation included a fine-grained matrix, which may have resulted in misidentification of minerals. Two quartz-sericite (±pyrite, ±tourmaline) altered samples (y695 and y574) show large QAP differences with the thin section results (figure 4.4, cluster e). Also in the case of these two samples, the discrepancies can partially be attributed to the fine-grained nature of the samples, which could hamper the identification of remaining feldspar relics under the microscope. An additional source of increased uncertainty for these samples is inherent to the modeling method itself: A PLSR model developed on a sample set with many typical and only a few extreme compositions has difficulties in predicting the extremes of the value range. This problem is evident in low plagioclase (figure 4.3b) and high quartz (figure 4.3c) samples that show large spreads in the measured versus predicted plots. The problematic samples are in both cases the quartz-sericite altered rocks. Since most (non-altered) samples do not contain any substantial amounts of white mica, the PLS models do not include any sericite features in the loading weights and appear to have problems modeling those samples properly. To increase the prediction accuracy it can be considered to model pervasively altered rocks separately in the future.

In order to put the modeled accuracies of this chapter into context, they can be compared to those reported with the commonly applied spectral mixture analysis (or unmixing): Feely & Christensen (1999) reported typical unmixing uncertainties for major minerals in igneous rock samples of ±5–10% absolute. For those results all types of feldspars were considered together. The results for alkali feldspar and plagioclase alone were considerably less reliable and were not specified. Wyatt et al. (2001) determined plagioclase modes to within 5–10% absolute. In comparison, the results presented here perform well (Afsp ± 5.1%, Plg ± 8.5%, Qtz ± 6.9% all absolute). Milam et al. (2007, 2004) deconvolved...
4. Laboratory TIR spectroscopy and PLSR modeling

TIR spectra of igneous rocks, coarse plagioclase sand, and polymineralic sand mixtures and modeled plagioclase compositions to within 6 mol% An. By comparison, plagioclase compositions modeled in this thesis had uncertainties of 7.8 mol% An.

While our PLSR error margins and those reported for SMA are comparable (see above), the two techniques have thoroughly different approaches and requirements. As mentioned in the introduction, the challenge of SMA is the *a priori* definition of a set of representative reference spectra for all expected mineralogic, compositional and structural variations in the rocks to be analyzed. Its strength, on the other hand, is that if a set of reference spectra can be defined accurately, SMA can be applied to different study areas without any additional field information available (e.g., planetary sciences). In contrast to SMA, PLSR does not link sample spectra to a spectral endmember reference library. Instead, existing modal mineralogy for a number of samples are used to train the model to extract the required information automatically from the thermal infrared spectra. While not required for building the model, a spectral library can be very helpful when interpreting the internal structures of a PLSR model: by comparing loading weights and regression coefficients to mineral spectra, one can analyze what minerals and mineral combinations drive a particular PLSR model.

PLSR is especially useful for many ongoing projects that do have existing information on composition for a number of samples on hand, which can be used to train the PLSR models and get modal estimates from TIR spectra on the rest of the samples. The most prospective sources of compositional information are mineral modes by thin section analysis or QXRD, since features in TIR spectroscopy are coupled to the mineralogic compounds in rocks. Alternatively, one could also attempt the use of whole rock or trace element geochemistry results as long as their concentrations are correlated with the mineral modes present in the rocks.

The minimum number of samples required to build a reliable PLSR models based on spectroscopy is 20–50 well defined samples (Esbensen, 2006). For mineralogic datasets with considerable uncertainties most authors prefer a slightly larger sample set of 50–100 samples. A prime example of where PLSR could be used on existing datasets would be a mining operation: data from different analytical methods for samples from diverse parts of the deposit exist and can be used to link TIR spectra to the existing datasets. While mineral modes are the TIR spectroscopy could be used at the mine face, on drill cores or in sorting operations to determine mineralogy and possibly ore content. However, care has to be taken when PLSR models are transported from one study area to another. The models and the estimated prediction errors (RMSEP) remain valid as long as the new samples come from the same population, that is, they have comparable mineralogic compositions. If that is not the case, prediction errors will increase and the model should be re-calibrated using samples from the new study area.

Thermal infrared spectra give us information on the average miner-
alogic composition of the sample, while thin section analysis with optical methods or electron microprobe can reveal information on compositional zonation of grains or whether a mineral was stable in a given assemblage. To combine spatial information with spectral information, drill cores or flat samples can be imaged in the shortwave infrared by hyperspectral sample imagers, such as SisuRock (Spectral Imaging Ltd., 2012b) for which a thermal infrared option is currently being developed. Furthermore, thermal infrared spectroscopy has the capacity to be scaled to routine measurements in the laboratory or field, or to airborne imagery. While the current measurement setup of directional-hemispherical reflectance was chosen for future comparison to airborne data, routine laboratory and field applications would benefit from the larger energy throughput of a bi-directional setup, which would reduce the measurement time to well under a minute per sample. A similarly operating system (bi-directional) has been developed by CSIRO Australia for routine drill core measurements and has recently been extended to TIR wavelengths (Huntington et al., 2010). Chapters 5 and 6 of this thesis will test, whether PLSR derived models can also be applied to airborne TIR imagery.

4.5 Conclusions

Thermal infrared spectroscopy in combination with partial least squares modeling can be used to estimate the modal mineralogy of igneous rock samples. In this chapter, TIR spectra were linked to thin section-determined alkali feldspar, plagioclase and quartz contents, as well as plagioclase composition. Rock samples were successfully classified in a QAP diagram based on TIR spectroscopy and PLSR modeling. PLSR-modeled alkali feldspar modes are within a ±5.1% estimated absolute error of those determined by thin sections. The plagioclase model performs well for all samples except those that contain very low or no plagioclase at all. Estimated errors for all samples are ±8.5% absolute. Modeled quartz modes stay within ±5.8% absolute for samples containing less than 30% quartz. If samples with high quartz contents (i.e., quartz-sericite altered) are included in the model, the estimated error increases slightly but remains below ±7% absolute. For the plagioclase group, a PLSR model was built that predicts plagioclase composition with discrepancies of ±7.8 mol% An.
Modeling the response of the airborne SEBASS sensor

5.1 Introduction

In Chapter 4, it was shown that thermal infrared laboratory spectra and PLSR modeling can successfully predict mineral modes of feldspar and quartz in a laboratory environment. Ultimately, the objective of this thesis is to assess the use of thermal infrared airborne imagery for quantitative mapping of feldspar abundances and plagioclase composition. The Spatially-Enhanced Broadband Array Spectrograph System (SEBASS; see description below) was chosen as the airborne data source for this purpose. Before the laboratory results are applied to the SEBASS data, it will first be investigated whether SEBASS would theoretically be able to detect feldspar minerals and quantitatively predict modes and compositions in igneous rocks. For that purpose, the laboratory signal was deteriorated to mimic the airborne SEBASS response, the PLSR prediction models were applied and the results compared to the original predictions.

5.1.1 Description of SEBASS

The Spatially Enhanced Broadband Array Spectrograph System (SEBASS) is a hyperspectral thermal infrared imaging instrument, built and operated by the Aerospace Corporation, USA (AERO) and first described by Hackwell et al. (1996). SEBASS is a push-broom imaging system with two detector arrays covering the atmospheric windows between 2.0 and 5.2 µm (mid-wave infrared; MWIR) as well as 7.8 and 13.5 µm (thermal infrared or long-wave infrared; LWIR). The two focal plane arrays have dimensions of 128 × 128 pixels resulting in two datacubes with 128 spectral bands and a narrow swath width of 128 pixels. Since silicates show their most diagnostic features in the Reststrahlen band (around 10 µm), only the LWIR SEBASS data is treated here. The signal-to-noise-ratio (SNR) of the LWIR sensor is quoted in the range of \( \approx 3000:1 \) (Kirkland

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5. Modeling the response of the airborne SEBASS sensor

et al., 2002) and \( \approx 2000:1 \) (Riley & Hecker, subm) and noise levels (NE\( \Delta T \)) are in the region of 0.05 K (Hackwell et al., 1996). To achieve these high SNR and low noise levels, the detector is cooled with liquid He to temperatures of 4 K. The SEBASS system is mounted on a roll compensation mount which also allows the sensor to be swung in front of hot cold calibration blackbodies that are mounted to either side of the instrument in the camera port of the plane.

5.2 Methodology

In this section, the different modifications applied to the laboratory sample spectra are described. The purpose is a progressive deterioration of the laboratory spectra in order to mimic typically occurring issues in airborne spectra.

5.2.1 Spectral resampling

As a first step, the ultra-high resolution laboratory spectra (4cm\(^{-1}\) resolution, 733 data points in the 7.5-16.0 \( \mu \)m range) were resampled to the SEBASS spatial range and band positions (from hereon referred to as "SEBASS-resampled"). Since SEBASS spectral response functions (the functions that define how each detector element reacts to incoming energy) are not public domain, they were approximated by a gaussian function using a central wavelength and a full-width at half maximum (FWHM) number. The central band positions were taken from the header of an actual SEBASS scene (see Chapter 6), while the extent of the band width (i.e., FWHM) was approximated by the half way points between adjacent bands. The spectrally resampled laboratory spectra were then re-calculated from reflectance to emissivity using Kirchhoff’s Law (Equation 3.7) in order to be optically more comparable to spectra recorded by the SEBASS sensor and displayed in Chapter 6.

5.2.2 Additive noise

In a second step, noise was added to the modeled SEBASS spectra to imitate the reduced SNR in airborne data. Uniform random noise was produced with peak-to-peak values of \( \pm 0.5 \), \( \pm 1.0 \), \( \pm 2.0 \) and \( \pm 5.0 \)% (in absolute emissivity percentages) and added to the SEBASS-resampled spectra. This process was repeated (applying new random noise values to the original SEBASS-resampled spectra) to produce a second set of noise-added spectra which was used to calculate the models RMSEP (see Section 5.2.4 for details).

5.2.3 Additive, multiplicative and tilt distortions

Existing literature reports substantial differences between airborne SEBASS spectra and TIR field or laboratory spectra of the same targets (e.g.,
5.2. Methodology

Table 5.1 Functions applied to spectra to investigate additive, multiplicative and tilt distortions.

<table>
<thead>
<tr>
<th>Distortion</th>
<th>Function(^{a,b})</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additive</td>
<td>(y_{\text{new}} = y_{\text{old}} - 0.2)</td>
<td>Spectrum down-shifted to 80% of normal values; spectral contrast kept same as in original</td>
</tr>
<tr>
<td>Multiplicative</td>
<td>(y_{\text{new}} = y_{\text{old}} \times 0.8)</td>
<td>Top edge of spectrum down-shifted to 80% and spectral contrast lowered to 80%</td>
</tr>
<tr>
<td>Additive and multiplicative</td>
<td>(y_{\text{new}} = (y_{\text{old}} \times 0.8) + 0.2)</td>
<td>Top edge of spectrum remains same as original; spectral contrast lowered to 80%</td>
</tr>
<tr>
<td>Additive tilting</td>
<td>(y_{\text{new}} = x - \left[ 1 - \left( \frac{\text{LN}(y_{\text{old}})}{3} + 0.13 \right) \right])</td>
<td>Tilt (short (\lambda) down) to (\approx 80%) of original values; spectral contrast kept same as original</td>
</tr>
<tr>
<td>Multiplicative tilting</td>
<td>(y_{\text{new}} = x \left[ \frac{\text{LN}(y_{\text{old}})}{3} + 0.13 \right])</td>
<td>Tilt (short (\lambda) down) to (\approx 80%) of original values; spectral contrast lowered to (\approx 80%) of original</td>
</tr>
</tbody>
</table>

\(^{a}\) Emissivity spectra \((y_{\text{old}}, y_{\text{new}})\) in \([0–1]\) value range

\(^{b}\) Wavelength of \(x\) in \([\mu \text{m}]\)

Vaughan et al., 2005; Cudahy et al., 2001b). Typical are reduced spectral contrast and drop-offs (spectral tilting) towards shorter wavelengths. To assess the influence of these reported distortions on the PLSR models, SEBASS-resampled spectra (without added noise) were subjected to a number of additive and multiplicative functions (see Table 5.1). Without specific knowledge of the exact degrees of distortions in SEBASS data, spectral contrasts of 80% of the original values and tilts to 80% of the absolute emissive values were assumed for this test. Then, each type of functions and the values of the factors and constants were chosen such that a particular scenario of change in absolute value, spectral contrast and/or spectral tilt was highlighted. For details see the comments in Table 5.1 and the graphical representation in Figure 5.4.

5.2.4 PLSR modeling

After the laboratory spectra had been treated as described in Sections 5.2.1 to 5.2.3, PLSR models were built and applied as described in Chapter 4 with the following two exceptions: (I) instead of using the RMSEP plot, the number of factors used was fixed to the values in Table 4.1 to allow for consistency and correlation between the different spectral treatments and (II) the set of spectra with additive noise were validated with a second
set of noise-added spectra (same base spectra but different random noise added) to avoid overfitting in the model calibration stage. This procedure prevents the PLSR models from giving overly optimistic error estimates. The PLS regression coefficients were applied to all spectra in the prediction stage, and the results were plotted against the validation value from thin section analysis and against the original laboratory PLSR results. Correlations between datasets were calculated using non-parametric Spearman’s correlation (i.e., correlation between the ranks in the ordered data rather than the values), since most variables show strongly asymmetric distributions, which make the use of a parametric Pearson’s correlator inappropriate.

5.3 Results and discussion

5.3.1 Changes in spectral shape

With 128 bands in the 7.5 – 13.5 µm region, the SEBASS instrument has a very high spectral resolution. This is corroborated by the fact that the SEBASS-resampled spectra are virtually identical to the original laboratory spectra, as demonstrated on a quartz-oligoclase dominated spectrum (Figure 5.1, first and second spectrum). The main difference is the reduced spectral range of the airborne data, which does cover the most important Reststrahlen features of the silicate minerals. Small differences can also be seen in areas with strong spectral changes (e.g., the central peak between the quartz doublet at 8.63 µm); while the SEBASS band width is still able to resolve the features, the finite spectral resolution modifies the feature’s shape. As higher noise levels are progressively added, spectral features start to deteriorate (Figure 5.1). Up to 1% noise, both quartz doublets are still identifiable with confidence. At 2% noise levels, the quartz doublets merge to single features but the (oligoclase) plateau at 9.6 µm is still discernible. At 5% noise levels, all individual spectral features have disappeared except for a general Reststrahlen feature centered at about 9 µm.

The spectral range of SEBASS is covering the most important spectral features in the Reststrahlen band. Secondary feldspar features around 13 µm (in Figure 5.1 faintly visible to the right of the secondary Qtz features) are at the edge of the sensor’s spectral range and may be difficult to resolve. Features beyond 13.5 µm cannot be utilized in terrestrial, airborne remote sensing studies anyhow, as they fall outside of the Earth’s atmospheric absorption window.

5.3.2 PLSR results with SEBASS-modeled spectra

The PLSR model predictions on SEBASS-resampled spectra are virtually identical to the predictions based on the original laboratory resolution spectral datasets. The spectral resolution of SEBASS is sufficient to model the spectral features in the rock samples appropriately. As an example,
5.3. Results and discussion

Figure 5.1 Example of TIR spectrum at full laboratory resolution, resampled to SEBASS band positions and with progressively more noise added (from top to bottom). Except for full resolution spectrum, all other spectra are downshifted by 0.10 emissivity units each for clarity. The spectral features in this sample (y653) are mainly due to quartz and plagioclase (Table A.1).

The results of the alkali feldspar model are presented (Figure 5.2, leftmost plot). Spearman’s correlation between the SEBASS-resampled and original laboratory results is $\rho = 0.995$. As noise is added the correlation starts dropping: at 1% noise, the correlation is still almost 0.98. After that, correlation deteriorates rather quickly with $\rho \approx 0.91$ (2% noise) and $\rho \approx 0.76$ (5% noise; Figure 5.2, rightmost plot).

To assess the influence of the added noise on the absolute prediction quality of the PLSR models (as compared to the thin section reference method), RMSEP values were calculated for all mineral/noise level combinations. The results show that RMSEP values generally do not increase when the laboratory spectra are resampled to SEBASS wavelengths (Figure 5.3). Even adding noise up to 1% only gently increases the prediction errors in the models (less than 0.4% absolute). For noise levels $\geq 2\%$,
5. Modeling the response of the airborne SEBASS sensor

![Fig 5.2](chart.png)

**Figure 5.2** Scatter plots comparing PLSR predictions [in areal %] for alkali feldspar based on the original laboratory spectra against those from SEBASS-resampled, noise-added spectra. Noise levels (from left to right): no noise, 0.5%, 1%, 2%, 5%. \( \rho \) indicates Spearman’s correlation factor of the two variables.

The results show that up to 1% added noise has a very limited effect on the interpretability as well as on the PLSR modeling results. This is demonstrated by the spectra in Figure 5.1, as well as high correlation factors and small RMSEP increases in Figures 5.2 and 5.3. Literature suggests SNR values for SEBASS that exceed 2000:1. However, these high SNR values were calculated on radiance-at-sensor data and also depend on the sensor setup for a given acquisition (Riley & Hecker, subm). Since the radiance spectrum is dominated by the object’s temperature rather than its emissivity, the SNR of the emissivity spectrum after atmospheric cor-
5.3. Results and discussion

Figure 5.3  PLSR model prediction errors (RMSEP; in % absolute) for laboratory spectra and SEBASS-resampled spectra with noise levels from 0% to 5%. Mineral abbreviations used are as follows: Afsp = alkali feldspar; Plg = plagioclase; Qtz = quartz; Plgcomp = plagioclase composition.

rection and temperature-emissivity-separation (TcS) is consequentially considerably lower than the published SNR values. Visual inspection of a SEBASS standard emissivity datacube (see Chapter 6) reveals noise levels in a typical spectral profile comparable with the 1% example in Figure 5.1. Hence, the SNR in the standard SEBASS emissivity product is theoretically sufficient to model feldspar amounts and compositions with PLSR.

5.3.3 Additive, multiplicative and tilt distortions

The functions applied to the SEBASS-resampled spectra and described in Table 5.1 instigated gradual spectral changes while leaving the general spectral shape intact (Figure 5.4). The main changes are (I) modification of the absolute emissivity values, (II) reduction of spectral contrast and (III) tilting towards shorter wavelengths.

When the PLSR models were run on these modified spectra and compared to the original laboratory resolution results, several effects could be observed:

• In the case of the plagioclase model (Figure 5.5B), absolute prediction values have changed, but the relative patterns remained the same (samples plot in the correct relative order). Hence, predictions
Figure 5.4  The effects of the additive, multiplicative and tilt distortions on the spectrum displayed on the example of sample spectrum y653 (Table A.1).

Based on shifted and tilted spectra are still giving useful relative plagioclase patterns but no absolute values.

- In the plagioclase composition models (Figure 5.5D), only the additive+multiplicative model shows useful relative patterns while the two tilting models show prediction patterns with a global maximum after which very high values are erroneously plotting at lower prediction values again. This effect is caused by the inverse of the arcsine square root function that is used at the end of the PLSR modeling to revert the results back to compositional information in the original units of areal percentages (see Sections 4.2.3.1 and 4.2.3.4). If the modified spectra cause (non-backtransformed) prediction values outside the $[0 - \pi/2]$-range, the squared sine function will cause data folding. For the additive and the multiplicative plagioclase composition model (Figure 5.5D) the data all fall in the $[-\pi/2 - 0]$-range and folding causes a total inversion of the data points.

- The alkali feldspar model (Figure 5.5A) shows an additional problem with data folding: in this model even the undistorted spectra cause a few samples to predict with negative values, which causes data folding as the data points approach the y-axis. Furthermore, the alkali feldspar model shows similar inversion of the data values as the plagioclase composition model does, but in this case the tilted spectra are inverted.

- Like the alkali feldspar and plagioclase composition models, the PLSR quartz model also uses an arcsine square root transformation.
5.3. Results and discussion

Figure 5.5  PLSR modeling results based on undistorted spectra against those from spectra with additive, multiplicative and tilt distortions. Thin solid line represents the 1:1 line. Values in areal%.

Unlike the Afsp and the Plgcomp models, however, nearly all raw quartz predictions fall in the usable value range of $[0 \, \pi/2]$. For that reason, the quartz models do not suffer from data folding and show excellent relative patterns, with even the absolute prediction values plotting in a sensible range (Figure 5.5C).

The experiment involving the additive, multiplicative and tilting functions revealed that only the additive+multiplicative distorted spectrum (same maximum values but lower spectral contrast) gave good relative and reasonable absolute results with all mineral models. Spectra with other distortions gave significantly different absolute results with even relative patterns often being obliterated. This illustrates that vertical shifts and tilts were more detrimental for the PLSR results than a simple change in "absorption depth" (dark blue spectrum and asterisks in Figures 5.4 and 5.5).

Airborne SEBASS spectra, however, show changes in "absorption depth" as well as tilts. Hence, the results demonstrate the acute need to correct the distortions before PLSR models are applied to SEBASS data.
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in order to get quantitatively reliable results. Chapter 6 will introduce a correction methodology that adjusts mean and standard deviation of airborne spectra to match the laboratory data, and compensates additive and multiplicative distortions, as well as spectral tilt.

5.4 Conclusions

Based on the results and discussion above, the following conclusions can be drawn:

1. SEBASS' spectral resolution and coverage are suitable for capturing spectral features in feldspars that fall within the LWIR atmospheric absorption window.

2. PLSR model results based on SEBASS band passes were nearly identical (correlation $\rho = 0.995$) to those based on laboratory resolution.

3. Modeled SEBASS data with up to 1% noise give PLSR modeling results that have RMSEP values within 0.4% (absolute) to the original laboratory PLSR predictions.

4. Noise levels in the standard SEBASS emissivity product appear to be similar to the modeled SEBASS data with 1% noise added. Hence, the SNR in the standard SEBASS emissivity product is theoretically sufficient to model feldspar amounts and compositions with PLSR.

5. In order to achieve reliable mineral estimates, spectral contrast, tilts and vertical shifts must be compensated for, before applying PLSR models.
Airborne thermal infrared imaging spectroscopy and partial least squares regression modeling

6.1 Introduction

In Chapter 4, the prediction of mineral modes and plagioclase composition from laboratory TIR spectra was tested with the help of partial least squares regression. In Chapter 5, the influence of lower spectral resolution, added noise and spectral distortions on the model predictions were investigated. The results have shown that the spectral resolution, spectral range and signal-to-noise levels of SEBASS are theoretically suitable to map feldspar modes and compositions on airborne data in a spatially coherent patterns.

In this chapter, the PLSR models that were developed in Chapter 4 are applied to multiple SEBASS images acquired over the Ann-Mason, Nevada test area in June 2008. First, a preprocessing chain is developed to specifically suppress as much noise as possible and to get the maximum ground-leaving radiance signal. Then, the images are normalized to match the mean and standard deviations of the laboratory spectra. In the final step, the PLSR models are applied and the resulting patterns compared to existing lithologic and alteration maps.

6.1.1 Existing work

Porphyry systems create distinct alteration zones containing diagnostic, infrared active minerals, and often produce a distinct arrangement of concentric zones at the erosional surface (e.g., Tangestani et al., 2008; Mars & Rowan, 2006). If porphyry systems occur in semi-arid to arid areas

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6. Airborne TIR imaging spectroscopy and PLSR modeling

with little vegetation cover, they are exceptionally suited for detection and mineral mapping with remote sensing techniques.

In the early work of Abrams et al. (1983), the authors used Landsat Multi Spectral Scanner (MSS) data to characterize porphyry systems in Arizona, but mainly managed to highlight areas rich in iron oxide. Simulated Landsat-4 TM data provided more spectral and spatial details and allowed them to differentiate several alteration zones. Other studies also used Landsat TM data and managed to delineate ferric iron and hydroxyl-bearing minerals through band ratios (e.g., Amos & Greenbaum, 1989; Green & Lyon, 1984).

From 1999 onward, the 14 band ASTER sensor became available for regional and even local mapping of porphyry systems. With the additional SWIR bands and a multi-spectral thermal infrared array, ASTER has a large advantage over the Landsat TM/ETM+ sensors for mineral mapping, and allowed mapping and identifying all porphyry copper related alteration zones (e.g., Pour & Hashim, 2012; Mars & Rowan, 2006; Rowan et al., 2006; Tangestani et al., 2005). Recent results show, that through careful radiometric calibration of the ASTER data and inclusion of the TIR bands in the analysis, the propylitic zone can even be subdivided into chloritic and carbonate, and quartz rich areas into clastic sandstones and hydrothermal silica without the need for extensive field visits (Mars, 2011; Mars & Rowan, 2010).

While multi-spectral spaceborne instruments are able to discriminate and identify mineral alteration zones, only the use of hyperspectral airborne data typically enabled the mapping and positive identification of individual minerals in those zones. Lyon & Honey (1990), Windeler Jr & Lyon (1991) and Windeler Jr (1993) used the 24 band airborne Geoscan AMSS instrument to map epithermal clay mineralogy, dolomitization patterns in carbonates and skarn mineralogy, respectively, in the Yerington area. Due to the relatively low spectral resolution available, differentiation between minerals were often not based on predictable differences in the target spectra but empirical, site-specific evidence gathered from field knowledge. As an example, calcite was discriminated from dolomite mainly by their contrasting albedo, caused by different levels of organic matter in the rock.

More recently, hyperspectral airborne systems were used to map mineral zoning over the Yerington batholith, such as the visible to shortwave infrared HyMap (Cudahy et al., 2001a,b,c) and AVIRIS (Cudahy et al., 2000) instruments, as well as the thermal infrared SEBASS sensor (Cudahy et al., 2001a,b,c,d, 2000).

Cudahy et al. (2001c, 2000) focused mainly on the skarn in Yerington and managed to identify and map the extent of several non-hydroxyl bearing silicate minerals and gradual change in garnet composition from SEBASS data. They also identified two spectral plagioclase types which they assigned to “sodium-rich” and “calcium-rich”. In a follow-up study, Cudahy et al. (2001b,d) investigated the epithermal and porphyry sections of the Yerington batholith in more detail and came up with a plagioclase composition index that gave relative composition results
6.1. Introduction

Apart from the studies by Cudahy et al., data from the SEBASS instrument has also been used in a small number of other published studies. Vaughan et al. (2003) created mineral maps in an acid-sulfate hydrothermal system as well as an active geothermal area in western Nevada. Vaughan et al. (2005) differentiated active geothermal deposits from older sinther terraces using SEBASS, and Kirkland et al. (2002) compared laboratory spectra to SEBASS data of carbonates near Mesquite, Nevada. Other SEBASS studies with mineral mapping content cover Yerington and Cuprite (Riley & Hecker, subm; Riley et al., 2007). Non-geologic applications of SEBASS include tree species mapping (Ribeiro da Luz & Crowley, 2010), inter-sensor comparisons studies (e.g., Raqueño et al., 2005) and spectral modeling with SEBASS data or its wavelength positions (e.g., Lammoglia & Filho, 2011; Richter et al., 2005; Ingram & Muse, 2001).

The remainder of this chapter builds mainly on the experiences from the SEBASS work done by the group of Cudahy et al. in the Yerington area. Contrary to their work, which determined qualitative plagioclase composition with band ratios, this thesis focuses on the use of PLSR to quantitatively extract mineral modes and plagioclase compositions over the entire Ann-Mason porphyry system.

6.1.2 SEBASS acquisition

Airborne data were acquired during the Joint Airborne Collection using Hyperspectral Systems (JACHS). Aerospace Corporation’s SEBASS instrument (2.4–5.5 µm and 7.6–13.5 µm) was flown in combination with SpecTIR LLC’s ProSpecTIR sensor (0.4–2.5 µm). The two instruments were installed together on a single roll-compensation mount on a Twin Otter plane, with a distance of just 30 cm between lenses (Figure 6.1). For this thesis the SEBASS LWIR data is used. Work combining these results with the other bandwidths will be the focus of future work.

The SEBASS LWIR sensor is a pushbroom sensor that records radiance in 128 spectral bands and 128 across-track spatial pixels at any given time (Hackwell et al., 1996). The forward motion of the plane generates the third dimension creating datacubes of 128x128 pixels and up to several thousand rows long. At the beginning and end of each flightline, the sensor is rotated in its mount to view a cold and a hot blackbody which are installed to either side of the sensor and used for radiometrically calibrating the data. The instantaneous field of view (IFOV) of the individual pixel is 1.1 mrad with a total field of view (FOV) of 7.8°. This particular survey was flown under clear sky conditions over the Yerington Batholith area between June 17 and 21, 2008. Average altitude was 12000 feet (ca. 3700 m) above ground level resulting in ground sample distance of about 4 m and a swath width of about 550 m. In order to cover the entire Yerington batholith target area, 36 parallel flightlines were flown in SE-NW direction. Of these, flightlines 22–29 were selected, which cover the Ann-Mason test area.
6. Airborne TIR imaging spectroscopy and PLSR modeling

6.1 SEBASS and ProSpecTIR sensors

Figure 6.1 SEBASS and ProSpecTIR sensors installed on the same roll-compensation mount on a Twin Otter plane. Photo credit: D. Riley, Aerospace Corporation.

6.2 Preprocessing of SEBASS data

With only a small number of existing SEBASS-based studies in literature (Section 6.1.1), preprocessing techniques and the understanding of their influence on the downstream results are still under development. The two standard data products typically distributed by the Aerospace Corporation (AERO) are Radiance at Sensor and Apparent Emissivity data. The radiance data is produced from the raw data with the help of the pre- and post-flightline measurements of the calibration blackbody, assuming linear detector response (Riley, 2012). This radiance dataset is the basis for any higher level products within the AERO workflow but also for the proposed processing chain explained in detail below. Figure 6.2 shows a color composite example of a SEBASS Radiance at Sensor strip, with RGB = (11.07, 9.59, 9.00 µm). The bands were chosen to highlight lithologic differences in the area. Quartz-rich rocks appear in yellow, the intermediate igneous rocks in magenta and skarn-affected sediments in cyan. Since TIR radiance bands are highly correlated, a decorrelation stretch (Gillespie, 1992a) was applied to enhance the color information in the composite.

While the SEBASS sensor is carefully calibrated, the current AERO Apparent Emissivity dataset still contains small striping and vignetting artifacts that influence the further processing results on the data. For
6.2. Preprocessing of SEBASS data

Figure 6.2  Example of decorrelation stretched SEBASS radiance at sensor color composite. RGB = (11.07, 9.59, 9.00 µm). The following rock types are labeled: (A) quartzite, (B) quartz monzodiorite, (C) McConnell volcanics, (D) skarn-affected sediments. Figure is of a subset of flightline 29, scanlines 500–2500, and cut in half for better displaying.

that purpose, destriping, bad pixel detection and spectral subsetting steps were inserted into the processing chain to increase the data consistency. Furthermore, a normalization step was included to make the airborne data more comparable to the laboratory data. For an overview of the preprocessing chain, see Figure 6.3.

6.2.1 Spectral Subsetting

Preliminary tests had shown that bands 125–128 developed striping towards the end of long flightlines on the starboard side. These artifacts are also found back in the MNF products (for MNF see Section 6.2.3) and in the final mineral maps if all 128 bands are entered into the processing chain. Cudahy et al. (2000) also reported that bands 125–128 did not contain any data in their dataset. To avoid noisy data from entering the next steps of the processing chain, which could spread the problematic values over the spatial and spectral dimension of the flightlines, the last four bands were culled and the spectral subset 1–124 was used for further processing.

6.2.2 Bad cell and destriping

A number of cells in the SEBASS LWIR array react differently from the average and require correction. If the cell response is slightly off, the values can be corrected by a destriping algorithm. If the response is considerably different to the typical behavior, the cell is flagged as bad, and its recorded values replaced. The bad cell detection and destriping algorithms applied here were based on pushbroom “plugger and destriper” (Mason, 2002). The fundamental assumption behind the algorithm is that when correcting a flightline of several thousand rows, the different ground compositions average out and all image columns of a particular band should record the same average radiance value. If the statistical moments (i.e., mean and/or standard deviation) of a single column differ
6. Airborne TIR imaging spectroscopy and PLSR modeling

Figure 6.3  Flowchart of the SEBASS preprocessing chain. Details on the individual steps are explained in the text.

more than 3 standard deviations from the moments of all columns in that band, the detector cell is flagged as "bad cell" and its values replaced with an interpolation of the (spatially) adjacent cells. The first spatial column (port side of plane) was consistently flagged "bad" through all wavelengths and flightlines. Typically, also some clusters of detector cells at the top left (port side/short wavelength) and bottom right corner (starboard side/long wavelengths) of the FPA were flagged and replaced.

After the influence of bad cells had been removed, each image band was destriped by normalizing the response of all cells of the same wavelength band. For each wavelength band, the mean and standard deviation were calculated for individual image columns ($\mu_x$ and $\sigma_x$), as well as for the the entire image band ($\mu_{total}$ and $\sigma_{total}$). The equations can then be formulated (after Mason (2002)):

$$\mu_x = \frac{1}{n} \sum_{y=1}^{n} Rad_{x,y}$$
$$\sigma_x = \sqrt{\frac{\sum_{y=1}^{n} (Rad_{x,y} - \mu_x)^2}{n}}$$

(6.1)

$$\mu_{total} = \frac{1}{mn} \sum_{x=1}^{m} \sum_{y=1}^{n} Rad_{x,y}$$
$$\sigma_{total} = \sqrt{\frac{\sum_{x=1}^{m} \sum_{y=1}^{n} (Rad_{x,y} - \mu_{total})^2}{mn}}$$

(6.2)

where $x$ and $y$ are column and row numbers, $m$ and $n$ are total number of
columns and rows, and $Rad_{x,y}$ is the original radiance value for pixel $x,y$ before destriping. The new, destriped radiance values are then calculated using:

$$Rad_{\text{new},x,y} = (Rad_{x,y} - \mu_x)\frac{\sigma_{\text{total}}}{\sigma_{x}} + \mu_{\text{total}}$$

where $Rad_{\text{new},x,y}$ is the new, destriped radiance value of pixel $x,y$. The process is repeated for each image band until all 124 wavelengths have been destriped.

Destriping and bad cell detection both rely on the assumption that the average composition is homogeneous across all image columns after a few thousand rows. To increase the prospect of this assumption being valid, spectrally extreme targets like built-up areas, water bodies and irrigated fields were manually digitized and excluded from the processing, allowing only bare ground to go into the statistics of bad cell detection as well as destriping.

### 6.2.3 MNF

To separate as much noise from the image data as possible before further processing, a minimum noise fraction (MNF) transformation was applied to the 124-band dataset (Green et al., 1988). The MNF transformation is a statistical operation with a double principal component analysis (PCA). It causes “noise whitening” and orders the final output components by their respective noise fractions (ITT Visual Information Solutions, 2010). MNF is preferred over standard PCA transformation, since MNF is condensing the bands with highest signal quality in the early components with most later bands consisting of mainly noise.

SEBASS bands 1–124 were entered into the MNF transform. Ideally, the MNF noise statistics are calculated on a homogeneous subset in the image. Since no sufficiently large, homogeneous areas could be found in each of the flightlines, the statistics were calculated on the igneous rocks of the Ann-Mason block, while other areas were masked out.

In order to use MNF transform for noise-removal, a selection of the "good" MNF bands has to be made before the inverse MNF transformation is applied. This process is rather arbitrary and depends on the further purpose of the data: As an example, selecting only a few, "noise free" MNF bands for the inverse transform gives the best noise removal but also has a strong smoothing effect. Since PLSR is not susceptible to random noise but relies on the subtle spectral information to still be present in the data, a more conservative culling threshold needed to be defined. Manual inspection revealed that the first $\approx 40$ MNF bands contained features linked to ground information, although with increasing levels of noise in the higher bands. Beyond MNF band 40, signs of ground influence started to get very faint. To exclude some noise from further processing steps but keep all spectral information from ground features intact, the arbitrary threshold of 40 MNF bands was chosen. These 40 bands were
entered into an inverse MNF to transform the MNF components with signal content back into image space.

Most other studies that apply MNF on hyperspectral TIR data choose to do the transformation after atmospheric correction and temperature/emissivity separation (Vaughan et al., 2005, 2003; Hewson et al., 2000). Since we apply MNF mainly to reduce noise in the data, and we transform back to image space afterwards, we prefer to do it right after removing systematic striping in the destriping step. This guarantees that noise is removed before the atmospheric correction, which is susceptible to elevated noise levels in the data.

6.2.4 Atmospheric correction and TɛS

The radiance measured at the SEBASS sensor \( L(\lambda) \) can be modeled by (Young et al., 2002):

\[
L(\lambda) = \langle \epsilon(\lambda)B(\lambda, T)\tau(\lambda) \rangle + \langle L\uparrow(\lambda) \rangle + \langle [1 - \epsilon(\lambda)]L\downarrow(\lambda)\tau(\lambda) \rangle \tag{6.4}
\]

where \( \lambda \) is wavelength, \( \epsilon(\lambda) \) the surface emissivity spectrum, \( \tau(\lambda) \) the transmissivity spectrum of the atmosphere, \( L\uparrow(\lambda) \) and \( L\downarrow(\lambda) \) the sky up- and down-welling radiance spectra, and \( B(\lambda, T) \) is the Planck radiation function at surface temperature \( T \). The angle brackets define three specific parts in Equation 6.4: the first part represents radiance radiated from the ground that is partially absorbed by the atmosphere before reaching the sensor. The second part represents radiance that is radiated upwards by the atmosphere within the optical path between the sensor and the ground. The final part represents the radiance that is radiated downwards by the entire sky and is reflected off the ground surface into the path of the pixel that is measured.

To correct for atmospheric effects in the data, the in-scene atmospheric compensation (ISAC) described by Johnson (1998), Young (1998) and Young et al. (2002) and implemented in ITT Visual Information Solutions (2010) was used. ISAC empirically estimates atmospheric properties based on statistical information it extracts from within the scene to be corrected. ISAC corrects for multiplicative transmissivity of the atmosphere (\( \tau \) in the first part of Equation 6.4) as well as for an additive up-welling radiance component (\( L\uparrow \) in Equation 6.4). Its main advantage lies in its simplicity and that it does not require any additional meteorologic information or complicated radiative transfer modeling. The main shortcoming is that it does not correct for reflected down-welling radiance (\( L\downarrow \) third part in Equation 6.4), which reduces the spectral contrast in the airborne data as compared to the real emissivity spectrum (Cudahy et al., 2000). Other assumptions of the method and their possible consequences are listed by Cudahy et al. (2000, p.28) and Vaughan et al. (2003, p.55).

After the atmospheric correction, the ISAC-corrected radiance data still contained the influence of the kinetic temperature and the emissiv-
6.2. Preprocessing of SEBASS data

![Graph showing different processing steps of SEBASS data]

**Figure 6.4** Pixel spectrum after different processing steps of the same airborne pixel (Flightline 23, col=15; row=2022). From bottom to top: (I) noise-removed radiance spectrum (still with atm. features), (II) atmosphere compensated radiance spectrum with corresponding Planck curve \((T=329.66 \text{ K, } \epsilon=0.96)\), (III) emissivity spectrum after emissivity normalization. Noise-removed spectrum is downshifted by 1.0 radiance units for clarity.

ity of the imaged ground (see Figure 6.4); a temperature-emissivity-separation (TeS) is required. Since emissivity (at each wavelength) and the temperature are not known, there is one more unknown than there is measured radiance bands in the image data. This underdetermined system always requires an assumption to reduce it to a solvable problem and different TeS algorithms are available (e.g., Kealy & Hook, 1993; Hook et al., 1992; Kahle & Alley, 1992). An emissivity normalization (ENorm) procedure was selected for this thesis (Kealy & Hook, 1993). For each pixel, temperatures are calculated from each band assuming a constant emissivity, with the maximum calculated value being set as the pixel’s temperature. With the temperature being known, the corresponding Planck curve and emissivity can be calculated for all other wavelengths (Figure 6.4). As constant emissivity a typical value of 0.96 from literature was chosen (e.g., Kealy & Hook, 1993). It was observed that a shortcoming of the ENorm method is its susceptibility to a single noisy band, that is, if a band sticks out above the general blackbody curve due to a slight calibration offset, that band singlehandedly determines the temperature of almost all pixels in the image.
6. Airborne TIR imaging spectroscopy and PLSR modeling

In an early stage of processing, experiments with masking and different spectral subsets were carried out to test their influences on ISAC and temperature-emissivity-separation(T\(\epsilon\)S), and ultimately on the resulting spectra. Results showed that masking out non-target areas was important, as they show different behavior with reflected down-welling radiance; built-up areas, for example, often contain zinc roofing with extremely high reflectance in the thermal infrared. Pixels imaging zinc roofs will show strong features related to reflected down-welling radiance. If they are included in the ISAC algorithm, they influence the regression, leading to less appropriate transmissivity and up-welling radiance estimates for the igneous areas. Another finding was that smaller spatial subsets often gave better atmospheric compensations with smaller residuals. This finding represents the fact that in ISAC, a homogeneous atmosphere is assumed for the entire image, which is an unlikely example especially for long flightlines. Since the target of interest are the igneous rocks of the Ann-Mason block, the same Ann-Mason mask was applied during ISAC and T\(\epsilon\)S as in Section 6.2.3.

Spectral subsetting does not influence the ISAC atmospheric correction, since each band is treated separately. The ENorm process, on the other hand, calculates on a spectral pixel-basis. If the band, on which the ENorm for a given pixel is calculated (often 892; 12.17 \(\mu\)m) is not part of the subset anymore, another band is used and set to \(\epsilon = 0.96\), leading to a vertical shift of the spectrum. Apart from removing bands 125–128 earlier, no further subsetting was performed, to allow the ENorm process to pick the appropriate band from as many bands as possible.

6.2.5 Normalization

In Chapter 5, it was demonstrated that spectral distortions, like differences in absolute values as well as spectral contrast, change the outcome of PLSR modeling when a laboratory-based model is applied to airborne data. Hence, systematic distortions in the airborne data (resulting from incomplete atmospheric correction, imperfections in the band-to-band calibration and problems with the T\(\epsilon\)S) need to be corrected before the modeling step. To get the airborne data to occupy the same value range as the laboratory samples from the test area, a mean and standard deviation (MASD) normalization was developed. For each SEBASS band, the mean and standard deviation of the pixels are compared to the mean and standard deviation of the laboratory spectra of 105 samples from the test area. The SEBASS pixels are then normalized to the laboratory spectra similarly to Equation 6.3:

\[
\epsilon_{SEB, new}(\lambda) = \left[ \epsilon_{SEB}(\lambda) - \mu_{SEB}(\lambda) \right] \frac{\sigma_{Lab}(\lambda)}{\sigma_{SEB}(\lambda)} + \mu_{Lab}(\lambda)
\]

where \(\epsilon_{SEB, new}\) are the MASD normalized SEBASS values, \(\epsilon_{SEB}\) are the SEBASS input emissivity values, \(\mu_{SEB}\) and \(\sigma_{SEB}\) are the mean and standard deviation of the entire (although input-masked) SEBASS band and \(\mu_{Lab}\)
and $\sigma_{\text{Lab}}$ are the mean and standard deviation of the same band in the laboratory spectra. The normalization is then executed on a band-by-band basis.

Each of the flightlines were acquired at a different time of day and had an individual atmospheric correction done, based on scene-dependent statistics. Therefore, the levels and types of distortions, as compared to laboratory spectra, may vary from one flightline to the next. This makes a normalization of the entire Ann-Mason block mosaic in one go not a suitable approach. On the other hand, applying the MASD normalization to individual SEBASS pixel would obliterate all amplitude information contained in the data. Hence, a normalization per flightline was chosen.

The main underlying assumption behind the MASD normalization is that the laboratory samples are a representative sample of the rocks in the SEBASS scenes. To increase the prospect of this assumption being valid, only the igneous rocks of the Ann-Mason block (where most of the 105 samples came from) were used in calculating the statistics for the normalization. Hence, the normalization statistics were calculated on the igneous, Ann-Mason parts (i.e., Ann-Mason mask) of an individual SEBASS flightline and then applied to the entire flightline.

### 6.3 Partial Least Squares Modeling

With the SEBASS spectra normalized to show laboratory-like mean and standard deviation, PLSR models developed on the laboratory data were applied to the airborne hyperspectral thermal infrared SEBASS data. The procedure of applying laboratory spectra-based models to SEBASS rather than using image spectra was preferred, as it proved to be challenging to find SEBASS pixels representative of the thin section locations for two reasons: (I) sample locations recorded on maps in pre-GPS era as well as the geocorrection uncertainties of SEBASS (see next section) lead to positional ambiguity between sample and image of several image pixels and (II) many thin section samples for alteration assemblage determination were collected from veins or alteration halos around porphyry intrusions and other fluid pathways and are not necessarily representative for an area surrounding the immediate sampling location.

The laboratory spectra-based models for alkali feldspar, plagioclase, quartz and plagioclase composition were developed as described in Chapter 5 except for the number of bands used; since SEBASS bands 125–128 were removed in the pre-processing, the laboratory spectra were resampled to the wavelengths of the remaining 124 bands and PLSR models built. The resulting regression coefficients were applied to the MASD-normalized SEBASS data.

In Section 5.3.3, it was shown that back-transformation of the results using a squared sine function can cause data folding for a small number of samples even if the spectra are not distorted. This is caused by individual spectra that are more extreme (in e.g., feature depth) than the typical values in the model. This causes the prediction value to
fall outside the $[0 - \frac{\pi}{2}]$-range and fold during the squared sine back-transformation. As a measure to prevent data folding with unexpected results, values in all four models were forced into the 0-100% range by assigning the minimum or maximum value, respectively, to pixels that were to fall outside the range.

6.4 Geometric correction

As part of the data delivery, AERO also provided a geographic location file for each SEBASS flightline. These files contain a geographic latitude and longitude for each individual pixel in the dataset. The coordinates were calculated from plane attitude data (IMU; inertia measurement unit) and differential GPS coordinates of the plane for each scanline. During the post-processing, AERO calculated coordinates for each pixel without including a digital terrain model, which can cause typical location errors of multiple pixels in hilly terrain like Yerington.

The geolocation files provided were used to georeference the individual flightlines and stitch them together into an eight flightline mosaic with 3.5 m pixel size. The georeferencing and mosaicing were the final two steps, after all earlier processing had been done on individual flightlines in their original, unrotated orientation. During georeferencing, nearest-neighbor resampling was used to maintain original data values while no feathering or other adjustments were employed to conceal issues with coherency at the edges of flightlines.

To test the spatial uncertainty in the geolocation information provided, the coordinates of 14 well-identifiable check points in the Ann-Mason SEBASS mosaic were compared to a 1 m orthophoto product (National Agriculture Imagery Program; distributed by seamless.usgs.gov). Results show that the total RMSE is 20.5 m, which is reduced to 13.2 m if the general bias in the results is removed (Appendix C). Scatterplots of error versus DEM-extracted altitude of the checkpoint show that the error in east-west direction is strongly related to the altitude, with positive errors at low altitude and negative errors at high altitude. The smallest positional error occurs at altitudes of about 1700 meters, implying that this height was chosen as an average ground elevation by the Aerospace Corporation processing.

6.5 Results

6.5.1 Preprocessing

6.5.1.1 MNF Bands

During the pre-processing of the SEBASS data, a vertical destriping and bad detector cell replacement was executed as the first step. The results of this treatment are difficult to visualize in image space, since the changes are small and the image data are still dominated by the large
6.5. Results

Figure 6.5 Example of signal and noise in MNF bands after destriping and spectral subsetting. 001–007 virtually noise free; 008–010 show horizontal striping; >040 dominated by random noise. Subset of flightline 22, scanlines 1300–1800.

...temperature effects of the ground. The improvements achieved by the destriping become visible in the MNF transformation (Figure 6.5). MNF 1–7, 11 are very rich in data content and virtually free from any visible noise in the data. MNF 8–10, 12 show sharp horizontal noise, that does not appear to repeat itself in regular patterns. This horizontal striping is difficult to correct for as any statistical technique would have to be applied to a very limited image width of only 128 pixels. Since the information content is still high in these bands, they were included for further processing. In MNF 13–20 the information content of the ground is still dominating, although with an increasing random noise component. Bands 21–40 are gradually dominated by noise but still show patterns of ground features. MNF 40 was chosen as the arbitrary cut-off, since MNF bands beyond this cut-off were strongly noise-dominated with no clear indication of coherent ground patterns. They were not included in the further processing steps.

These results are very different from earlier studies (Vaughan et al., 2005, 2003; Cudahy et al., 2000), which reported broad, vertical banding that dominated the first three MNF bands (an effect of “spectral smile” in the data) and sharp, column-specific detector noise in bands higher than MNF ≈11. In comparison, the results presented in Figure 6.5 show...
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![Graph showing emissivity and normalized data](image)

**Figure 6.6** Comparison between different processing steps and products of the same airborne pixel (Flightline 23, col=15; row=2022). ENorm(AERO) is the standard emissivity normalized or apparent emissivity product by the Aerospace Corporation. The arrow indicates residual atmospheric features in the data. Lab(y691b) is the laboratory spectrum of the quartz monzodiorite sample taken from the same location imaged by the pixel. Vertical lines mark features that are visible in all four spectra. Except for Aero spectrum, all other spectra are downshifted by 0.10 emissivity units each for clarity.

ground information from the first MNF band onward and no vertical banding and sharp striping in any of the MNF bands. This improved result has two causes: (I) instrument adjustments have reduced the "spectral smile" effect since the earlier acquisitions and (II) the applied destriping approach has effectively corrected any remaining small calibration misalignments. Cudahy et al. (2000) report oblique noise in the MNF bands, possibly relating it to a misaligned prism that projects dispersed light across the FPA. No indication of any oblique striping noise could be found in the 2008 data, indicating a successful realignment of the optical components by the AERO.

### 6.5.1.2 MASD Normalization

The noise-removal steps and the atmospheric compensation, which were restricted to igneous pixels of the Ann-Mason area, have created ENorm
6.5. Results

Table 6.1  Summary statistics of SEBASS model results for igneous units of the Ann-Mason area.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Mean</th>
<th>Stdev</th>
<th>5 percentile</th>
<th>95 percentile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Afsp</td>
<td>12.5</td>
<td>13.7</td>
<td>0</td>
<td>40.3</td>
</tr>
<tr>
<td>Plg</td>
<td>45.0</td>
<td>11.8</td>
<td>23.7</td>
<td>61.8</td>
</tr>
<tr>
<td>Qtz</td>
<td>16.2</td>
<td>6.29</td>
<td>7.8</td>
<td>27.1</td>
</tr>
<tr>
<td>Plgcomp</td>
<td>23.4</td>
<td>10.2</td>
<td>8.5</td>
<td>41.2</td>
</tr>
</tbody>
</table>

spectra that show better band-to-band consistency and smaller residual atmospheric features than in the original AERO ENorm product (Figure 6.6; top two spectra). Both spectra do show a spectral tilt towards shorter wavelengths, strongly reduced spectral contrast and some major artifacts between 7.5–8.5 µm. Although the spectral contrast is very low, some of the main Reststrahlen features (marked by vertical lines in Figure 6.6) are identifiable in the ENorm spectra as well.

After the mean and standard deviation normalization, the same airborne pixel shows spectral values and contrast comparable to the set of laboratory spectra (Figure 6.6; bottom two spectra). The spectral tilt and 8.0 µm artifacts have been corrected for and the spectral contrast has been hugely increased. The general spectral shape of the Reststrahlen band and relative depths of individual features match well with the laboratory spectrum of a sample taken nearby the airborne pixel location.

6.5.2 PLSR results

In the following sections the results from the PLSR models applied to airborne SEBASS data are presented. By normalizing the image data mean and standard deviation to those of laboratory spectra, PLSR model results are achieved that fall into the correct value range and create functional image patterns.

For the reasons mentioned in Section 6.3, a quantitative validation of the results with the thin section samples seems futile. Instead it was decided to use published lithologic and alteration maps (Dilles & Einaudi, 1992; Proffett & Dilles, 1984) to validate resulting patterns and compare the results of traditional field geologic work to the remote sensing products. Figures 6.7 and 6.8 show the lithologies and alteration zones, while Figures 6.9 to 6.13 show resulting mineralogic maps from PLSR prediction on SEBASS. Areas of interest that are mentioned in the text are highlighted in Figures 6.7 to 6.13 by lines of different colors to allow comparison of features in the PLSR products with those in the published reference maps. For names of geologic and/or alteration zones, the reader is referred to Figures 6.7 and 6.8, as well as Section 1.3 with the Ann-Mason test area description.
6.5.2.1 Alkali feldspar results

The map resulting from the Afsp model (Figure 6.9) shows coherent patterns across the nine flightlines with only a small amount of differences across flightline boundaries. Typical Afsp values (5 to 95 percentile) for the Ann-Mason area range from 0% to 40% (Table 6.1). The lower margin of values corresponds well with values of sericitized granodiorite rocks in the area. The upper margin reaches values about 5% higher than typically found in ground samples (Table A.1), but can be reached in the most Afsp rich parts of the Border Phase of the Bear quartz monzonite (Dilles, 2012). As expected Triassic sedimentary rocks (southern end) as well as quaternary material show up with very little Afsp. Most outcrops of igneous rocks of the Ann-Mason block show values above 20% Afsp, while lose material in the valley bottoms have Afsp values close to zero, probably due to weathering.

Two areas in the McLeod granodiorite are notably low on alkali feldspar. The first area (thick red line in Figure 6.9) is situated in the NW part of the area. The line demarcates a sharp change to rocks with greatly reduced Afsp content to its west (up direction in original position of the porphyry system). The part of the Ann-Mason block coincides with the general area where sodic-calcic alteration changes to sericitic and sodic alteration in the published alteration map (Dilles & Einaudi, 1992). The boundary between the Afsp rich and poor area in the SEBASS data is irregularly shaped and undulating, hinting to possible fluid pathways in an ESE-WNW direction, parallel to the porphyry dike system in the area. However, no apparent link is visible between the undulating boundary and individually mapped porphyry intrusions, which typically constitute the main fluid pathways in Porphyry Copper systems (Sillitoe, 2010; Dilles et al., 2000b). The main mineral reactions in the sodic and sericitic alteration zones involving feldspar are the alkali feldspar consuming reaction to albite and to sericite, respectively.

The second area displaying low Afsp compositions in the SEBASS data is situated at the top end of the Luhr Hill granite cupola and along its northern and southern contact with the McLeod granodiorite (black lines with white backing in Figure 6.9). The area coincides mainly with strong, pervasive sodic-calcic alteration and to a lesser degree with the top of the potassic alteration and some endoskarn. The main mineral reaction in the sodic-calcic alteration involving feldspar is

$$\text{Afsp} \rightarrow \text{Olg} + \text{Qtz}$$

and in the endoskarn is

$$\text{Afsp} + \text{Hbl} \rightarrow \text{Olg}/\text{And} + \text{Qtz} + \text{Dio} \pm \text{Hbl}$$

All mineral reactions mentioned are consuming Afsp and explain the drop in this mineral's concentration in the sericitic, sodic, sodic-calcic and endoskarn zones. The fact that a small part of the low-Afsp area in the SEBASS data overlaps with the area mapped as potassic zone in
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The published alteration map is surprising. The potassic zone is defined by the alteration of Hbl to hydrothermal Bt. While Afsp is generally stable in the potassic zone, very little added Afsp is actually visible at the surface. Reportedly, in some drill cores of the Ann-Mason area, Afsp is even broken down in intense potassic alteration (Dilles, 2012) and forms an additional source of Al and K for the formation of hydrothermal Bt following:

\[
\text{Hbl} + \text{Afsp} + \text{acid} \rightarrow \text{Bt} + \text{Ca}^{2+}
\]

While this reaction could explain low Afsp results inside the potassic alteration zone, it has not been observed on surface outcrops in the indicated region (Dilles, 2012).

Cutting north-south across the sodic alteration zone, a unit is visible with distinctly increased Afsp content (thin red line in Figure 6.9). This zone was identified by Dilles (2012) as older quaternary gravel deposit that is dissected by more recent drainage patterns. The high Afsp and low Qtz and Plg content (see below) is distinctly different from the sericite altered igneous units directly uphill (east) from the location of these gravels. Possible source locations would be the spectrally similar units 1-2 km SE of their current location, below the sericite zone in original alteration system orientation.

6.5.2.2 Plagioclase results

The SEBASS derived plagioclase map (Figure 6.10) shows coherent patterns across eight of the nine flightlines. The southernmost flightline partially overestimates the high plagioclase amount as compared to its neighboring line. This artifact can be traced back to the atmospheric correction which is based on igneous parts of the Ann-Mason block only; since flightline 29 contains mainly Triassic sedimentary rocks, the in-scene atmospheric correction statistics were based on too small an area for representative results. Typical SEBASS-derived plagioclase values (5 to 95 percentile) for the Ann-Mason area range from 24% to 61% (Table 6.1), a reasonable range as compared to the ground data (Table A.1). SEBASS estimated plagioclase values of 0% are observed in intensely sericitized areas with total destruction of plagioclase to sericite. The general pattern of the plagioclase concentration shows that the Triassic McConnell Canyon volcanics as well as the lower units of the Tertiary Singatse volcanics are considerably lower in plagioclase than the Jurassic intrusive rocks. One zone with consistently low plagioclase values (thick black line Figure 6.10) was identified inside the Jurassic intrusives. The area has a funnel-shaped connection to the Triassic sediment units in the south of the Ann-Mason block and connects with the main porphyry dike swarm just below the sodic alteration zone.

The sodic altered areas that showed very low Afsp values (thick red line in Figure 6.9), shows elevated plagioclase modes that can reach up to 60% (Figure 6.10). Furthermore, the Quaternary gravels identified in the Afsp product also show in the plagioclase map (thin red line,
6. Airborne TIR imaging spectroscopy and PLSR modeling

Apart from those areas mentioned above, the patterns inside the intrusive granodiorite and granitic units are not very clear and difficult to link to lithology or alteration.

6.5.2.3 Quartz results

The quartz content map from the airborne SEBASS data (Figure 6.11) shows clear patterns with excellent coherence across all flightlines. Typical Qtz values (5 to 95 percentile) for the Ann-Mason area range from 8% to 27% (Table 6.1), which correspond well with value from ground data (Table A.1). Extreme values of quartz content in Figure 6.11 are found in quartz-sericite altered areas (up to 60% Qtz), Jurassic quartzites (90-100% Qtz), Triassic sediments and hornblende gabbro (both <5% Qtz). Since quartz is less affected by metasomatism than the feldspars, the quartz content layer still shows different lithologic units, such as quartz porphyry dikes (Figure 6.11A) or a lens of gabbro (Figure 6.11A) inside the McLeod Hill Qtz monzodiorite. Among the Jurassic magmatic rocks, the Luhr Hill granite and its associated porphyry dikes as well as the border phase of the Bear quartz monzonite can all be differentiated from the McLeod Hill quartz monzodiorite based on its lower quartz content. The SEBASS-derived quartz content map also shows more intra-unit variability in the McLeod Hill mapping unit (thick green lines in Figure 6.11) which can be attributed to multiple, separate intrusions in the pre-alteration McLeod Hill unit (Dilles, 1987).

Quartz fractions in alluvial/colluvial quaternary sediments are expectedly high due to the resistance to chemical weathering. The quartz map also shows clear differences in quartz content between various units of the Singatse tertiary volcanics, where a clear line separates the so called "Mickey Pass Tuff" (right of dashed green line in Figure 6.11) from the Qtz-poorer "Singatse Tuff" (Proffett & Dilles, 1984).

Another noticeable feature is a late, NE striking quartz-calcite vein (Figure 6.11C) that occupies a steeply east-dipping Cenozoic normal fault (Dilles, 2012). The vein can be followed in the airborne data for over 2 km as it is cutting through all units from the Luhr Hill cupola in the NE to the Triassic sediments in the SW. At one location the vein splits up in several splays and at its southwestern end, appears to be boudinaged or offset by local faulting.

6.5.2.4 Plagioclase composition results

The plagioclase composition layer depicts patterns of variable mol% An in the plagioclase throughout the area (Figures 6.12 and 6.13). Its value range (5 to 95 percentile) is of 9 to 41 mol% An (with an average of An$_{23}$) which correspond well with value from ground data (Table A.1). The contrast of spatial patterns in this layer is quite low and it suffers from striping across flightlines as well as some minor influence of slope aspect (i.e., brightness temperature) on the data. If the data layer is stretched and color coded from green ($\leq$ 10 mol% An) to red ($\geq$ 40 mol% An) a zone
with predominantly more calcic plagioclase is enhanced (Figure 6.12). This zone reaches from the sediments in the south through endoskarn altered areas all the way to the main dike swarm and encompasses mainly the sodic-calcic altered zone. The area of Ca-rich plagioclase has a concave eastern margin (downward curving lower margin in original position) that follows the Luhr Hill granite cupola (and with it the potassic zone) quite closely. The western margin is concave as well with a deep paleodepth level close to the sediments and curving upwards to shallower levels closer to the central part of the dike warm. The upper end of the zone with Ca-rich plagioclase appears truncated by the sodic alteration zone, while the eastern margin is covered by the Singatse volcanic rocks. Within the Ca-plagioclase zone, the rocks with the highest An compositions appear in the central part and line up in a wide curve (blue, dashed arrow in Figure 6.12) indicating a general fluid pathway for sedimentary brines through the system. The plagioclase composition changes gradually from the central axis towards the edge of the zone. No sharp changes in plagioclase composition along lineaments could be detected in the airborne data.

Apart from the central zone with calcium-rich plagioclase, the plagioclase composition layer also contains information on rocks with strongly sodic composition. For that purpose, the layer was stretched (Figure 6.13) to only highlight areas that contain more than 30% plagioclase of albic (<10 mol% An) compositions. The results show that albic plagioclase is detected mainly in the western half of the area, where propylitic and late sodic alteration occurred (Dilles & Einaudi, 1992), both producing albic plagioclase. Some of these zones rich in albic plagioclase follow porphyry dikes (Figure 6.13A).

At the southwestern end of the test area, albic plagioclase is detected in the talus of the quartzites as well as in a unit just north of it. The quartzites can be arkosic (see Section 1.3) but since the spectrum itself is very strongly dominated by quartz features, this unit appears wrongly classified as albite-rich. Just north of the quartzites, a lens (black ellipse; Figure 6.13C) inside the igneous units shows very high albic plagioclase values. The lens has been mapped as "undifferentiated breccia" in an unpublished field map (Dilles, 1984). The SEBASS thermal infrared spectra of that area are perfect examples of a pure albite spectrum. The exact composition and the provenance of the lens requires further investigation.

East of the sodic-calcic alteration (i.e., "below" in original orientation of the alteration system), a few areas inside the Luhr Hill cupola show albic plagioclase patterns as well (e.g., Figure 6.13B). These occurrences of albic plagioclase can be linked to the late, low-T Ep + Ab ± Chl alteration that has been observed in the cupola just west of the range front fault (Dilles, 2012).
Figure 6.7  Simplified geologic map after Proffett & Dilles (1984). Interpreted boundaries of patterns stem from the airborne PLSR products and are explained in the text.
Figure 6.8 Alteration map after Dilles & Einaudi (1992). Interpreted boundaries of patterns stem from the airborne PLSR products and are explained in the text.
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Figure 6.9  Airborne PLSR-derived alkali feldspar map. Linear contrast stretch from 5% (black) to 40% (white). Black line and thick red line mark zones of low Afsp content in strong sodic-calcic and sodic alteration zones, respectively. Thin red line marks area of Quaternary gravel deposits.
Figure 6.10  Airborne PLSR-derived plagioclase mode map. Linear contrast stretch from 10% (black) to 60% (white). Black line marks central zone of reduced plagioclase modes. For solid red lines, see Afsp.
6. Airborne TIR imaging spectroscopy and PLSR modeling

Figure 6.11 Airborne PLSR-derived quartz map. Linear contrast stretch from 5% (black) to 40% (white). Blue dashed lines mark a few of the porphyry dikes with higher Qtz content. Thin green line marks gabbro lenses and the thick green line other Qtz poor inclusions in the McLeod unit. Dashed green line separates Qtz-rich and poor Tertiary volcanic units. Dashed red line traces a Qtz-Cc vein. For solid red line, see Asp. Insets show details of A) porphyry dikes, B) gabbro lens and C) Qtz-Cc vein.
Figure 6.12  Airborne PLSR-derived plagioclase composition map. Linear contrast stretch from 10 mol% An (green) to 40 mol% An (red) highlighting changes in the central part of the area. Black dashed lines show limits of area with Ca-richer plagioclase. Blue dashed line shows interpreted main fluid pathway of sedimentary brines, following highest Ca-component. Only the Jurassic intrusions are shown to facilitate interpretation.
Figure 6.13  Airborne PLSR-derived albitic plagioclase map, highlighting pixels with more than 30% plagioclase and <10 mol% An composition. Background is generalized geologic map after Dilles & Einaudi (1992). Only the Jurassic intrusions are shown to facilitate interpretation.
6.5. Results

6.5.3 Mapping the Batholith

The PLSR models applied to SEBASS have created quantitative mineral abundance and plagioclase composition maps (Figure 6.9 to 6.13) that compare well with published lithologic and mineral maps of the area. In the following sections, a reverse look is taken and it is discussed, which units (lithologic or alteration) can be discriminated from each other based on the discussed PLSR data products.

6.5.3.1 Mapping lithologies

*Quaternary* alluvial and colluvial can be differentiated from *outcrops* with the help of its high (detrital) quartz content and its low alkali feldspar content. It is best assessed when the products are draped over a DTM so the morphology can be used as input as well to reduce false positives.

The *McLeod Hill quartz monzodiorite* is the main magmatic body of the batholith. It can be differentiated from the triassic and tertiary volcanic units by the plagioclase content product and from the Luhr Hill granite and the triassic sediments by the quartz product. Variations within the unit, such as gabbroic rocks and other patches of quartz-poor rocks, can be detected in the quartz product as well.

The *Luhr Hill* unit is a granitic cupola that is the source intrusion for the porphyry dike swarm. The boundary with the McLeod Hill unit is clear (although not sharp) in the quartz product. At the top of the cupola, the boundary is a bit more fuzzy than towards its side, due to the large number of porphyry dikes intruding the McLeod unit through the apex of the cupola. The top of the cupola also lines up with the boundary between Na-rich and more Ca-rich plagioclase. The bottom of the unit is fault controlled and borders mainly Quaternary alluvial. Variations within the Luhr Hill granite are minimal in the quartz layer, but the plagioclase composition layer shows some strongly albitic zones inside it.

Mapping *Quartz porphyry dikes* is key to the understanding of fluid pathways and areas with highest potential for Cu-mineralization. The dikes have a higher quartz content than the McLeod unit, which makes them often (though not always) visible in the quartz content map. Where the dikes pass through Luhr Hill granite or the border phase of the Bear unit, the difference in the quartz content is minimal and it was not possible to detect it in the airborne data. Above and below the sodic-calcic alteration, the porphyry dikes often show up as linear aggregations of very albitic plagioclase which can help to map dikes that pass through Luhr Hill and border phase units.

*Jurassic* *Aplites, Pegmatites* and *late andesitic intrusions* occur as small intrusive bodies, cutting through older units. The andesites can be identified by their low quartz values and the Ca-rich plagioclase composition. Wider aplites and pegmatites are detectable by their higher quartz content than the surrounding rocks, but since they don’t show up
on the alkali feldspar map, they can often not be identified as a particular intrusion.

6.5.3.2 Mapping alteration zones

Most alteration in the Yerington batholith is not pervasive but follows porphyry dikes and fractures. A few meters away from the main fluid pathways, the host rocks can be entirely unaltered. This makes detection of alteration from airborne data challenging and success is only possible if the density of fractures and veinlets is high enough to cause a detectable change in the rocks at a 3.5 m pixel size. In the following section it is analyzed, whether or not particular alteration zones were detectable from airborne TIR data.

Potassic zone: Since mapping copper mineralization (usually manifested as a few percent of copper sulfide or oxide in the Yerington batholith rocks) directly from airborne TIR data is not possible, mapping the associated potassic alteration zone would help significantly in pinpointing locations for follow-up visits. The potassic zone in the Yerington batholith is defined by the replacement of Hbl with secondary, hydrothermal Bt in the rocks. Total percentages of Bt is usually no more than a few percent with occurrences of >10% being rare (see Table A.1). Furthermore, Bt is spectrally difficult to recognize in thermal infrared spectra of rocks. Feely & Christensen (1999) determined a detection limit of \( \approx 10\% \) (twice the amount of most other minerals) for their unmixing studies on laboratory rock samples. Hence, mapping potassic alteration through airborne detection of small Bt flakes is unfeasible.

Alkali feldspar is a second mineral indicative of potassic alteration. However, most observations of plagioclase being altered to alkali feldspar in the potassic zone stem from drill cores and very little added Afsp is actually visible at the surface (Dilles, 2012). Consequently, the alkali feldspar product did not show any patterns that coincided with the potassic alteration zone and it would not have been possible to map it based on the presented spectral products.

Strong sodic-calcic alteration (S2) is visible in the alkali feldspar map, where contents typically drop from 30% to close to 0%. Furthermore, the plagioclase composition in the strongly Na/Ca-altered areas is typically \( >35 \text{ mol}\% \text{ An} \). If these two maps are combined, strong Na/Ca alteration can be mapped and identified quite successfully. The less intense Na/Ca alteration west (formerly above) the pervasive S2 alteration is not detectable in the products.

The sodic alteration shows up with alkali feldspar values close to 0%, but opposite to the strong Na/Ca-zone, the plagioclase composition is not elevated and stays around or below \( \approx 25 \text{ mol}\% \text{ An} \). Plagioclase modes are also elevated sometimes reaching \( >60\% \).

The sericite alteration zone shows a decrease in plagioclase modes from \( \approx 50\% \) to \( \approx 15\% \). The most strongly altered areas also contain Qtz-Ser alteration that have clearly elevated quartz mode values (typically 40-50%). Compared to a pure quartz spectrum, Qtz-Ser has an asym-
metically deepened, second lobe which helps to differentiate Qtz-Ser altered areas from sandstones and quartzites. The chlorite-sericite zone could not be differentiated from the sericite zone, as both have similar compositions in the spectral TIR products. The main difference lies in the chloritized mafic minerals, which are difficult to detect in the TIR. Ideally, the shortwave infrared spectrum should be consulted as well. Not only would the SWIR make sericite detection simpler, it would even allow the differentiation of sericite into white mica and chlorites of various chemical compositions.

Propylitic alteration coincides with the western part of the system, where albite plagioclase compositions were found. Opposite to the sodic alteration zone, alkali feldspar modes are not visibly reduced. Combined SWIR/TIR analysis could be helpful here as well, in order to detect other propylitic alteration minerals, like epidote and calcite.

The endoskarn zone is similar to the sodic-calcic zone, where Afsp values are reduced and plagioclase compositions tend to be more calcic. Based on the TIR products of this thesis, the two zones cannot be differentiated. Focusing on diopside and garnet in the TIR, and epidote in the SWIR and TIR, should allow the differentiation of endoskarn from strong sodic-calcic alteration.

6.6 Discussion

6.6.1 The SEBASS dataset

The thermal infrared images recorded by SEBASS are of excellent signal quality, but show minor vertical striping effects, and band-to-band noise. The currently applied atmospheric compensation is creating substantial atmospheric residuals and low spectral contrast in the data. The results presented in this chapter show that the new pre-processing chain developed for airborne SEBASS data successfully suppresses striping, residual atmospheric features and image noise. The realignment of SEBASS optical components by the Aerospace Corporation has also helped to further reduce the broad vertical banding and oblique noise reported by Cudahy et al. (2000) in older datasets.

Towards the end of the flightlines, the radiometric calibration of the sensor seems less controlled, especially towards the longest wavelengths, along the starboard side of the swath and when south-facing (i.e., hot) surfaces are imaged. This could be related to current SEBASS calibration practices where calibration measurements are taken before and after each flightline and the gain and offset of the instrument are calculated for the central part of each flightline (Riley, 2012). Hence, for long flightlines (exceeding several thousand scanlines), calibration should deteriorate towards their beginnings (not observed) and ends. The problem was alleviated by removing the most affected bands 125–128 early in the processing chain. In the future, long flightlines may require a different
calibration procedure, where gain and offset are calculated per scanline rather than the central part of the flightline.

The currently used atmospheric correction, ISAC, is a simple approach based on many assumptions and does not correct for reflected down-welling radiance. This creates spectra that have very little spectral contrast and sometimes even inverted atmospheric features in highly reflecting urban areas. Better atmospheric correction tools for hyperspectral thermal infrared data are needed and several efforts are currently ongoing: The Aerospace Corporation is developing ISAC-Gates (Genetic Algorithm TeS), an extension to the traditional ISAC algorithm, that includes an estimation of the down-welling sky radiance component. Another approach, called Automatic Retrieval of Temperature and EMissivity using Spectral Smoothness (ARTEMISS), is developed at the Air Force Institute of Technology (Borel & Tuttle, 2011; Borel, 2008). ARTEMISS works with a combination of in-scene information and radiometric transfer model-based look-up tables. While a general description of the code is available, the tool itself is subject to US export restrictions and could not be tested.

In the temperature-emissivity-separation (TeS) step, the commonly applied emissivity normalization was used to keep it in line with the approaches of the Aerospace Corporation as well as Vaughan et al. (2005, 2003). The ENorm approach was originally developed for multi-spectral TIMS data (Gillespie, 1985) and the chosen emissivity of 0.96 is a good compromise for rock and soil spectra in such a multi-spectral system. As Figure 6.4 demonstrates, the Planck curve determined on the hyperspectral radiance data can be far from ideal and leads in this case to a tilted emissivity spectrum after ENorm. For hyperspectral thermal infrared data, an approach could be investigated that optimizes the fit between top of radiance spectrum (determined by a convex hull function) and a Planck curve as a function of emissivity and temperature. The "best fit" criteria could involve a measure of residuals versus wavelength, making sure that the relationship includes only noise and no structure.

After ENorm, the SEBASS apparent emissivity data still contains some spectral artifacts. Other authors used a spectral three-point moving mean filter and restrictive spectral subsets (Vaughan et al., 2005, 2003) to cope with spectral noise, and used convex hull removal to correct for the tilt in spectra (Vaughan et al., 2005, 2003; Cudahy et al., 2000). The presented MASD normalization not only corrects for spectral tilt, band-to-band noise and residual atmospheric features in the data, but it also enhances the spectral contrast to a level that is comparable to laboratory data of similar compositions. This enables the quantitative PLSR model to run on the airborne data as well. Basic prerequisite for MASD normalization is a set of field or laboratory spectra of samples that can be considered representative for the rock compositions in the area. Hence, it cannot be applied blindly to a new area without any prior knowledge or a few field samples.
6.6.2 PLSR results

The results from the PLSR modeling are presented in four mineral maps: Alkali feldspar, plagioclase and quartz modes, as well as plagioclase composition in mol% An. Where the outcrop situation is good, all models perform well, although the plagioclase composition model shows small information contrast. The patterns detected in the airborne data are strongly influenced by erosion and weathering; valley bottoms and alluvial fans, for example, appear as units rich in quartz and poor in alkali feldspar, merely because of their different resistivity to weathering. This could lead to misinterpretation of a Quaternary cover for Qtz-rich, Afsp-poor outcrops.

While automatic rejection of anomalies by certain landforms may be technically possible, a simple image draped over a digital terrain model during the interpretation of the results is certainly more effective. To the trained earth scientist, the combination of topographic and compositional information in the same image is very valuable.

Similarly, units that occupy topographic highs can cover the downslope outcrops with their scree appearing larger or with a different shape than they are in reality. This effect may have had some influence on the N-S axis of Ca-plagioclase zone in the plagioclase composition map (Figure 6.12): the strike direction of the main ridges is about N70W, with slopes roughly towards north and south. Since sodic-clastic altered rocks are quite resistant to weathering (Dilles, 2012), more calcic plagioclase from the ridge tops could have tumble down-slope in the talus smearing out the Ca-plagioclase signal in a N-S orientation in the process. Indication of erosional processes affecting patterns can be seen in several places. Therefore, it is plausible that Ca-plagioclase mainly occurs in ESE-WNW oriented ridges (following porphyry dikes) at paleodepths of 3-5 km and that the patterns of the individual ridges are connected by erosional processes in N-S direction.

6.6.2.1 Application to other areas

The strength of combining PLSR and TIR imaging spectroscopy is that detailed knowledge that exists for a few field samples, is used to predict the same parameters for the entire extent of the airborne imagery. In the case of the Yerington batholith, the PLSR models are directly transported to any of the other fault blocks that share similar lithologies and alteration histories. A good example is the Blue Hill area, situated just north-west of Ann-Mason (Figure 1.2). Detailed alteration mapping in the Blue Hill area is still ongoing. Hence, Blue Hill did not lend itself as the test area, but would make an excellent follow-up study at this point. A different set of flightlines could be chosen and the same processing chain applied as described above. The products could be used to increase the speed of the traditional field mapping that is currently carried out by connecting the dots and by optimizing precious field time by highlighting the most interesting areas.
If the presented PLSR model was to be applied to another porphyry system, the existing model could be directly applied as a first approximation, as long as lithologies and alteration zones were comparable to the Ann-Mason block. For best results, a new set of field spectra and accompanying compositional information should be collected and a dedicated PLSR model should be built, based on those samples.

6.7 Conclusions

In this chapter, SEBASS data and PLS regression were used to produce the first ever quantitative airborne maps of plagioclase composition as well as alkali feldspar, plagioclase and quartz abundances. Based on the results and discussion above, the following conclusions can be drawn:

- The mineral mode and plagioclase composition maps show coherent patterns across flightlines. The major patterns coincide with lithologies and alteration zones of the Ann-Mason area from literature. In an absolute sense, the "typical" values (5, 50 and 95 percentile) in the airborne data compare well with those known from field samples.

- For mapping lithologies, the Plg mode layer differentiates between the Tertiary and Triassic volcanic rocks, and the plagioclase-richer Jurassic intrusives. Qtz mode map can differentiate between most igneous lithologic units, such as three main intrusive bodies, and porphyry dikes, gabbroid and aplitic rocks in the McLeod unit.

- The plagioclase composition map revealed a central zone of Ca-richer plagioclase indicating a general fluid flow direction of sedimentary brines through the batholith.

- In alteration zone mapping, strong sodic-calcic and endoskarn alteration can be identified by their drop in Afsp and increase in Ca-rich plagioclase. Differentiation between the two is not possible without mapping Ep. Sodic alteration can be identified in the airborne data by the drop in Afsp and by albitic plagioclase composition. Propylitic alteration shows slight increase in Na-rich plagioclase but is difficult to map based on TIR alone. Sericite and chlorite-sericite alterations are visible through a decrease in plagioclase mode. Strong Qtz-Ser alteration considerably increases the Qtz mode. To map weak Qtz-Ser alteration and differentiate between Ser and Chl-Ser alteration, SWIR bands must be used. No indication of potassic alteration could be detected in the mineral mode products.

As a byproduct, a renewed preprocessing chain for SEBASS data was developed. It corrects calibration issues and removes noisy components at an early stage and has helped to remove vertical striping and spectral noise from the dataset. Furthermore, the Mean And Standard Deviation (MASD) normalization between airborne and laboratory spectra was introduced. It successfully restored the spectral contrast of the airborne
6.7. Conclusions

SEBASS data to match those of laboratory spectra, after which laboratory-developed PLSR models can be applied to airborne TIR data yielding realistic quantitative results. Apart from restoring spectral contrast in the images, MASD normalization also corrects spectral artifacts such as spectral tilt, band-to-band noise and residual atmospheric features.
7.1 Introduction

The general goal of geologic remote sensing is to equip the modern geologist with state-of-the-art tools. The tools can help to speed up the process of data collection by giving a synoptic view of patterns in a study area, producing preliminary mineralogic or lithologic maps and pinpointing the most interesting locations for follow-up field work. The objective of this thesis was to determine whether airborne hyperspectral thermal infrared imagery could be used to identify major feldspar mineral groups and quantitatively map their abundances as well as the chemical compositions of the plagioclase group. In this chapter, the findings of the previous Chapters 3 to 6 are summarized and the outcomes are discussed in relation to the original research objectives which were defined as:

- to develop a thermal infrared laboratory measurement procedure that results in repeatable and accurate spectral measurements of the sample material (Section 7.2)
- to develop a quantitative link between TIR laboratory spectra and mineral information from traditional analytic methods (Section 7.2)
- to apply this quantitative link to airborne hyperspectral TIR data (Section 7.3)
- to evaluate the resulting mineral maps for accuracy and added value as compared to ground-based methods (Section 7.3)

The following sections are structured by results in the laboratory and airborne domain, and are followed by a summary of the progress made during this research. The final section deals with recommendation for future research.

7.2 Laboratory domain

The first objective of this thesis was to develop a suitable laboratory measurement procedure. At the beginning of this research, no spectro-
meter was available at UT-ITC, able to measure thermal infrared spectra of rock samples. Furthermore, the collective expertise of the thermal infrared realm within the research group was based on extrapolation from years of shortwave infrared experience and years of researching temperature anomalies in coalfire areas. In order to achieve the first research objective of developing a sound TIR spectroscopic measurement procedure, contacts with other TIR spectroscopy laboratories were of great importance. Through the course of this research, different measurement setups and procedures were developed, cross-referenced with results from other laboratories, leading to a well-calibrated, reliable instrument setup as described in Chapter 3.

As usual, the devil is in the detail and the more closely one studies the repeatability and noise statistics of spectrometers, the more problems one encounters. A rather unexpected (and serendipitous) discovery in the first part of the thesis was the realization that even a coarse calibration quartz sand (free of clinging fines) seems to be hygroscopic such that its reflectivity is lowered by several percent if exposed to air (Chapter 3). As a consequence, the standard should be oven dried and cooled in a desiccator before every standard measurement if maximum accuracy is required. Alternatively, a homogeneous solid standard could be developed, which is expected to be less susceptible to the influence of humidity (until proven otherwise).

The second objective was to quantitatively link the TIR spectra with mineral modes from an existing study by Dilles (1984). PLSR was chosen over the often applied spectral mixture analysis (SMA) as it did not require a large, spectral database of pure spectral endmembers. Especially with complex mineral groups (like feldspars), it would be challenging to acquire pure sample material and representative spectra for all compositional variations within the group. By using PLSR, the existing tabular rock composition information (mineral modes from thin section study) were used to build a quantitative model between the thermal infrared spectra and the alkali feldspar, plagioclase and quartz modes, and plagioclase compositions.

The results of Chapter 4 showed that it was possible to predict mineral modes and plagioclase composition with PLSR from TIR spectra with slightly smaller or similar uncertainties than SMA reports (e.g., Feely & Christensen, 1999) but without having to supply a spectral endmember database. The error analysis in Chapter 4 also showed that errors in the PLSR model were similar to those of the reference method used (thin section). Since uncertainties in the predicted values can never be lower than the uncertainties in the reference method, it is believed that the calculated RMSEP values are not yet a true measure of the accuracy that can be achieved with TIR spectroscopy and PLSR statistics. But to test this hypothesis, a highly accurate reference method is required (like point-counting in thin sections) which was not available for testing at this time.
7.3 Airborne domain

After demonstrating that the mineral modes could be extracted from laboratory spectra, the next research objective involved applying of the results to airborne data. Before doing so, it was decided to first investigate whether airborne SEBASS data would theoretically be able to detect feldspar minerals and quantitatively predict modes and compositions in igneous rocks. For that purpose laboratory spectra were spectrally down-sampled and noise was added in order to mimic typical airborne data conditions. Results showed that the spectral resolution, spectral range and signal-to-noise levels of SEBASS were theoretically suitable to map feldspar modes and compositions on airborne data. When theory was put to practice, geolocation issues and scale differences between thin section samples and airborne data made it impossible to build and validate a PLSR model on airborne data itself. On the other hand, applying a laboratory PLSR model to airborne data was only possible if image spectra were as free of distortions as possible and similar in shape to the laboratory spectra. A long series of pre-processing tests started, culminating in the newly proposed MASD normalization, which was necessary to get realistic model predictions.

The last research objective required the assessment of the results and its added value. Due to the scale and geolocation issues mentioned above, the sample locations (and their mineralogic compositions from thin section) could not be linked to individual image pixels for a direct quantitative assessment of the results. Instead, two approaches of validating the results were used: firstly, the patterns in the predictive model output maps were compared to patterns of lithologic and alteration maps in literature. Secondly, the "typical" value range (5–95 percentile) of the absolute predictive values were compared to the compositions known from field samples. The coherence of the patterns with lithologies and alteration, and the general value ranges in absolute sense fitted remarkably well.

The added value of this research for the airborne domain clearly lies in the unbiased approach that was followed. Too often remote sensing involves processing steps where parameters are tweaked until the resulting patterns fit the expected output. Through that conduct, we make algorithms fit local geology and return to us what we already knew rather than building models that are generally applicable with surprising results. In this thesis, quantitative mineral products were created without the need for operator interference. Admittedly, PLSR as well as MASD normalization both require field samples with accompanying spectra and auxiliary information. These field data were the only input for the modeling; no use was made of the existing geologic and alteration maps until the validation stage. Therefore, the resulting prediction results would have looked identical with or without the existing maps and independent of the operator. Since the method was not geared towards reproducing a map of existing knowledge, the PLSR result maps showed
7. **Synthesis: Mapping feldspars, what’s new?**

areas with clear discrepancies as compared to the published maps. These are the interesting areas to check during a field campaign.

In terms of making field work more efficient, the techniques tested on the Ann-Mason block could immediately be applied to other, less studied area in the Yerington batholith. With lithology and geologic history between blocks being comparable, most of the lithologic boundaries and alteration zones would be reasonably captured even without new field sampling, giving the field geologist immediately a starting point from which to plan future field work. Definitely, this is an added value compared to starting with a blank map sheet.

A multitude of recent instrument developments demonstrate that the TIR remote sensing domain is thriving. Numerous multi- to hyperspectral airborne TIR instruments are either being designed or have recently had first test flights (Table 2.2). The most recent developments are the Aerospace Corporation’s 32-channel TIR Mineral and Gas Identifier (MAGI) (Hall et al., 2008), and a 128-channel TIR imager, MAKO (Hall et al., 2011a). With a 128 spectral bands in the 7.8-13.4 \( \mu \text{m} \) range, MAKO is a potential successor of SEBASS in terms of spectral resolution. With its whiskbroom design, however, MAKO is able to image wide areas in a single flight strip, overcoming the disadvantage of SEBASS’ very narrow swath. NASA JPL is reportedly scheduled to fly its airborne Hyperspectral Thermal Emission Spectrometer (HyTES) in late 2012 or 2013 (Riley & Hecker, subm). All these technical advances are very encouraging and will drive the development of algorithms and new application fields in the years to come.

### 7.3.1 No more dirty hands?

With hyperspectral airborne sensors getting increasingly sensitive in spatial and spectral resolution, the end of geologic field work may appear near. By combining different wavelength ranges (e.g., VIS-SWIR-TIR, but also RADAR, \( \gamma \)-ray and other geophysical techniques) we can almost image everything we want. Almost! An important concept to keep in mind is the difference between discrimination and identification of features (Kirkland et al., 2002). *Discrimination* is seeing patterns of units and the boundaries between them, while *identification* is unambiguously knowing what they actually represent or consist of. With its synoptic view, discrimination on remote sensing data is often simple (frequently even easier than when standing in the field). Identifying materials correctly is a lot more difficult especially for multi-spectral data but often for hyperspectral datasets as well.

The same holds for this research. Many units could be discriminated and most discriminated units could be identified. Nevertheless, some of the resulting patterns divert from existing maps and could not be explained from the airborne data alone. These areas are of particular interest and should be checked during a future field visit.

Apart from field validation of the airborne results, field work also remains important to fill the gaps, which remote sensing cannot fill.
A typical example in this case is the alteration of minerals. Thermal infrared spectra give us information on the average mineralogic composition of a certain surface area at the time of acquisition. It lacks information on, for example, compositional zonations which can give indications on the alteration history, or whether or not a detected mineral was actually stable in a given assemblage.

7.4 Progress made

7.4.1 Spectroscopy of feldspars

At the beginning of this research, quantitative mineral mode extractions from TIR laboratory spectra were possible through spectral mixture analysis with reasonable error margins. The main crux of the method was the definition (and acquisition) of a representative suite of endmember spectra that incorporated all naturally occurring mineral variability in a study area.

The outcome of this work has demonstrated that the PLSR approach can determine mineral modes with similar error margins but without the need of an endmember library. Instead, existing modal mineralogy for a number of samples are used to train the PLSR model to extract the required information automatically from the thermal infrared spectra of all other sample. Hence, the two approaches have fundamentally different requirements and application fields.

- Since PLSR requires a small set of samples for which compositional data are available, it lends itself to ongoing studies in, for example, the mining sector, where samples are tested on a regular basis anyways, and the results are extrapolated to other parts of the mining operation.

- Since SMA does not require any sample material from the study area, it lends itself to studies where no field work is possible, like planetary exploration, or for a first assessment of a remote study area, where no sample material is available.

Have we then managed to make TIR spectroscopy and PLSR a routine analytical tool, similar to XRD or XRF? One of the advantages of TIR laboratory spectroscopy, as used in this thesis, is the simple sample preparation, which does not require any powdering or pressing pellets. This thesis used offcuts from thin sections but any reasonably flat surface that covers the sampling port will do. For the purpose of this research, however, a DHR measurement method was chosen which takes 30 minutes measurement time per sample, totally obliterating the advantage of minimal sample preparation. While the current DHR measurement setup was chosen for comparison to airborne data, routine laboratory and field applications would benefit from the larger energy throughput of a bi-directional setup, which would reduce the measurement time to well under a minute per sample, making the method much more applicable for routine measurements. As a pure laboratory tool it would not matter
that the results are not quantitatively comparable to airborne emission spectra.

In the airborne domain, the starting point were studies by Cudahy et al. (2001b,c,d, 2000). They mapped feldspar mineral occurrences by classifying the image, and produced a qualitative plagioclase composition layer with band ratios of SEBASS data. In Chapter 2, existing information and studies were reviewed prior to the start of this research and in Section 2.4, a number of feldspar products were proposed that could be helpful to exploration geologists in the future. From the proposed products, quantitative plagioclase composition and abundance products for Afsp and Plg were developed. For the Afsp composition and structural state, insufficient auxiliary information was available in the reference dataset used.

The outcome of this thesis has demonstrated that airborne SEBASS data, in combination with PLSR, are not only theoretically able to map feldspar modes and plagioclase compositions, but can actually produce quantitative mineral maps that compare well with documented lithology and alteration zones of the area, and mineral modes in field samples. In a next step, these products should be applied to a similar area in the Yerington batholith to demonstrate the applicability to less studied areas. It is then to the exploration companies to decide whether they see use in these datasets. But as a colleague from the mining sector once put it: "If you can manage to make airborne feldspar maps, we will find a way to use them" (Antonio Arribas Jr., pers. comm., 2006).

### 7.4.2 Yerington Porphyry Copper System

For the purpose of this research, the Ann-Mason porphyry copper system was a test case rather than the object of study. Nevertheless, a few interesting observations were made on the batholith itself, that differ from the existing maps and would require detailed attention in the future. A few examples include:

- The results showed areas of very low Qtz content in the McLeod unit. While some of them were mapped as gabbro lenses, several are newly discovered and need verification in the field.

- The boundary of the sodic alteration (as mapped in airborne data) closely follows the lithologic boundary of the border phase of the Bear unit (as mapped on the ground). Nearby areas are currently mapped as McLeod unit even though they look spectrally identical to the sodic-altered Bear unit. Field checks have to confirm if the boundaries of the units have to be re-drawn.

- A spectrally rather unusual unit of reportedly Quaternary gravels, dissected by younger drainage systems, occurs in the very northwest of the test area. The materials in the gravels are spectrally distinct from the directly neighboring sericite-altered units. With the spatially continuous airborne data the gravels can be linked
to a spectrally similar source locations 1–2 km southeast of their current location.

### 7.5 Future work

While a first step has been made towards reliable, quantitative airborne feldspar products, this research offers a number of natural follow-up opportunities.

- **Atmospheric correction.** The currently used ISAC is fast and simple but has disadvantages. There is a need for better atmospheric correction tools for hyperspectral TIR sensors. None of the commercially available model-based atmospheric correction tools seem to be able to properly handle the high spectral resolution of SEBASS data.

- **A quantitative validation program of the mineral mapping results.** This would require a specific sampling approach where samples from large homogeneous areas are taken. The values and the variability in the airborne feldspar product could be used as a guide to design an appropriate sampling scheme.

- **Include other TIR minerals.** Quantitative mineral maps for feldspars and quartz were produced for the Ann-Mason area. Additionally, SEBASS data could also be used to detect or quantify other minerals that help in mapping lithologies and alteration zones. Examples would be epidote, carbonates, diopside and possibly garnets for the skarn areas.

- **Combining the wavelengths.** Combine the VIS-SWIR with the TIR data in the Ann-Mason area to profit from the complementary nature of the wavelength ranges.

- **Extension to other areas.** A future contribution of this research to the understanding of porphyry systems will be the application of the Ann-Mason results to less studied areas within the Yerington batholith and beyond. Alteration mapping in the Blue Hill area (see Figure 1.2) of Yerington is still ongoing. The area is also covered by airborne VIS-SWIR-TIR data and readily lends itself to a directly application of the acquired knowledge from the Ann-Mason block to an area with less detailed existing knowledge.
This appendix contains compositional information on the 105 samples that were used in the study. The left half show the mineralogic compositions as determined by thin section analysis during the PhD study of Dilles (1984). Mineral modes were determined in percent of the thin section area (areal%) with traditional polarization microscopy. Error estimates for the modal mineralogy are similar to those typically quoted in literature, with accuracies of $\pm 5$–$15\%$ for major minerals ($\geq 10\%$ of area) and $\pm <5\%$ for minor minerals ($<10\%$ of area) (Feely & Christensen, 1999; Hamilton & Christensen, 2000). In altered samples, for each mineral phase the percentage of alteration as well as the alteration product was taken into account. This ensures that the tabular modal descriptions represent the current mineral composition of the samples (after alteration).

Plagioclase composition was determined using the a-normal method (Deer et al., 1992) on several grains per thin section, and confirmed with electron microprobe on selected samples, with corresponding errors approximately $\pm 1$–$2$ mol% and $\pm 1$ mol%, respectively. In samples with zoned plagioclase, compositions were estimated on several spots from core to rim of individual grains and the results were averaged.

The right half of the table shows the modal estimates from TIR spectrosocopy and PLSR modeling (this study). Estimated errors for the compositional model results were found to have root mean square errors of prediction (as compared to thin section results) of $\pm 5.1\%$ (absolute) for alkali feldspar, $\pm 8.5\%$ (absolute) for plagioclase and $\pm 6.9\%$ (absolute) for quartz. The regression model for plagioclase composition predicted with estimated errors of $\pm 7.8$ mol% anorthite.
## A. Sample descriptions

**Table A.1:** Modal mineralogy of samples determined from thin section study (left half) and PLSR modeling on TIR spectra (right half).

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*Minerals in CAPITALS cover >10% of the sample area each, mineral names in (brackets) <5% each.

act=actinolite, ana= analcime, ap=apatite, aug=augite, bt=biotite, cc=calcite, chl=chlorite, chr=chrysocolla, clay=clay minerals (without subdivision), dio=diopside, ep=epidote, gnt=garnet, goe=goethite, hbl=hornblende, hm=hematite, jar=jarosite, mgt=magnetite, rt=rutile, ser=sericite, sph=sphene, tm=tourmaline.
PLSR model details

Introduction

This appendix contains supplemental information on the laboratory partial least squares regression (PLSR) models. Additional figures of root mean square error of prediction (RMSEP) plots, loading weights and regression coefficient spectra are shown and discussed here. Some figures and descriptions of the alkali feldspar were already treated in Chapter 4 but are repeated here for completeness. This appendix was published as supplemental text to Chapter 4 in: Hecker, C.A., Dilles, J.H., van der Meijde, M. and van der Meer, F.D. (2012) Thermal infrared spectroscopy and partial least squares regression to determine mineral modes of granitoid rocks. Geochemistry, Geophysics, Geosystems (G3), 13(3), 1–15.

Alkali feldspar model

RMSEP

The RMSEP plot shows the predicted mean error (from the cross validation analysis) as a function of the number of factors used (Figure B.1). After a global minimum at six factors, the predicted error increases again, as the model starts fitting noise in the data. Since the gain in RMSEP between a model of 5 factors and the model of 6 factors is minimal, it was decided to use the more robust 5 factor model (see also Table 1).

Loading weights

Since our predictor variables are spectral data, the resulting loading weight and regression coefficients can be plotted and interpreted as spectra as well. The loading weights of a factor show which wavelengths were important in defining that particular factor. Through spectral interpretation of the loading weights, we can understand which minerals and mineral combinations drive the particular PLSR model. For the alkali feldspar model, the loading weights of factor 1 (Figure B.2) are strongly dominated by microcline, with reststrahlen features at 8.56, 9.24, 9.48 and 9.81 (all wavelengths are in units of µm). There are also features at
B. PLSR model details

Figure B.1  RMSEP plot for alkali feldspar. The plot indicates prediction errors for various numbers of factors used in the alkali feldspar model. The selected number of factors is indicated by the dashed vertical line.

12.98, 13.37 and 15.35 that are all caused by microcline. Loading weights of factor 2 show a negative link with the quartz spectrum and a positive link with a couple of microcline features at 9.49 and 9.82. Loading weights of factor 3 show a negative link with a few albite features at 9.78 and 15.25, and a weak positive link with microcline features at 8.57, 8.76, 9.28, 9.47, 9.66, 12.69, 13.45. The 8.31 feature was not assigned to a mineral. Also the loading weights of factor 4 are dominated by albite. The features show a negative link with albite at 8.58, 9.64, 9.81, 9.95, as well as the four features between 12.5 and 14 and the feature at 15.21. Furthermore, a broad feature at 10.78 indicates a link with more Ca-rich plagioclase, such as labradorite or bytownite. The loading weights of factor 5 (not displayed here) show clear structure but the features could not be assigned to a particular mineral spectrum.

Regression coefficients

The regression coefficient spectrum of the alkali feldspar model combines the information from the loading weights of factors 1 to 5. Most spectral features are linked positively to spectral features of microcline (8.62, 8.99, 9.28, 9.40, 9.47). The feature at 8.21 and 8.62 are negatively linked to quartz, and features at 12.69, 13.12, 13.43 and 15.21 are negatively linked to albite. At the 10.78 wavelength, typical for Ca-rich plagioclase, the coefficients are nearly zero, thus showing that this wavelength region is not relevant in determining alkali feldspar modes. No evidence of other minerals was detected in the regression coefficients of the alkali feldspar model.
Figure B.2 Loading weights (factors 1 to 4) and regression coefficients of the alkali feldspar model displayed as functions of wavelength. Wavelengths with values far from zero are influential for the PLSR model.

**Plagioclase model**

**RMSEP**

The RMSEP plot of the alkali feldspar model shows a minimum at factor 4 (Figure B.3). Hence, four factors were used to create the final alkali feldspar PLSR model.

**Loading weights**

Loading weights (Figure B.4) of factor 1 are strongly dominated by a lack of quartz (features at 8.63, 9.19, 12.53 and 12.82) as well as a weak small positive link with albite (8.40, 9.71). The feature at 8.17 could be related to the Christiansen feature often seen in fine-grained muscovite, but no other muscovite features were detected. Loading weight 2 is dominated by albite with features at 8.39, 9.67, 9.93, 15.35 and the quadrouple feature at 12.5 to 14 microns. While the wavelengths of the features
B. PLSR model details

Figure B.3  RMSEP plot for plagioclase. The plot indicates prediction errors for various numbers of factors used in the plagioclase model. The selected number of factors is indicated by the dashed vertical line.

...fit albite, the relative height/depth varies. The most important feature is at 8.39 microns. Loading weight 3 shows a strong negative link with microcline (8.63, 9.48, 9.81, 12.98, 13.74). The 8.30 feature was not assigned to a mineral. Loading weights of factor 4 is dominated by a positive link with albite. Compared to factor 2, the main albite features in factor 4 (9.64, 9.91) are at a slightly shorter wavelength.

Regression coefficients

The loading weights show that the model for plagioclase is driven by the lack of quartz and microcline (factors 1 and 3) as well as a positive link with two types of albite features (factors 2 and 4). When the four loading weights are combined in the regression coefficients of the model, the influence of quartz is no longer visible (except for a small feature at 8.63) and the combination of albite features are now driving the model. Surprisingly, no Ca-rich plagioclase features were identifiable in the loading weights. When they are combined in the regression coefficients, however, a broad feature at about 10.7 \( \mu \text{m} \) becomes visible and this was attributed to Ca-rich plagioclase (anorthite).

Quartz model

RMSEP

The RMSEP of the quartz model (Figure B.5) shows that the first two factors are very important (RMSEP reduces dramatically when they are included). The graph shows a minimum at four factors but factors 3...
Figure B.4 Loading weights (factors 1 to 4) and regression coefficients of the plagioclase model displayed as functions of wavelength. Wavelengths with values far from zero are influential for the PLSR model.

and 4 reduce the predicted error minimally and were not included in the final model. Since the quartz model works well with all spectral information compressed into only two factors, the model is very simple and is expected to behave very robustly when applied to other datasets.

Loading weights
Loading weights (Figure B.6) of factor 1 are strongly dominated by quartz spectral features (8.22, 8.63, 9.15, 12.51 and 12.80). The second factor shows some quartz features (8.63, 12.51) but is dominated by a negative link with albite (9.03, 9.65, 9.92, 12.69, 13.10, 13.41, 13.85 and 15.25).

Regression coefficients
The regression coefficient spectrum combines the two factors used and dominantly shows quartz features and a negative link with albite.
B. PLSR model details

**Figure B.5** RMSEP plot for quartz. The plot indicates prediction errors for various numbers of factors used in the quartz model. The selected number of factors is indicated by the dashed vertical line.

### Plagioclase composition model

#### RMSEP

The RMSEP graph of the plagioclase composition (Figure B.7) shows that the model is far from ideal. The two local minima at factors 1 and 5 indicate that the dataset probably still contains one or several outliers in the plagioclase composition model. Since all reasonable outliers (e.g., vague data description, uncertain mineral identification in thin section study) had been removed from the dataset earlier, no unjustifiable outlier removal, to artificially improve model performance, was implemented at this stage. The global minimum in the RMSEP plot is at factor 8. The model using eight factors was observably overfitting the calibration data, with the loading weights higher than factor 5 becoming noisy. Hence, the local minimum at factor 5 was used as the cut-off for building the plagioclase composition model.

#### Loading weights

Loading weights (Figure B.8) of factor 1 show a negative link with anodesine, an intermediate composition plagioclase. Features are visible at 8.51, 9.22, 9.60 and 15.25. The two broad features at about 10.7 and 12.1 are positive links to more calcic plagioclase. They are usually observed in plagioclase compositions ranging from labradorite to anorthite. Loading weights of factor 2 show features of quartz (8.63, 9.0, 12.48 and 12.80) as well as Na-rich plagioclase like albite and oligoclase (9.0, 9.63, 15.25) and again a broad feature at about 10.8 which is attributed to Ca-rich plagioclase. Factor 3 shows a positive link with albite features (8.85, 9.43,
Figure B.6  Loading weights (factors 1 and 2) and regression coefficients of the quartz model displayed as functions of wavelength. Wavelengths with values far from zero are influential for the PLSR model.

9.64, 9.95, 13.08) and again a 10.8 Ca-rich plagioclase feature. Factor 4 (9.00, 9.29, 9.51, 9.61, 9.82, 9.97, 12.70, 13.08, 13.44 and 15.16). The features at 8.21 and 8.63 show an influence of quartz, and the feature at 10.9 shows a minor influence of Ca-rich plagioclase on this factor. The feature at 12.47 was not assigned to a specific mineral. Factor 5 still shows distinct spectral features but they could not be attributed to individual minerals.

Regression coefficients

The regression coefficients of the plagioclase composition model combine the loading weights of factors 1 to 5. Its spectrum is difficult to interpret as it contains little distinct spectral features of known minerals but is more an accumulation of many mineral features and possibly noise. Features that can be identified are those of albite, quartz and a 10.8 feature of Ca-rich plagioclase. Hence, the plagioclase composition model is driven by sodic and calcic plagioclase features as well as quartz content. Plagioclase composition and quartz content are negatively correlated in this dataset. This relationship is also represented in the plagioclase composition PLSR model.
B. PLSR model details

Figure B.7  RMSEP plot for plagioclase composition. The plot indicates prediction errors for various numbers of factors used in the plagioclase composition model. The selected number of factors is indicated by the dashed vertical line.
Figure B.8 Loading weights (factors 1 to 4) and regression coefficients of the plagioclase composition model displayed as functions of wavelength. Wavelengths with values far from zero are influential for the PLSR model.
Spatial uncertainty in SEBASS georeferencing

To estimate the spatial uncertainty in the georeferenced Ann-Mason SEBASS mosaic, the coordinates of 14 check points spread over the mosaic area were compared to the NAIP 1m orthophoto product (National Agriculture Imagery Program; distributed by seamless.usgs.gov) and root mean squared error values were calculated without and with a correction for error bias.

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Table C.1 SEBASS spatial uncertainty test [all values in meters].


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Samenvatting

Dit proefschrift is de uitkomst van een onderzoek dat een nieuwe methodiek beschrijft om via Aardobservatie kwantitatief veldspaat mineraalvoorkomens en de samenstelling van de plagioklaas mineraalreeksen te karteren. Om op objectieve wijze goede kwantitatieve resultaten te verkrijgen, is tijdens dit onderzoek gebruik gemaakt van thermische infrarood (IR) spectroscopie in combinatie met de statistische methode Partial Least Squares Regressie.

Voor het classificeren van bijvoorbeeld vulkanisch gesteente, of het bepalen van meta-somatische condities bij metamorfisme zijn zowel het voorkomen als de samenstelling van het mineraal veldspaat belangrijke indicatoren. Traditionele laboratoriumtechnieken om veldspaten te determineren vergen veel tijd, zijn kostbaar en zijn vaak slechts toepasbaar op een eindig aantal puntobservaties verkregen uit gesteentemonsters in het veld. Via thermische IR-spectroscopie zijn spectrale kenmerken te detecteren die gerelateerd kunnen worden aan fundamentele trillingsfrequenties in het Si—O silicaatkristallooster van veldspaten. Door het gebruik van thermische IR-spectroscopie vanuit een vliegtuig kan de beperking van een eindig aantal puntobservaties vermeden worden. Via deze techniek ontstaat namelijk een generiek overzicht over een geografisch gebied, en maakt het mogelijk om de ruimtelijke verspreiding van veldspaten en andere gesteentevormende mineralen te karteren. Doordat de te analyseren gesteentes veelal bestaan uit een mengsel van verschillende silicaten, vertonen hun thermische IR-spectra overlappende kenmerken, bestaande uit de specifieke spectra van elk van de afzonderlijke mineralen in het mengsel. Dit kan de identificatie en kwantificering van de mineralen (ver)hinderen. Om dit probleem te ondervangen, is in dit onderzoek gebruik gemaakt van de statistische methode partial least squares regressie. Het grote voordeel van deze methode is dat het geen uitgebreide spectrale database van pure mineralen vereist, iets dat in de praktijk moeilijk samen te stellen is.

Dit proefschrift geeft de analyseresultaten van thermische IR-spectra, welke zowel in het laboratorium als via vliegtuig-gedragen sensorbeelden zijn verkregen. In het laboratorium zijn mineraalvoorkomens met behulp van slijpplaatjes geschat om een kwantitatief voorspelling partial least squares model op te bouwen tussen enerzijds de thermische IR-spectra en anderzijds de alkali-veldspaat, plagioklaas, kwarts (in oppervlakte
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%) en plagioklaas samenstellingen (in mol% An). De studie met laboratoriumspectra laat zien dat de, via partial least squares gemodelleerde, alkali-veldspaat en plagioklaas voorkomens respectievelijk binnen een absolute ±5.1% en ±8.5% van de waardes verkregen bij analyse met slijpplaatjes liggen. In de plagioklaas samenstelling zijn, vergeleken met slijpplaat analyse, variaties te zien van ±7.8 mol% An. Deze foutmarges zijn iets kleiner of vergelijkbaar met foutmarges in spectraanalysen van mineraalmengsels ("spectral unmixing") gerapporteerd in literatuur, terwijl er geen uitgebreide spectrale database van pure materialen benodigd is.

Voor het bestuderen van spectra verkregen uit vliegtuig-gedragen sensoren zijn hyperspectrale thermische IR-beelden van de SEBASS sensor gebruikt, die zijn opgenomen boven een testgebied van de Yerington batholiet, Nevada. Uit voorbereidend onderzoek met gesimuleerde SEBASS data is gebleken dat de spectrale resolutie en het ruisniveau van deze sensor geschikt zijn om veldspaatvoorkomens en plagioklaas samenstellingen te karteren tot op 0.4% van de absolute waardes van de voorspellingen gebaseerd op de originele laboratorium spectra. Verstoringen in spectra, zoals kanteling en verminderd contrast, bleken wel nadelig te zijn voor de voorspellingsresultaten. Dit is in deze studie vertaald naar een correctie.

In dit proefschrift is de "gemiddelde en standaard deviatie normalisatie" methode voorgesteld bij de ontwikkeling van een nieuwe beeldverwerkingsmethode om te corrigeren voor kanteling en herstellen van spectraal contrast in de SEBASS beelden. Hierna zijn de partial least squares voorspellingsmodellen toegepast op de beelden. Op deze wijze zijn voor het eerst kaarten uit vliegtuig-gedragen sensoren geproduceerd met daarop de samenstelling van plagioklaas en de hoeveelheden alkali-veldspaat, plagioklaas en kwarts op de grond. Deze kaarten laten consistentiepatronen zien tussen opeenvolgende reeksen van beeldopnames. De grootschalige, gekarteerde patronen komen overeen met gesteentetypes en omzettingszones die voor het testgebied bekend zijn uit literatuur. In absolute zin laten de waardes van deze kaarten (5, 50 en 95 percentiel) zich goed vergelijken met waardes verkregen uit gesteente monsters afkomstig uit het veld.

De toegevoegde waarde van dit onderzoek ligt duidelijk in de kwantitatieve, en tegelijkertijd objectieve aanpak die ontwikkeld is voor vliegtuiggedragen Aardobservatie. Een bijkomstige maar niet minder belangrijke uitkomst is de nieuw ontwikkelde methode om spectra, verkregen via vliegtuiggedragen sensoren, zodanig te corrigeren dat deze goed vergelijkend kunnen worden met spectra verkregen in een laboratorium. Het belangrijkste voordeel hiervan is dat statistische modellen die kwantiteit voorspellen op basis van laboratoriumonderzoek nu toegepast kunnen worden op beelden van vliegtuiggedragen sensoren. Dit proefschrift levert niet alleen een significante vernieuwing in de Aardobservatie door het gebruik van thermische IR beelden van vliegtuiggedragen sensoren, maar ook door de presentatie van de allereerste kaart met kwantitatieve plagioklaas samenstelling verkregen uit een vliegtuiggedragen sensor.
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A staff PhD cannot be done alone. Especially in the final two years, Freek and Victor have given me a reduced workload so I could focus on
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Biography

Chris Hecker was born in Binningen, Switzerland on August 15, 1974. From 1996 to 1999 he studied Earth Sciences at the University of Basel, specializing in structural geology and tectonics. His MSc research focused on the alpine deformation history and low-grade metamorphism in the Engadin Valley, eastern Switzerland. From 2000 to 2001 he worked at the Belize Audubon Society, a conservation NGO. There he implemented and managed a small GIS and Remote Sensing unit, supporting sustainable decision making of tropical natural resources. In 2001 Chris joined the then International Institute for Aerospace Survey and Earth Sciences (ITC), where he combined his background in earth sciences with remote sensing and GIS. In 2003 he joined the department of Earth Systems Analysis, where he currently holds the position of lecturer/researcher in geologic remote sensing. In his work he teaches in the Applied Earth Sciences programme and tailor-made courses in Enschede and abroad. His research interests are laboratory, field and imaging spectroscopy in the thermal infrared out of which the idea for this thesis emerged. In the process, he initiated and coordinated the setting up of the TIR spectroscopic facilities at ITC. Chris Hecker is co-founder and joint chair of the Special Interest Group on Thermal Remote Sensing (SIG-TRS), which is a subgroup of the European Association of Remote Sensing Laboratories (EARSeL).

Chris Hecker currently lives in Enschede, The Netherlands with his wife Jeanna and their son Kaden.
Author’s publications


ITC dissertations

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This dissertation has number 214.