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Infrared Reflection Spectroscopy of Microscopic Mineral Grains

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Abstract

The method and instrumentation described permit mid-infrared reflection spectra to be recorded from a 100 micrometer diameter sample area on thin sections which are placed on the stage of a polarizing microscope. Applications for research and analytical purposes are discussed.

Introduction

Mid-infrared spectroscopy has been extensively used as an analytical tool in the study of silicate minerals and rocks, both in the laboratory (*e.g.*, Coblenz, 1906; Lyon, 1964; Rutstein and White, 1971), and in remote sensing applications (*e.g.* Salisbury *et al*, 1969; Logan and Hunt, 1970).

In the laboratory, two qualities of most silicate minerals and rocks introduce particular problems. First, even extremely thin samples are essentially opaque in the 10 μm range and, second, samples are not compositionally homogeneous over an area as big as the minimum cross-sectional size of the infrared beam in commercially available spectrometers. It is possible to acquire a transmission spectrum of a mineral or rock by crushing it to a fine powder, and then suspending the powder as a mull (in nujol), or in an alkali halide matrix. However, these techniques introduce complicating scattering effects and destroy the textural and orientational information contained in the original sample. Reflection measurements, on the other hand, allow study of opaque samples without destroying their texture, but the heterogeneity problem can only be solved by using smaller sample sizes.

Recently, micro-reflectance attachments have become available for use with the commercial spectrometers. For example, the attachment for the Perkin Elmer Model 621 first optically condenses the beam and then masks the sampled area down to 1.5 × 4.0 mm with 15 percent energy throughout. Estep, Kovach, and Karr (1973) used such an attachment, but masked the area down still further to the usable limit, which provided a 1 mm diameter spot size. This proved to be satisfactory for studies of single crystals isolated from lunar soils. However, a detailed spectroscopic analysis of minerals embedded in a fine grained rock requires still smaller sample areas. It would not appear reasonable, though, to record mid-infrared spectra from grains smaller than 50 micrometers in diameter if thin sections 30 micrometers thick are used as samples, because of the increasing likelihood of measuring overlapping grains of different composition as the spot size approaches the sample thickness. The design of a suitable spectrometer has to evolve around methods to select and identify microscopic samples as well as to efficiently collect and process mid-infrared energy from their small areas.

Spectroscopic Considerations

The mid-infrared spectrum provides information that is characteristic of the basic molecular structure of a material and is frequently referred to as a "fingerprint." In isolated molecules, the individual spectral bands can be assigned to specific vibrations, and the number of such bands and their precise wavelength values can be calculated from a knowledge of the number and kind of atoms, their geometry, and the interatomic forces operative in the molecule.

In silicates, the molecular structure is predominantly represented by the Si-O and Al-O bonds, and it is their fundamental stretching motions which cause up to seven resolvable bands to appear between 8 and 11 μm in each reflection spectrum. While the (Si, Al–O) structure of a silicate crystal is too complex a "molecule" to allow a correlation of these bands with specific vibrations, its spectrum still maintains the fingerprint characteristic. Differences between the spectra of two or more minerals are based primarily upon (Si, Al–O) structure differences and, more subtly, on compositional substitutions.

If a sufficiently small area can be sampled by the infrared beam, single crystals can always be selected as objects of study. In this case, as for visible light, the optical properties at each wavelength vary with crystal orientation for non-isotropic crystals. However, in the mid-infrared, refractive indices are not useful because they vary rapidly and cannot be directly measured in the vicinity of reflection bands. The information to be gained from the reflection spectra is sufficiently described by a plot of the percent reflection *vs* crystal orientation for each reflection band. Thus, spectra have to be obtained at various crystal orientations, preferably with polarized radiation. Also, appropriate data reduction has to be applied to account for masking of weak bands by overlapping strong bands and for apparent shifts in the wavelength of maximum reflection of strong bands caused by band overlap. For purely analytical purposes, of course, a library of spectra suffices.

Instrumentation

The instrument design fulfills the requirement that a reflection spectrum at a small reflection angle could be recorded from a microscopic area on the polished surface of a thin section, and that this area could be readily chosen and identified on the sample surface.

The central component of the instrument is a research polarizing microscope which accepts thin sections prepared for electron microprobe analysis. An optical diagram of the microscope-spectrometer is shown in Figure 1. A small two-position plane mirror is located beneath the microscope stage. When this mirror is in one position, the normal illumination optics of the microscope allow a petrographic analysis of the sample to be made. When the mirror is in the other position (shown in Fig. 1), the Nernst glower is imaged at *f*/10 on the sample. The infrared energy reflected by the sample is directed by the same mirror onto a spherical mirror which forms a 1:1 image of the sample on the entrance aperture of a spectrometer. The radiation from the sample is chopped against a black body reference, and a circular variable filter[1] is used to scan the wavelength range between 7 and 14 micrometers, with a half bandwidth of 1.5 percent. A liquid-helium-cooled, copper-doped germanium detector then senses the intensity of the reflected radiation as a function of wavelength.

The target spot on the sample is defined by restricting the spectrometer entrance aperture, rather than by placing a mask on the sample itself. This permits an extended area of the sample to be viewed during the selection of the target; it also avoids problems associated with spurious reflections from the mask. Because mirror transfer optics are used throughout, the process of aligning the spectrometer with the microscope, of focussing the infrared beam onto the sample, and of selecting an aperture to match the desired target area can be performed using visible light. The image of a lamp (= "visible source" in Figure 1) positioned behind the aperture is projected back onto the sample so that the illuminated spot precisely defines the area on the sample from which the spectrum is recorded. Thus, on the microscope stage, the selected area on the sample surface can be examined through the microscope and the necessary adjustments made. The choice of spot size is, of course, limited by detector sensitivity and by aperture diffraction limits. With the present system, a 100-micron-diameter sample spot may be studied with adequate signal-to-noise ratio. However, alternate transfer optic designs are studied and appear to make smaller spot sizes feasible. Also, the circular variable filter could be replaced by a more complex but far less expensive grating monochromator.

Applications

Mid-infrared mineralogy and petrology can be usefully applied in both research and analytical situations. For analytical applications, emphasis is

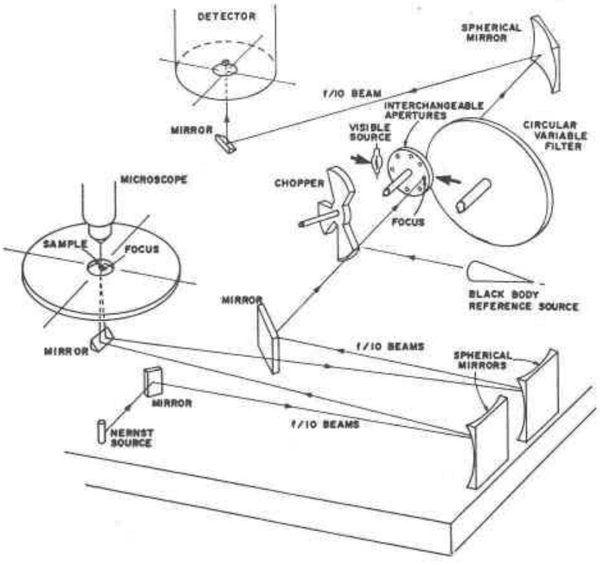

FIG. 1. Optical diagram of the microscope-spectrometer.

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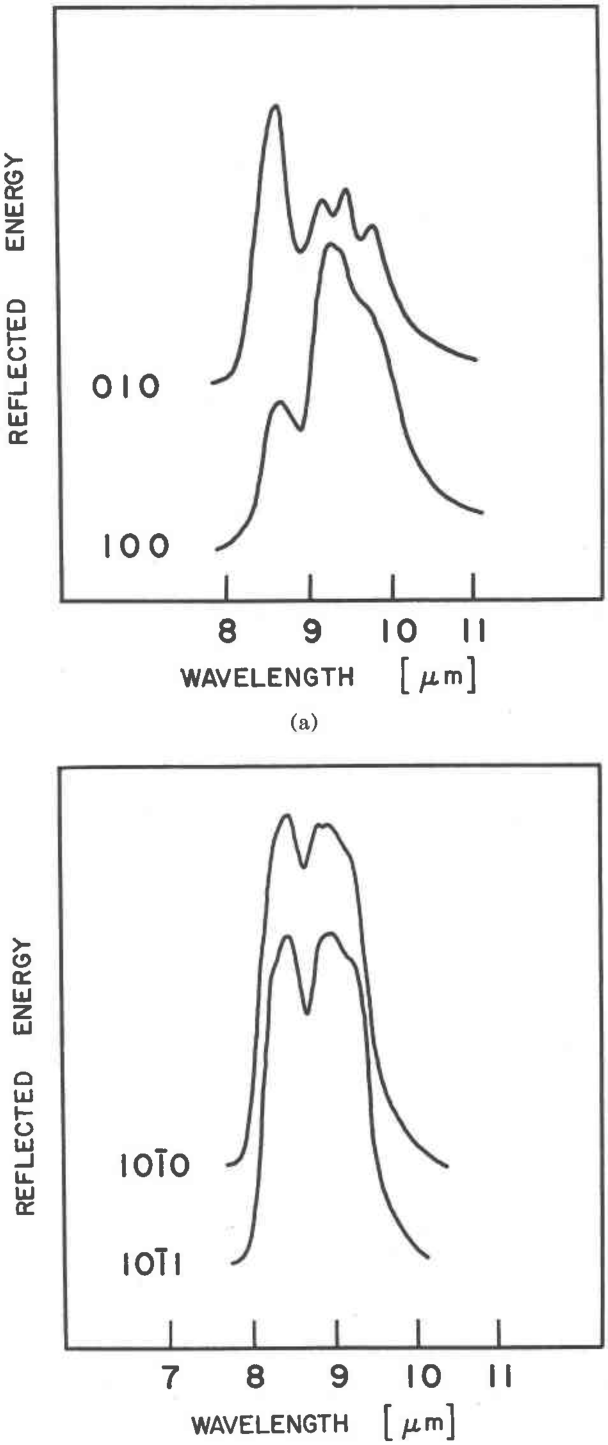
[1] Manufactured by Optical Coating Laboratory, Inc., Santa Rosa, California.



(a)

(b)

FIG. 2. Infrared spectra demonstrating the variability of bands with orientation. The variations are large for microcline (a) and minor for quartz crystals (b). The base lines of the spectra are vertically offset, and the absolute values for the reflected energy have been omitted.

placed upon the speed and ease of data acquisition, on its characterizing nature, and upon the feasibility of developing semi-automatic systems. For research purposes, on the other hand, interest is in the particular infrared properties of the samples. In either case, absolute values of the reflected energy can be obtained by calibrating the instrument with a front-surface mirror placed in the specimen position.

Research Applications

Among the many grains in a thin section, single crystals of desired orientations can normally be chosen with the aid of the polarizing microscope incorporated in the instrument. Polarized spectra of grains sectioned along the optical axes of the crystal allow a detailed study of the infrared properties of a mineral species to be performed. While the microscope spectrometer permits investigation of those members of a mineral series which cannot be obtained as large natural or artificial specimens, the narrowness of its infrared beam can also be used to advantage on larger crystals to study the variation of spectral features with respect to crystal orientation. Because the sampled area on a sphere with a 3 millimeter radius is flat to within one degree, the amount of energy collected from a rounded

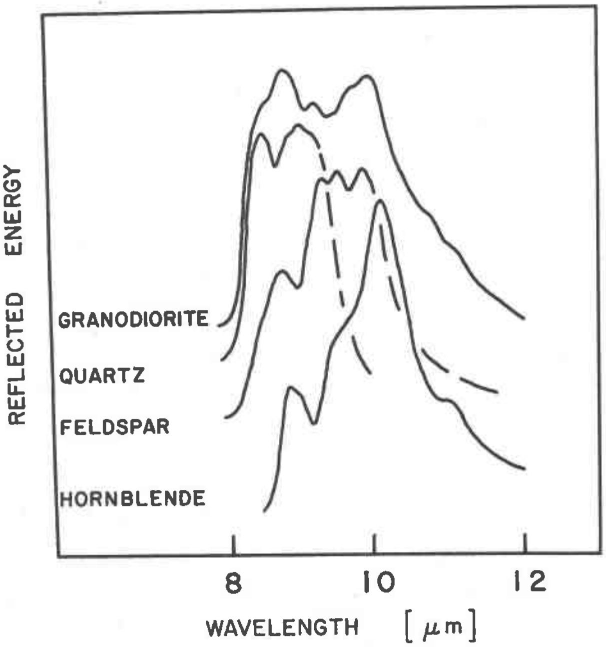


FIG. 3. Infrared spectra of a polished 1 × 2 cm granodiorite thin section and of component mineral grains 100 micrometers or larger in diameter. The base lines of the spectra are vertically offset and the absolute values for the reflected energy have been omitted.

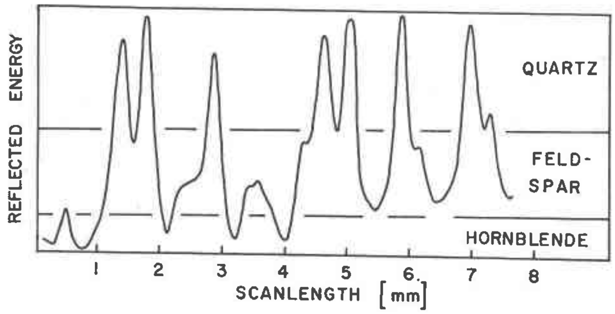


FIG. 4. Scan across a polished granodiorite thin section at 1150 wavenumbers and 100 micrometers sample spot size. The trace represents diagnostic differences in reflectivity of component minerals at the selected wavelength.

sample of this dimension is almost as large as energy collected from a flat section. Successions of spectra at closely spaced orientations can be obtained if the microscope is replaced by a goniometer. Conveniently, randomly rounded samples are accommodated, because the detector may be used to indicate when specular reflection from the sample has been achieved.

Further applications involve the correlation of infrared spectroscopy of thin sections with electron microprobe data based on the convenience of the common sample preparation technique. Variations in crystal growth and surface phenomena, such as the amount of shallow radiation damage (Dybwad, 1971), can be studied.

Analytical Applications

The "fingerprint" characteristic of mid-infrared mineral spectra permits a rapid recognition of minerals after a library of spectra has been compiled. Spectra recorded at various orientations have to be included for those minerals having particularly orientation-sensitive bands (see Fig. 2). The *X-Y* format of the data output invites use of a computer for data processing. This appears particularly profitable for quantitative mineral analysis of rocks by either of two methods:

(1) *The summing method.* Here a spectrum of the total thin section area is acquired. Then, for each component mineral, the spectra of several differently oriented grains are measured and averaged. For the component minerals, the weighted sum of the resultant orientation-averaged spectra must then produce the total (= rock's) spectrum. Consequently, the fraction of each mineral component in the rock can be calculated with a computer. The elements of the summing method are illustrated in Figure 3 where the total spectrum of a rock, granodiorite, is shown together with the spectra of its constituent minerals.

(2) *Scanning method.* In this technique the first step is to record spectra of individual grains. Comparisons of these spectra will allow selection of the wavelengths which best discriminate between the different constituent minerals. The monochromatic beam is then scanned across the thin section, and the intensity variations at that wavelength are plotted against location, as shown in Figure 4. Several different wavelengths may be used to refine the discrimination, and the method can be made quantitative quite easily. This technique can be readily used to produce mineral maps of thin sections by raster scanning and visually displaying the detector output on a TV screen or recording it photographically.

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