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IDENTIFICATION OF KAOLINS AND ASSOCIATED MINERALS IN ALTERED VOLCANIC ROCKS BY INFRARED SPECTROSCOPY

Key Words—Alunite, Identification, Infrared spectroscopy, Kaolinite, Remote sensing, Volcanic rocks.

Mid-infrared spectroscopy (2.5–50 μm) has been extensively used to identify and characterize clays and associated minerals in rocks and soils, with particular emphasis on the 3-, 10-, and 20-μm regions (Farmer and Russell, 1967; Farmer, 1968; White, 1971; Van der Marel and Beutelspacher, 1976). However, application of mid-infrared spectroscopy in remote-sensing activities has been restricted because the spectral information occurs only as a small perturbation to the emitted radiation from the earth's surface, and much of that which is especially relevant to clays (e.g., the 3.0-μm region) is obscured by atmospheric absorption.

Visible (0.4–0.7 μm) and near-infrared (0.7–2.5 μm) laboratory spectroscopy has shown that unique diagnostic features occur for clay minerals between 1.3 and 2.5 μm (Hunt and Salisbury, 1970; Hunt *et al.,* 1971, 1973; Hunt, 1977, 1979; Hunt and Ashley, 1979). For remote-sensing purposes, spectral information in the visible and near infrared regions is contained in reflected sunlight. Vast quantities of data have been collected in the 0.4- to 1.1-μm range by multispectral scanning instruments on aircraft and by the series of Landsat satellites. Some data have been acquired in the 1.6- to 2.2-μm regions by the now defunct NASA/Bendix 24-channel scanner and by the NASA Thematic Mapper Simulator; these data have been used to demonstrate the feasibility of the near-infrared region for remote-sensing purposes (Abrams *et al.,* 1977; Rowan *et al.,* 1977).

Hydrothermal alteration in Tertiary volcanic terranes in many parts of the world has formed extensive bodies of siliceous alunite-bearing rock surrounded by zones of clay-rich soil (Hall, 1978). The use of near-infrared spectroscopy could be valuable in exploring for such potentially important non-bauxite ore deposits. In addition to alunite, such hydrothermally altered areas typically contain dickite, kaolinite, illite or sericite, montmorillonite, pyrophyllite, diaspore, hematite, goethite, jarosite, anatase, and rutile. In addition, alunite and clay-bearing altered areas are favorable exploration targets for nonferrous metal deposits (Kerr *et al.,* 1950; Steven and Ratte, 1960; Tooker, 1963; Creasey, 1966; Stringham, 1967; Gustafson and Hunt, 1975; Corn, 1975).

Examples of visible and near-infrared spectra of altered volcanic rocks and their mineral constituents from Utah and Arizona are presented here to illustrate the potential of this spectral range. Other examples of the spectra of hydrothermally altered rocks from Nevada are given by Hunt and Ashley (1979).

EXPERIMENTAL

The locations and descriptions of the mineral and rock samples used in this study are listed in Table 1.

The spectra were recorded using a bidirectional reflection attachment (Hunt and Ross, 1967) fitted to a Beckman[1] 5270 spectrophotometer, which allows spectra of particulate materials to be recorded from the top surface of horizontal samples. The spectral bandpass used to record the spectra was about 1.5 nm. Although the technique used is reflection, the bands that appear in the spectra are caused by the absorption process that occurs when incident light is scattered in the upper surface layers before leaving the sample. Energy is absorbed only when it interacts with the material, and in the visible and near-infrared ranges this interaction in geological materials takes place almost entirely as electronic processes involving iron, or as vibrational processes involving water or hydroxyl groups. Other ions or molecular groups may be involved, such as the manganese, copper, cobalt, nickel, chromium, or lanthanum ions, for electronic interactions, but, with the exception of carbonates and phosphates, they occur less frequently, commonly display characteristic spectral signatures, and are not pertinent to the present discussion.

The presence of clay minerals in altered volcanic rocks is indicated by overtone and combination bands of hydroxyl-group vibrations in near-infrared spectra. Also apparent in the rock spectra are broad bands diagnostic of the presence of various forms of iron. Substances that do not contain these ions or molecular groups, including most unaltered silicates and especially quartz, produce no absorption, and, consequently, display no diagnostic bands in the 0.4- to 2.5-μm wavelength range.

RESULTS AND DISCUSSION

Figure 1 shows the visible and near-infrared (0.4- to 2.5-μm) spectra of several altered rock samples. The presence of iron is indicated by the bands and slopes that appear in the curves at wavelengths shorter than 1.3 μm. The features are best illustrated in the spectrum of sample RM 91A. The major band near 0.85 μm is caused by a crystal-field transition in the ferric ion in hematite, and it is distinguishable from a similar band

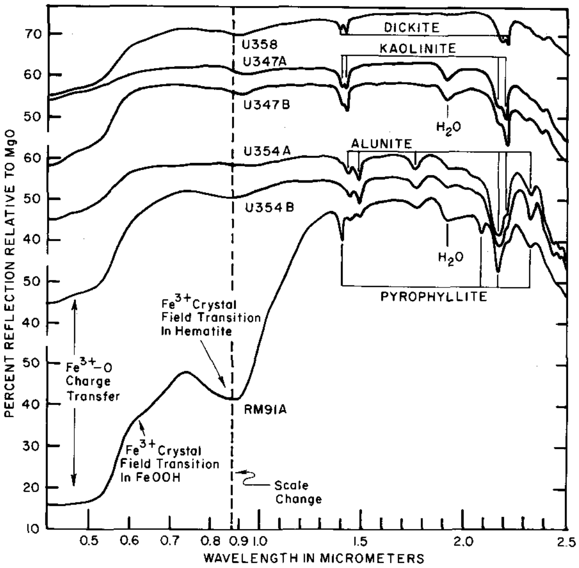

Figure 1. Visible and near-infrared (0.4- to 2.5-μm) reflection spectra of crushed samples of altered volcanic rocks. Bands caused by charge transfer, crystal field, and vibrational transitions are indicated.

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[1] Brand or manufacturers' names used in this report are for descriptive purposes only and do not constitute endorsement by the U.S. Geological Survey.

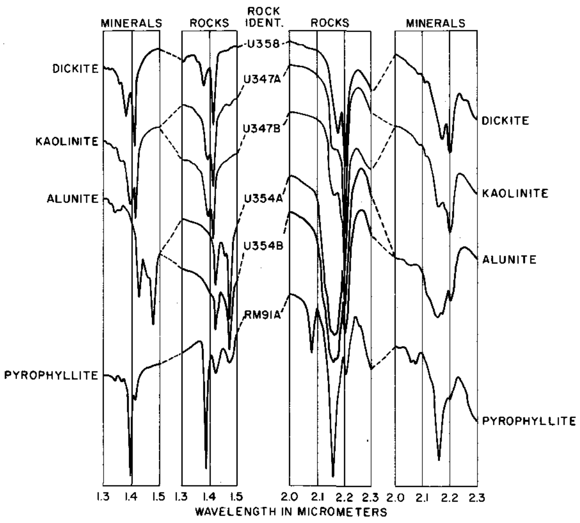

Figure 2. Segments (1.3- to 1.5-μm and 2.0- to 2.3-μm) of near-infrared reflection spectra of alteration minerals (shown in the two outside blocks) and altered volcanic rocks (shown in the two inside blocks). The dotted lines between the blocks link a mineral spectrum with the feature its presence is responsible for producing in the rock spectrum.

which occurs in goethite, which typically is centered at slightly longer wavelengths, near 0.93 μm. The shoulder near 0.65 μm is due to a crystal-field transition in the ferric ion in FeOOH, and the intense absorption band between 0.4 and 0.5 is due to a charge-transfer transition between the ferric ion and the oxygen ion. The spectra of samples U347 and U354 illustrate additional diagnostic features at wavelengths shorter than 1.3 μm. These spectra show the most obvious differences between the A and B samples; the B sample in each pair shows the more intense absorption, indicating the presence of more iron oxide than in its A counterpart.

The presence of clay minerals is indicated by the much sharper multiple bands due to hydroxyl-group vibrations between 1.3 and 2.5 μm. The A and B samples for U347 are essentially identical; the same holds true for the A and B samples of U354. However, these two pairs are distinctly different from each other and from samples U358 and RM 91A. The bands near 1.4 μm are due to overtones of the fundamental OH-stretching modes near 3 μm, and those near 2.2 μm are characteristic of combinations involving OH-stretching and AlOH-bending modes. The band near 1.9 μm indicates the presence of molecular water, and that near 1.775 μm is characteristic of alunite.

The location and relative intensity of the groups of bands in the 1.4- to 2.2-μm region are characteristic of specific clay minerals. Four such groups of bands are shown in Figure 1 and indicate the presence of dickite, kaolinite, alunite, and pyrophyllite. In Figure 2 the bands near 1.4 and 2.2 μm are presented in an expanded manner. In the left box, the bands be-

Table 1. Composition, location, and description of samples examined by visible and near-infrared spectroscopy.

Sample number	Mineral composition[1]	Location and description
U358	Microcrystalline quartz, dickite	Beaver County, Utah; Blawn Mountain, southern Wah Wah Mountains. Strongly altered rhyolitic(?) ash-flow tuff of Tertiary age.
U347A	Microcrystalline quartz, kaolinite, cristobalite, alunite	Sevier County, Utah; Mill Creek Canyon, Tushar Mountains. White altered Joe Lott Tuff (Miocene); mineral quarried for ceramic raw material.
U347B	Microcrystalline quartz, kaolinite, cristobalite, alunite, hematite	Same as U347A; pink.
U354A	Microcrystalline quartz, alunite, very minor kaolinite	Beaver County, Utah; southern Wah Wah Mountains. Strongly altered rhyolitic(?) lithic tuff of Tertiary age; quarry where cream alunite "ore" extracted for metallurgical testing.
U354B	Microcrystalline quartz, alunite, minor kaolinite, minor hematite	Same as U354A; with purple mottling.
RM 91A	Microcrystalline quartz, alunite, pyrophyllite, hematite	Santa Cruz County, Arizona; Patagonia district, southwest flank of Red Mountain. Strongly altered volcanic rock of Tertiary age.
Mx 10	Dickite, trace of illite or sericite	State of Zacatecas, Mexico; 4 km east of Guadalupe. White altered rhyolite of Miocene age; quarried for refractory raw material.
220 3B	Kaolinite	Aiken County, South Carolina; near Bath. Sedimentary kaolin of early Tertiary(?) age.
295 3B	Alunite	Piute County, Utah; Alunite Ridge, Marysvale district. Vein alunite.
221 3B	Pyrophyllite	Moore County, North Carolina; near Robbins. Pyrophyllitized rock in Volcanic Slate belt.

[1] Mineral constituents listed in decreasing order of abundance.

tween 1.3 and 1.5 μm for four pure minerals are shown; these curves are joined by dashed lines to the spectra of the rocks in the same wavelength range. A similar arrangement is shown on the right side of the figure for the 2.0- to 2.3-μm range.

It is clear that the spectra of the pure minerals in both the 1.3- to 1.5-μm and the 2.0- to 2.3-μm regions are different from each other, and that the mineral spectra correspond closely to the rock spectra to which they are linked. In the RM 91A spectra, features corresponding to both pyrophyllite and alunite indicate the presence of both of these minerals in the rock.

The spectra presented here show that the presence of iron and of clay minerals in volcanic rocks and soils can be readily detected by visible and near-infrared spectroscopy. They also suggest that near-infrared from 1.3- to 2.5-μm could be a significant remote-sensing tool for such materials.

U.S. Geological Survey GRAHAM R. HUNT
Denver, Colorado 80225 ROBERT B. HALL

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