

gravimetric geoid: 16th
t. Union Geodesy and Geophys.,
975 (preprint, 22 p.).
Possible late Precambrian subduction
Africa: Nature, v. 259, p. 471-473.
5, Colors and the meso-structure of
VII, pt. II, Experimenters' analyses
Calif. Inst. Technology, Jet Propul-
t. 32-700, p. 29-39.
ii, N., Conte, C. N., Zir Filho, J. A.,
1974, Carta geológica do Brasil ao
Porto Alegre (SH.22): Dept. Nac.
1.
d Laznicka, P., 1972, Copper belts,
mer-lead lines of the world: 24th Int.
Montreal, Canada, Sec. 4, p. 37-51.
new class of faults and their bearing
Nature, v. 207, p. 343-347.

SPECTRAL SIGNATURES OF PARTICULATE MINERALS IN THE VISIBLE AND NEAR INFRARED

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The utility of multispectral remote sensing techniques for discriminating among materials is based on the differences that exist among their spectral properties. As distinct from spectral variations that occur as a consequence of target condition and environmental factors, intrinsic spectral features that appear in the form of bands and slopes in the visible and near infrared (.325 to 2.5 μm) bidirectional reflection spectra of minerals (and, consequently, rocks) are caused by a variety of electronic and vibrational processes. These processes, such as crystal field effects, charge-transfer, color centers, transitions to the conduction band, and overtone and combination

tone vibrational transitions are discussed and illustrated with reference to specific minerals.

Spectral data collected from a large selection of minerals are used to generate a "spectral signature" diagram that summarizes the optimum intrinsic information available from the spectra of particulate minerals. The diagram provides a ready reference for the interpretation of visible and near infrared features that typically appear in remotely sensed data.

In the visible-near infrared region, the most commonly observed features in naturally occurring materials are due to the presence of iron in some form or other, or to the presence of water or OH groups.

INTRODUCTION

The purpose of this paper is to provide the necessary information to answer the question, "What is responsible for the presence of a feature at a specific wavelength in the spectrum of a particulate mineral?"

A large body of data exists dealing with the visible and near-infrared (VNIR) spectra of minerals, which covers the range from 0.325 to 2.5 μm . Nowhere, to the author's knowledge, are the results of these studies collected and summarized so that they can be rapidly utilized by investigators not necessarily interested in the spectroscopic arguments presented, but who are interested in the application of the VNIR to remote sensing problems. In many cases, these studies were performed to provide a detailed analysis of either a single band or multiple features in the spectrum of a single mineral; often the investigation was carried out using oriented single crystals with carefully polished surfaces so that polarization studies could be made. In other studies of the VNIR spectra, additional data were acquired from a variety of

techniques to assist in the interpretation—techniques such as mid- and far-infrared, Mossbauer and Raman spectroscopy, magnetic susceptibility, and electron spin resonance.

The best collection of pertinent data currently available is contained in Burns's (1970b) text on the mineralogical applications of crystal field theory. Although all the spectra included are the results of his own studies, he references over 200 papers which cover much of the work done up to 1969. Since then a multitude of publications have appeared in the attempt to clarify the many problems that still existed, some of which have provided considerable controversy. Burns's text is concerned exclusively with the electronic processes involved in producing spectral features. However, much of the information there and in the literature is more detailed and complex than is necessary for remote sensing applications. Although extensive use was made of the data in Burns's book to identify many spectral features, the experimental data used here were derived from a series of six papers by

Manuscript received by the Editor August 6, 1976; revised manuscript received October 1, 1976.
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BERYL 108B MAINE

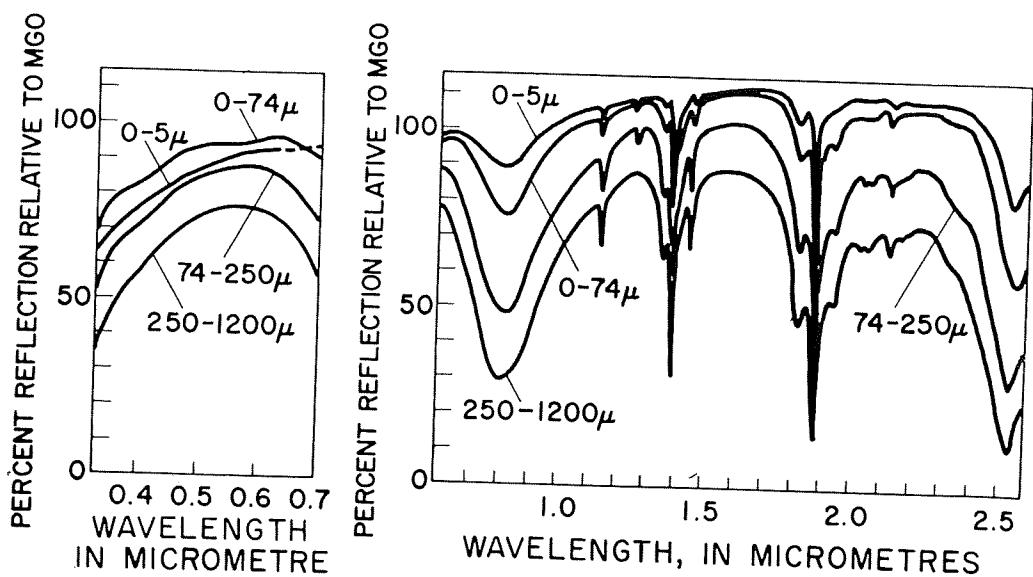


FIG. 1. Bidirectional reflection spectra of four different particle size range samples of the mineral beryl. The smallest particle size range displays the highest relative reflection, but shows the least contrast in its spectral bands.

Hunt and Salisbury (1970, 1971) and Hunt et al (1971a, 1971b, 1972, 1973), which deal with the bidirectional reflection spectra of particulate samples of over 200 minerals. In addition to those features that arise from electronic processes, features of vibrational origin are included, and the prime intention here is to condense all this information into a single diagram.

EXPERIMENTAL DATA

In light of the large number and diverse nature of the minerals investigated, it is perhaps surprising that all the pertinent spectral features can be represented on a single diagram. It should be recalled, however, that the major constituents of most minerals, namely silicon, aluminum, magnesium, and oxygen, do not produce absorption features in the VNIR range. Consequently, the information that is available results from absorptions due to electronic processes, involving a relatively few constitutional or substitutional ions, and vibrational processes involving a limited number of anionic groups.

The basic data used here were originally presented as bidirectional (VNIR) spectra obtained from appropriately characterized mineral samples ground and sieved into four particle size ranges. For example,

Figure 1 shows the spectra of the mineral beryl in four particle size ranges.

It is important to realize that the spectra shown here present in an optimum form the intrinsic data that are available as a consequence of the chemistry and structure of a single mineral. Data collected in a terrestrial remote sensing experiment will be considerably inferior to these laboratory data, even though the recording techniques may be equivalent. This is because the terrestrial atmosphere attenuates energy and restricts the wavelength range, often excluding the most useful data. Also natural surfaces are rarely, if ever, composed of pure, size-sorted minerals; natural surfaces are commonly composed of assemblages of minerals in a variety of shapes and sizes with surfaces stained by weathering and alteration. Also, the contained water and organic materials in soils, or their vegetation covers, contribute to the total spectrum, often dominating it. Finally, remotely sampled areas rarely are homogeneous in composition or texture.

ELECTRONIC PROCESSES

The subject of electronic energies is broad and complex. The VNIR region spans an energy range sufficiently wide to encounter effects due to several different electronic processes.

Crystal-field effect

Isolated atoms in energy states. At wavelengths of electrons as changes from one state to another. These changes are

The energy values may be calculated by band group theoretic methods to admit the nature of electronic transitions specified. When these are plotted on an energy level diagram, they represent an energy level which characterizes the state of the atom.

Certain atoms, as cause when embedded in a crystal lattice or as an impurity, may be shared by the electrons. The electrons are no longer bound to a single atom. The electron may move over a range of values between "energy bands" of the solid. The energy originated becomes part of the bound electrons of the crystalized energy states at

In the case of the rare earth elements, the transitions involve deep lying electrons which are shielded from outside influences. The solid remains essentially like the free ion. On the other hand, the transition elements (e.g., Ni) have most electrons principally in the outer shell, the energy levels; and they can be greatly influenced by the electrostatic field of the surrounding ions. These fields originate from the positive charges and dipolar groups, the ligands, which surround the ions, and the resulting fields. The changes in the energy levels depend upon the type, position, and coordination ligands.

The most frequently observed features in the VNIR spectra of rocks and soils are due to iron in some form. For the unfilled d orbitals of the isolated ion, but when the ion is surrounded by other ions, the energy levels are split, with the surrounding cations. The change in these energy levels is dependent on the valence state of the ion, its coordination number, and the ligands it occupies. The levels are

Crystal-field effects

Isolated atoms and ions may exist only in discrete energy states. Absorption or emission of specific wavelengths of electromagnetic radiation takes place as changes from one energy state to another occur. These changes are referred to as transitions.

The energy values of the possible electronic states may be calculated by employing quantum mechanical and group theoretical considerations, which also permit the nature of each electronic energy level to be specified. When the results of such calculations are plotted on an energy scale, the resultant figure constitutes an energy level diagram that completely characterizes the state of the atom or ion.

Certain atoms, as such, do not exist in minerals because when embedded in a solid, either as a constituent or as an impurity, one or more of their electrons may be shared by the solid as a whole, and those electrons are no longer associated with any particular atom. The electron energy levels become smeared over a range of values which are then called the "energy bands" of the solid, and the atom from which it originated becomes an ion. However, the remaining bound electrons of the resultant ion still have quantized energy states associated with them.

In the case of the rare earth ions, the unfilled shells involve deep lying electrons which are well shielded from outside influences, so that their energy levels in the solid remain essentially unchanged from those of the free ion. On the other hand, for ions of the transition elements (e.g., Ni, Cr, Co, Fe, etc.), the outermost electrons principally determine the location of the energy levels; and because they are not shielded, they can be greatly influenced by interaction with the electrostatic fields which surround the ions. These fields originate from negatively charged anions and dipolar groups, the so-called "ligands" which surround the ions, and they are referred to as crystal fields. The changes induced in the ion are dependent upon the type, position, and symmetry of the surrounding ligands.

The most frequently encountered electronic features in the VNIR spectra of minerals (and consequently of rocks and soils) are due to the presence of iron in some form. For all of the transition elements, the unfilled *d* orbitals have identical energies in the isolated ion, but when the ion is located in a solid, the energy levels are split and displaced by interaction with the surrounding crystal field. The location of these energy levels is primarily determined by the valence state of the ion (Fe^{2+} or Fe^{3+} , for example), its coordination number, and the symmetry of the site it occupies. The levels are secondarily determined by

the type of ligand formed, the extent of distortion of the metal site, and by the value of the metal-ligand interatomic distance.

The very different arrangement of the energy levels for different crystal fields leads to the appearance of quite different spectra for the same ion. However, not all possible transitions between these levels may occur equally strongly. Information concerning whether a particular transition should occur is provided by "selection rules," of which the most pertinent is that relating to the electron spins of the states involved. This rule states that transitions between states with the same spins are allowed, and those between states with unlike spins are forbidden. The consequence of this rule is that transitions which are allowed produce intense features in the spectrum, while forbidden transitions are completely absent or else produce very weak features.

Ferrous ion Fe^{2+} .—For a ferrous ion in a perfectly octahedral site, only one spin allowed transition gives rise to a feature in the VNIR spectrum; but when the octahedral site is distorted, the field experienced by the ion may cause some levels to be split further, so that additional allowed transitions may occur. In some materials, such as olivine, the ferrous ions may reside in two nonequivalent sites, and transitions in each of these ions contribute differently to the spectrum.

Figure 2 shows the bidirectional reflection spectra of several minerals that contain ferrous iron. Because spectral features due to ferrous iron occur at different wavelengths for different minerals, the data relate mostly to the nature of the site in which the ion resides. Consequently, important information concerning the bulk structure of the mineral is provided in this somewhat indirect manner. This type of information is extremely valuable from a remote sensing viewpoint.

Bands in the VNIR spectra due to allowed transitions in the ferrous ion are indicated by a vertical line that locates the minimum of the band. These lines are joined to a solid area covering a wavelength range corresponding approximately to the half-width of the band. These solid areas are transferred to the composite diagram (Figure 10) and locate the positions of all the features commonly encountered in the VNIR spectra of minerals. This transferal method is used for all the spectral features that are discussed in this article. Only one mineral spectrum is included to illustrate each type of feature, but many of these features occur repeatedly in the spectra of many different minerals.

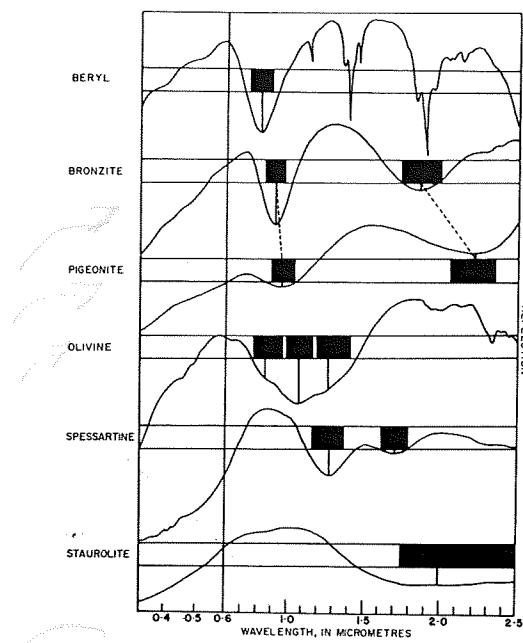


FIG. 2. Spectra of six minerals which contain ferrous ions, either in different crystal fields or in different sites. All the features indicated in these spectra are due to spin-allowed transition in the ferrous ions contained in the mineral. Solid areas show wavelength range of half-width spectral bands and vertical lines locate the minimum of each band.

The top spectrum in Figure 2 is that of beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$). The indicated band is due to the ferrous ion in six-fold coordination located in an almost perfect octahedral Al^{3+} site, and is due to a single spin-allowed transition (Grum-Grzhimailo et al., 1962; Wood and Nassau, 1968).

The bronzite $[(\text{Mg}, \text{Fe})\text{SiO}_3]$ and pigeonite $[(\text{Mg}, \text{Fe}, \text{Ca})(\text{Mg}, \text{Fe})\text{Si}_2\text{O}_6]$ spectra both display a band near $1.0 \mu\text{m}$ and another at wavelengths longer than $1.8 \mu\text{m}$. Both these features arise from transitions in the six-fold coordinated ferrous ion located in one of two possible sites. Here the octahedron is so highly distorted that the degeneracies of the levels in the pure octahedron are removed, providing levels for two distinct spin-allowed transitions (White and Keester, 1966; Burns, 1970a). The ranges of values which these two features can adopt in terrestrial and extraterrestrial pyroxenes have been summarized by Burns et al (1972) and Adams and McCord (1972).

The olivine $[(\text{Mg}, \text{Fe})_2\text{SiO}_4]$ spectrum displays a very broad absorption region centered near $1.0 \mu\text{m}$ composed of at least three separate features. The olivine structure contains two six-fold coordinated sites,

and some controversy has recently existed concerning the spectral contributions from the ferrous ions located in these sites (Burns, 1970a; Runciman et al, 1973). The most recent evidence indicates that the ions in one site produce the intense central features, while those in the other produce the features on either side (Burns, 1974; Runciman et al, 1974).

The spessartine $[\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3]$ spectrum shows two features located at longer wavelengths than the most intense features of minerals containing ferrous ion in six-fold coordinated sites. The garnet structure consists of independent SiO_4 tetrahedra linked by trivalent ions in six-fold octahedral coordination, and divalent ions in eight-fold coordination. In the distorted eight-fold coordinated sites, two Fe^{2+} levels are resolved, and it is the transitions between these levels that give rise to the two features indicated in this spectrum (Clark, 1957; Manning, 1967a; Burns, 1968).

In staurolite $[(\text{Fe}, \text{Mg})_2\text{Al}_9\text{Si}_4\text{O}_{23}(\text{OH})]$, the Fe^{2+} ions are in tetrahedral coordination; in this site the Fe to O distances are shorter than in the six coordination sites in the ferro-magnesium silicates (Burns, 1970a), and it is these ions which produce the spectral features indicated.

The intense features indicated in Figure 2 are all due to spin-allowed transitions. The very weak features due to the spin-forbidden transitions are weakly expressed as shoulders on the broad absorption feature which is responsible for the fall-off in intensity toward shorter wavelengths.

Figure 3 shows the spectra of six minerals, each of which exemplifies features typical of each of the six transition metal ions occasionally present in mineral spectra.

Nickel Ni^{2+} .—The divalent nickel ion can form octahedral, square planar, or tetrahedral complexes. Transitions from the ground state to three upper states produce bands near 1.25 , 0.74 , and $0.4 \mu\text{m}$, respectively (McClure, 1957); and because such transitions are spin-allowed, they produce pronounced absorption bands, such as those in the spectrum of annabergite $[(\text{Ni}, \text{Co})_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$ shown in Figure 3.

Copper Cu^{2+} .—Cupric ions are stabilized in deformed octahedral sites. In the chrysocolla $[\text{Cu}_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ spectrum, shown second from the top in Figure 3, the intense feature near $0.8 \mu\text{m}$ is due to the spin-allowed transition from the ground state to the upper state. Distortion of the octahedral site should permit further splitting of the levels, resulting in resolution of this band, but it is not evident

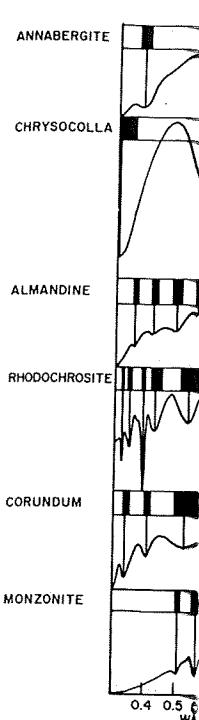


FIG. 3. Spectra of six minerals which contains the transition metal ions, and the features typical of each of the six transition metal ions occasionally present in mineral spectra (of monzonite due to the presence of Fe^{3+}).

in this particular sample (Clark, 1957; Clark and Burns, 1967).

Ferric Ion Fe^{3+} .—The ferric ion can form octahedral, square planar, or tetrahedral complexes. The locations of such transitions of the ferric ion in various crystal fields are summarized by Burns (1970a). The ferric ion has a symmetric ground state in any crystal field. Transitions from the ground state to the first three quadrupole states are spin-forbidden, but features arising from weak and diffuse bands in the long-wavelength end of the visible region are most clearly observed in the spectra of annabergite and beryl. The feature in annabergite occurs near $0.44 \mu\text{m}$.

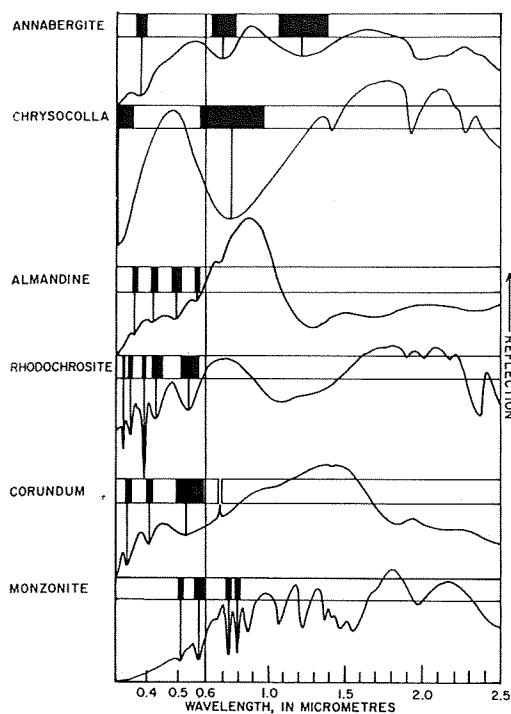


FIG. 3. Spectra of six minerals, each of the top five of which contains the ion of a different transition element, and the features indicated are characteristic of the crystal field transitions in that ion. In the bottom spectrum (of monzonite), the features indicated are due to the presence of a rare earth element.

in this particular spectrum (Holmes and McClure, 1957; Clark and Burns, 1967).

Ferric Ion Fe^{3+} .—Numerous attempts have been made to identify and assign spectral features due to transitions of the ferric ion in a variety of minerals. The locations of such features are identified in the almandine $[Fe_3Al_2(SiO_4)_3]$ spectrum (Figure 3). Fe^{3+} has a symmetric ground state that is not split in any crystal field. Transitions from this field independent ground state to higher levels that arise from quadrupole states are all spin-forbidden. Consequently, features arising from such transitions appear only as weak and diffuse bands, and the difficulty of observing them is compounded by the fact that they occur in the same region as the very much more intense ligand to metal charge transfer bands which are responsible for the sharp drop off in intensity at the short wavelength end of the visible spectrum. Ferric ion features are most clearly observed in the spectra of garnets and beryl. The feature most firmly assigned to ferric ion occurs near $0.44 \mu m$ [in beryl, Dvir and Low

(1960), Wood and Nassau (1968); in garnets, Bailey (1960), Manning (1967b, 1968); in oxides, Wicker-sheim and Lefever (1961), Tandon and Gupta (1970), Lehmann and Harder (1970), Faye (1971); and in other minerals, Clark (1957), White and Keester (1966, 1967), Faye (1968, 1972), Manning (1970a, 1970b, 1971), Tossel et al (1973)].

Manganese Mn^{2+} .—Figure 3 illustrates features due to the presence of the manganese ion in the spectrum of the mineral rhodochrosite ($MnCO_3$). All transitions are spin-forbidden but features do appear in the spectrum at $\sim 0.34 \mu m$, $0.37 \mu m$, $0.41 \mu m$, $0.45 \mu m$, and $0.55 \mu m$ (McClure, 1959).

Chromium Cr^{3+} .—The Cr^{3+} ion readily substitutes with no charge discrepancy into Al^{3+} sites (as in αAl_2O_3 , in ruby). Transitions produce the features displayed in the corundum spectrum, shown in Figure 3, near $0.4 \mu m$ and $0.55 \mu m$, respectively (Poole and Itzel, 1963). The chromium ion is also responsible for the most unusual sharp emission feature near $0.7 \mu m$, and it is this transition which produces the best known ruby laser line.

Rare earth ions: Lanthanum La^{2+} .—The indicated bands in the spectrum of monzonite (Figure 3) are assigned to transitions in the La^{2+} ion. Although electronic transitions in trivalent lanthanum do not produce features in the VNIR spectrum (Adams, 1965), those in the divalent lanthanum ion do. Bands essentially identical to those shown in the monzonite spectrum are displayed in the flame emission spectrum of lanthanum oxide (Menis et al, 1958; Spedding and Doane, 1959).

Titanium.—Although the Ti^{4+} ion does not produce any features in the VNIR, the Ti^{3+} ion in octahedral coordination should. The data available on spectral features due to Ti^{3+} in minerals are limited, and interpretation somewhat speculative. No such features were observed in the mineral spectra used here but several features have been reported. Mao and Bell (1973) report a single feature near $0.55 \mu m$ in silicate glasses; Prewitt et al (1972) report a band near $0.64 \mu m$ in synthetic Ti pyroxenes; Burns and Fyfe (1967), and Manning and Nickel (1969) a band near $0.45 \mu m$ in titanaugite; and Clark et al (1969), Burns and Huggins (1973), and Dowty and Clark (1973) report two features near 0.45 and $0.60 \mu m$ in a pyroxene crystal from the Allende meteorite.

Charge-transfer

Charge-transfer, or inter-element electron transition, refers to the process whereby absorbed energy

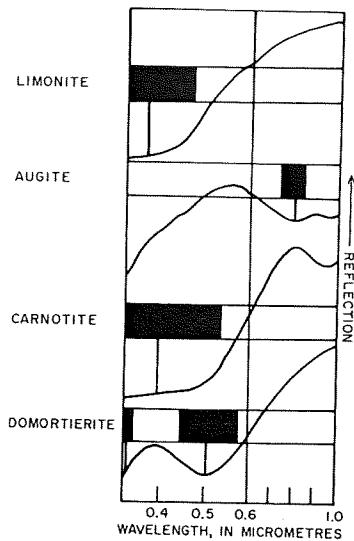


FIG. 4. Spectra of four minerals, the top three of which illustrate various types of charge-transfer spectral features. The bottom spectrum (that of dumortierite) illustrates bands due to $\pi-\pi$ transitions.

causes an electron to migrate between neighboring ions, or between ions and ligands. Although an electron is actually transferred, it remains localized in its new position and does not enter into the conduction band.

In crystal structures, an electron localized mainly in a ligand orbital can be excited to an orbital localized mainly on a central metal ion, or vice versa. Such transfers may also occur between adjacent ions of the same metal in different valence states, so that the process is essentially one of photochemical oxidation-reduction. This is frequently the case when pairs of ions, such as Fe^{2+} and Fe^{3+} , Mn^{3+} and Mn^{2+} , or Ti^{3+} and Ti^{4+} , are suitably located adjacent to each other.

The spectral features which occur as a result of "charge-transfers" typically are very intense, usually hundreds of thousands of times more intense than allowed crystal field transitions; the process is facilitated when a local misbalance of charge occurs accompanying isomorphous substitution such as, for example, in the replacement of Fe^{2+} and Mg^{2+} by Al^{3+} and Fe^{3+} ions in ferromagnesian silicates (Burns, 1970b).

One of the most commonly observed features in the spectra of terrestrial geologic materials is a pronounced decrease in spectral intensity from the visible into the ultraviolet, and this intensity fall-off is particularly evident in the spectra of weathered materials where both iron and oxygen are present. Unless the

minimum of such a feature is observed in the ultraviolet region, it is difficult to tell whether the feature observed in the visible represents the wing of a charge-transfer band, or the edge of the conduction band where the electrons are not located at specific excited sites, but become delocalized. Hunt et al (1971a) suggested that in some iron oxides this fall-off may be due to the conduction-band edge. As Huguenin (1973) points out, in magnetite (Fe_3O_4) continuous absorption extends across the entire VNIR due to β -spin electrons migrating over the B-site sublattice, giving it a high electrical conductivity under an applied field. When magnetite is oxidized to hematite ($\alpha\text{-Fe}_2\text{O}_3$), the spectrum changes to display an apparent band edge near $0.7 \mu\text{m}$, and in geothite [$\alpha\text{FeO(OH)}$], this edge does not extend as far into the visible. Tandon and Gupta (1970), as well as observing Fe^{3+} crystal field bands near $.86$ and $.47 \mu\text{m}$, observed three minima, near $.35 \mu\text{m}$, $.29 \mu\text{m}$, and $.23 \mu\text{m}$, in the diffuse reflectance spectra of ferric oxide. These minima are considered to be due to Fe-O charge-transfer band. These charge-transfer bands are commonly observed to extend further toward the red when the iron is associated with oxide rather than hydroxide groups.

The intense feature indicated in the limonite ($2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) spectrum (Figure 4) is due to the tail of the Fe-O charge-transfer band, while the additional band at longer wavelengths is due to a crystal-field transition.

The feature indicated in the augite [$(\text{Ca}, \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Ti}, \text{Al})_2(\text{Si}, \text{Al})_2\text{O}_6$] spectrum (Figure 4) is due to the charge-transfer transition between a ferrous and ferric ion, while the feature indicated in the carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$] spectrum (Figure 4) is due to at least three charge-transfer transitions between the uranium and oxygen atoms (McGlynn et al, 1961).

Dumortierite [$\text{Al}_8\text{BSi}_3\text{O}_{19}(\text{OH})$] is composed of a network of SiO_4 tetrahedra, AlO_4 octahedra, and BO_3 triangles. Its spectrum (Figure 4) shows a strong feature in the visible due to a $\pi-\pi$ transition in the π electron orbitals of the boron-oxygen triangles. This phenomenon, rare in inorganic materials, is very common in unsaturated organic substances. It is this type of transition which is responsible for the intense "chlorophyll band" present in spectral recordings of vegetated areas.

Color centers

A limited number of colored materials, particularly halides, display spectral features in the visible that cannot be explained by their chemistry or the presence

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FIG. 5. Spec
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color-centers

of impurities but are caused by the presence of electronic phenomena called "color centers."

Irradiation of a perfect crystal with a completely periodic field potential would have no permanent effect, because as soon as the radiation is removed, the excited electrons would return to the positively charged holes they vacated. In real crystals however, lattice defects exist that disturb the periodicity; these defects can produce discrete energy levels into which excited electrons can fall, and such electrons can become bound to the defect.

There are many different types of defects, and they have been studied extensively (Przibaum, 1956; Fowler, 1968), but the most commonly encountered color center is referred to as the "F-center."

Spectral features due to color centers in natural crystals are illustrated in three fluorite spectra displayed in Figure 5. The colors of the fluorite samples were yellow, purple, and blue.

Conduction band transitions

In some periodic lattices, the discrete energy levels of the outer shell electrons of the ions composing the lattice are broadened into energy bands by their proximity to each other. There are then two energy bands in which the electrons may exist: a higher energy region called the "conduction" band, and a lower energy region called the "valence" band. Electrons in the conduction band have so much energy that they are not attached to any ion, but are free to wander throughout the crystal lattice, and they are referred to as "free" or "conduction" electrons. Electrons in

the valence band, however, are attached to specific ions or bonds.

Between these two energy bands is a zone of energies that electrons may not adopt; this is called the "forbidden" band or gap. Metals display very high conductivity, indicating an abundance of free electrons, and they display a very narrow or nonexistent forbidden gap. In this case the conduction and valence bands touch. In dielectric materials, on the other hand, the valence electrons are so tightly bound that large amounts of energy are required to set them free; the conduction band does not commence until well into the vacuum ultraviolet region. Dielectrics typically have very wide forbidden gaps.

In semiconductors, the width of the forbidden gap is intermediate between that for metals and dielectrics, and the edge of the conduction band is marked by the appearance of an intense absorption edge in the VNIR. The sharpness of this absorption edge is a function of the purity and crystallinity of the material. In particulate materials, grain boundaries, lattice defects, lack of periodicity, and compositional impurities, all operate to produce more sloped absorption edges than are observed in pure single crystals.

Figure 6 shows the spectra of four minerals, three of which, sulphur (S), cinnebar (HgS), and stibnite (Sb_2S_3) show well defined absorption edges marking the transition from intense absorption in the conduction band at shorter wavelengths to complete transmission in the forbidden gap at longer wavelengths. The fourth mineral spectrum, arsenopyrite (FeAsS), shows the conduction band extending completely across the VNIR range.

VIBRATIONAL PROCESSES

The apparently random motions of any vibrating system are made up from a restricted number of simple motions, which are called the normal modes or fundamentals. For a system of N particles, there are $3N-6$ normal modes. Thus the number and form of the normal vibrations, and the values of the permitted energy levels for any material are determined by the number and type of its constituent atoms, their spatial geometry, and the magnitude of the binding forces between them.

Each normal vibration has a quantum number v_i associated with it and a normal frequency ν_i . The i th vibration is usually described in terms of the motion involved. For the water molecule, which has just 3 normal modes, the symmetric OH stretch is designated v_1 or ν_{OH} ; the HOH bend v_2 ; and the asymmetric OH stretch v_3 .

When a fundamental mode is excited with two or

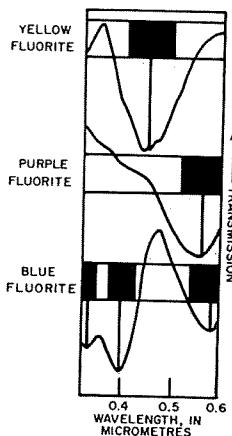


FIG. 5. Spectra of three different colored samples of fluorite, illustrating features due to the presence of color-centers in a mineral.

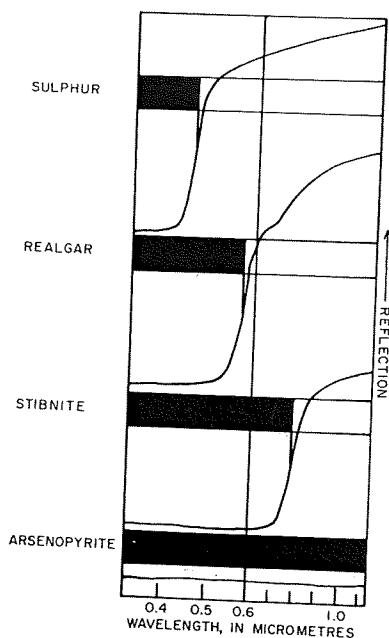


FIG. 6. Spectra of four minerals which illustrate the sharp transition between intense absorption and transparency in materials which display features due to the presence of a forbidden gap and a conduction-band. In the lowest spectrum, the absorption edge occurs in the mid-infrared.

more quanta of energy an overtone occurs, producing a band at (or near) twice (or some multiple integral value) of the fundamental frequency, i.e., $2\nu_1$, $3\nu_1$, $4\nu_1$, etc. When two or more different fundamental or overtone vibrations occur, a combination tone feature appears located at (or near) the sum of all the fundamental or overtone frequencies involved.

The energy required to excite the fundamental modes of all geologically important materials fall in the mid- and far-infrared regions. All the fundamentals of silicon, aluminum, or magnesium associated with oxygen occur near $10\text{ }\mu\text{m}$ or at longer wavelengths. The first overtones of these fundamentals, which should be most intense near $5\text{ }\mu\text{m}$ or at longer wavelengths, are not observed. Consequently, because higher overtones would be even weaker, any evidence for them is not expected in the VNIR.

What is observed in the NIR are features due to overtones and combinations of groups that have very high fundamental frequencies. There are, however, relatively few groups which provide such high fre-

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quencies, and by far the most important of these is the OH group.

Evidence for OH occurs far more frequently than evidence for any other group in the spectra of terrestrial materials, both because the OH group is constitutionally present in many substances, and because hydroxyl features appear whenever water is present.

Water

Liquid water has three fundamental vibrational modes which were mentioned above. The location of the features which appear when these modes are excited are ν_1 at $3.106\text{ }\mu\text{m}$; ν_2 at $6.08\text{ }\mu\text{m}$; and ν_3 at $2.903\text{ }\mu\text{m}$. The overtones and combinations which may appear in the NIR are $(\nu_2 + \nu_3)$, near $1.875\text{ }\mu\text{m}$; $(2\nu_1 + \nu_3)$ near $1.454\text{ }\mu\text{m}$; $(\nu_1 + \nu_3)$ near $1.38\text{ }\mu\text{m}$; $(\nu_1 + \nu_2 + \nu_3)$ near $1.135\text{ }\mu\text{m}$; and $(2\nu_1 + \nu_3)$ near $0.942\text{ }\mu\text{m}$.

Spectral features in minerals due to the presence of water are illustrated in Figure 7. Water may be present in a mineral as individual or clusters of molecules at specific sites essential to its structure, as in hydrates such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (Figure 7). It may be present in various quantities in specific locations not essential to the crystal structure, as in zeolites, such as natrolite ($\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) (Figure 7). It may be present in various amounts, together with considerable quantities of constitutional hydroxyl groups, as in the clay-like group of minerals illustrated here by montmorillonite. The general formula of montmorillonite can be expressed as $[(\text{Al}, \text{Mg}, \text{Fe})_4(\text{OH})_n - (\text{Si}, \text{Al}, \text{Fe})_8\text{O}_{20-n}(\text{OH})_n \cdot 6\text{H}_2\text{O}]$. Water molecules are typically both physically and chemi-adsorbed on the crystal surfaces. Water may also be present trapped in fluid inclusions in the crystal structure, as in milky quartz (SiO_2).

In these spectra the features due to the presence of water vary in intensity, and somewhat in location, and this is a consequence of the variety of locations and sites it can occupy and the different environments in which it can be located. However, whenever molecular water is present in minerals and rocks, two features always appear—one near $1.4\text{ }\mu\text{m}$ and the other near $1.9\text{ }\mu\text{m}$. They may be broad, indicating that the molecules occupy unorganized, or several non-equivalent sites, but the presence of these two features together is completely diagnostic of the presence of the water molecule.

Hydroxyl

There is only one fundamental stretching mode for the hydroxyl ($-\text{OH}$) group, which is infrared active and produces a feature somewhere near $2.75\text{ }\mu\text{m}$.

FIG. 7. § contained

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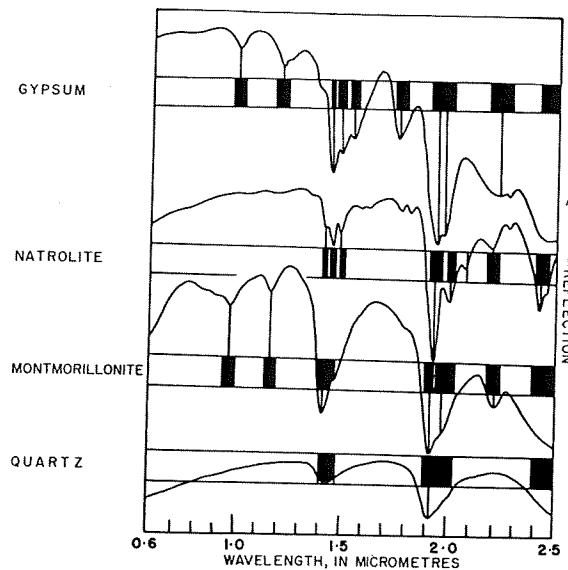


FIG. 7. Spectra displaying features due to the vibrational combinations and overtones of molecular water contained in various locations in the minerals.

μm . Exactly where this feature will appear depends upon what the OH is directly attached to, and where it is located in the material. Because OH groups may be located on several different sites, and hence are located in different potential fields in the same material, several bands may appear in a spectrum, all due to the fundamental OH stretching mode. For example, in the spectrum of talc there are three sharp bands that occur at 2.719, 2.730, and 2.743 μm . These have been related to the OH groups that are located in positions where the closest octahedral sites are occupied by 3 Mg^{2+} ions; 2 Mg^{2+} and Fe^{2+} ; or Mg^{2+} and 2 Fe^{2+} ions, respectively (Vedder, 1964).

The bands due to the fundamental OH-stretching mode lie just outside the NIR range, so that what is observed in the NIR are features due to the first overtone of the OH stretch (which is responsible for probably the most common feature of all, the band near 1.4 μm), or due to combination bands of the fundamental stretch with an $X - \text{OH}$ bending fundamental (where X is usually Al or Mg), or due to the OH stretch in combination with some lattice or librational mode. Pronounced well-resolved OH features occur in the spectra of micas, clay minerals, and amphiboles.

Combination bands in the 2 μm region that involve the OH fundamental stretching mode generally appear in pairs, with the shorter wavelength member typically near either 2.2 or 2.3 μm , and the accompanying

feature near either 2.3 or 2.4 μm . The location of the more intense feature appears to depend upon whether aluminum is present, in which case it occurs near 2.2 μm , or whether magnesium is present, in which case it appears near 2.3 μm .

The above variables are illustrated in Figure 8 for micas, a clay mineral, and an amphibole. In muscovite $[\text{K}_2\text{Al}_4(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH},\text{F}_4)]$, which is a dioctahedral phyllosilicate with OH groups coordinated around aluminum, the feature appears near 2.2 μm , and is considered to be due to the combination of the OH stretch with the fundamental AlOH bending mode. In phlogopite $[\text{K}_2(\text{Mg},\text{Fe}^{2+})_6(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH},\text{F}_4)]$, which is a trioctahedral member, the OH groups are coordinated around magnesium, and the major feature occurs near 2.3 μm and is assumed to be due to a combination of the OH stretch with the MgOH bending mode. This situation is repeated in the spectra of kaolinite $[\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8]$ and the amphibole, actinolite $[\text{Ca}_2\text{Mg}_5(\text{Si}_8\text{O}_{22})(\text{OH},\text{F})_2]$. In the spectrum of kaolinite the features are doubled, indicating that there are slightly different sites in which the OH groups are located. Other features in these spectra can be assigned as combinations of the OH stretch with the silicon-oxygen stretching fundamentals, and the presence of the band near 1.9 μm in kaolinite indicates that some water is present in this sample.

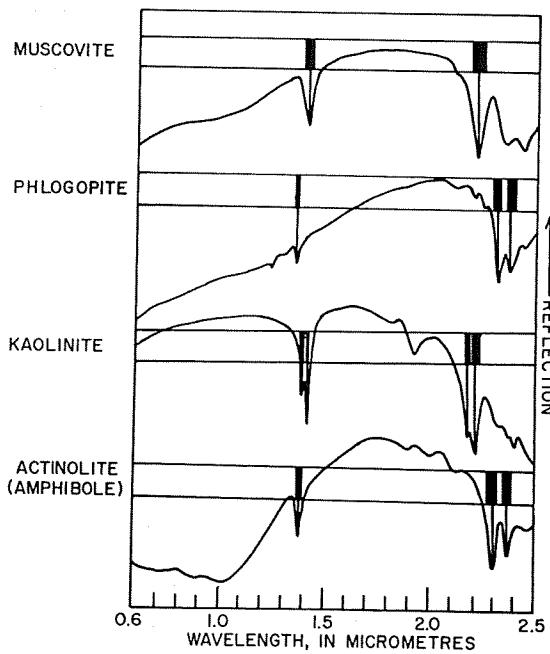


FIG. 8. Spectra displaying features due to the overtone and combination tones of the hydroxyl group present in different environments in various minerals.

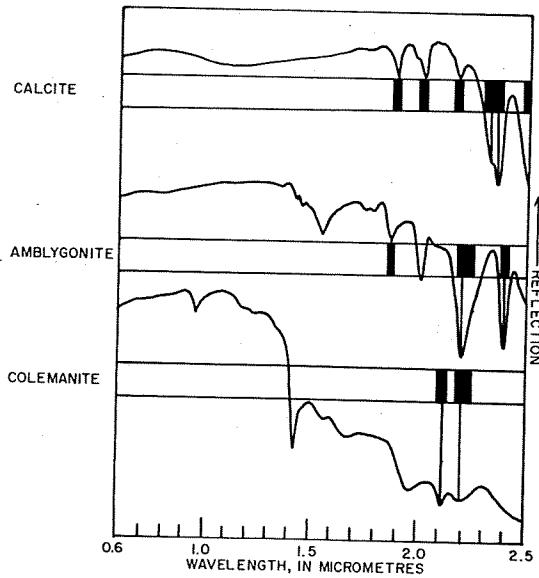


FIG. 9. Spectra displaying features due to overtones and combination tones of internal vibrations of various anionic groups.

Carbonate, borat
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There are six
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FLUORITE

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REALGAR
STIBNITE
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TRANSMISSION
 O_2, CO_2

Carbonate, borate, and phosphate

Features occur in the NIR spectra between 1.6 and 2.5 μm as a result of overtone or combinations of the internal vibrations of the carbonate ion. Such features are usually quite distinctive. Carbonates are not usually associated with water, so intense water features are frequently not present to confuse the spectra.

There are six fundamental modes of the planar CO_3^{2-} ion. Because there are two doubly degenerate modes, a total of four instead of six fundamental frequencies is listed. They are ν_1 , the totally symmetric C–O stretch which is infrared inactive, however its Raman feature occurs near 9.23 μm (Griffith, 1969);

ν_2 , the out-of-plane bending mode, occurring near 11.36 μm ; ν_3 , the doubly degenerate antisymmetric C–O stretching mode, occurring near 7.0 μm ; and ν_4 , the doubly degenerate in-plane bending mode, that appears near 14 μm .

In the NIR, carbonates typically display a series of five very characteristic bands, the first two of which, at the longer wavelengths, are quite clearly doubled and are considerably more intense than the three features at shorter wavelengths, which generally have shoulders on their short wavelength sides. The doubling can be explained in terms of lifting of the degeneracies.

hydroxyl group present

internal vibrations of various

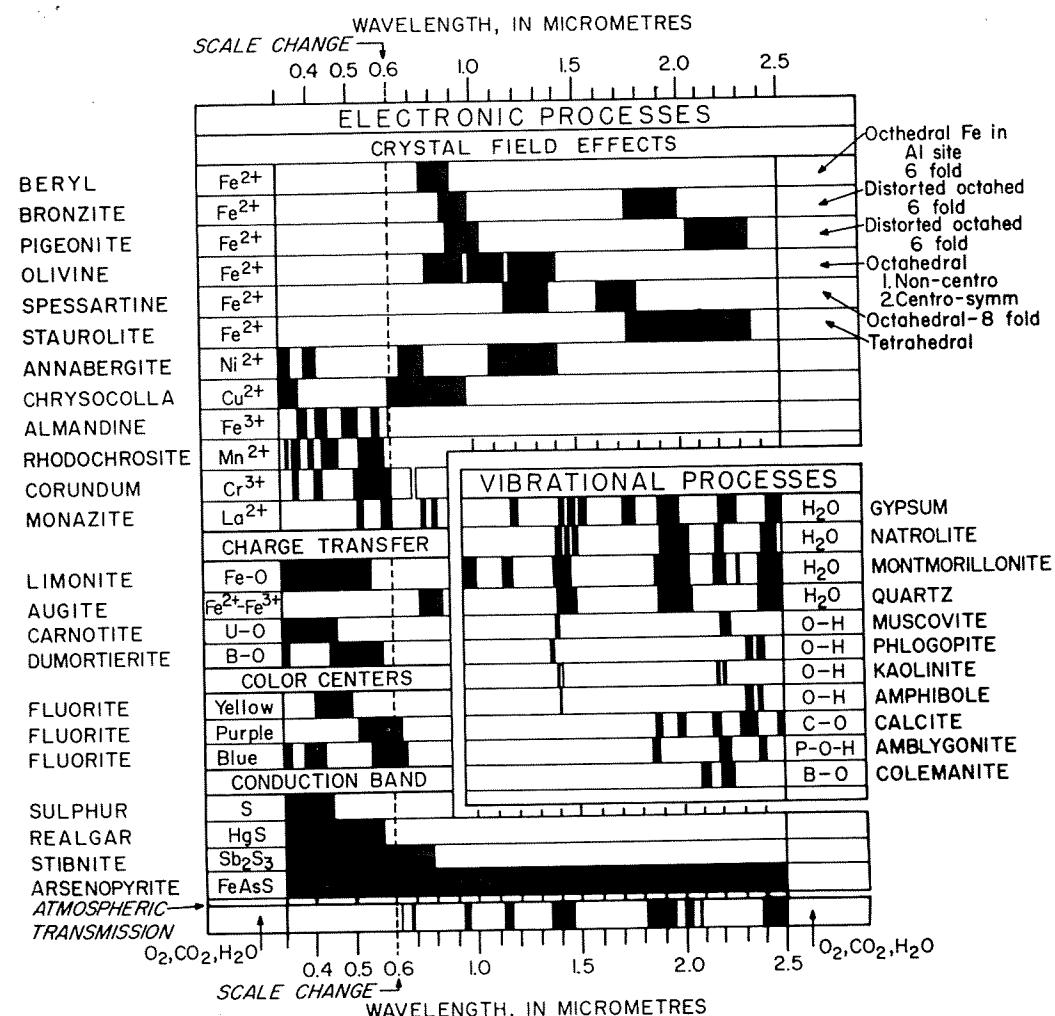


FIG. 10. Spectral signature diagram.

The bands, which are displayed in the calcite (CaCO_3) spectrum (Figure 9) can be attributed to the following overtones or combinations: $v_1 + 2v_3$ near 2.55 μm ; $3v_3$ near 2.35 μm ; $v_1 + 2v_3 + v_4$, or $3v_1 + 2v_4$ near 2.16 μm ; $2v_1 + 2v_3$ near 2.00 μm ; and $v_1 + 3v_3$ near 1.90 μm .

The spectrum of amblygonite $[(\text{Li}, \text{Na})_4 \text{Al}_4(\text{PO}_4)_4(\text{F}, \text{OH})_4]$ (Figure 9) shows features attributed to the P-O-H group. In phosphates, arsenates, and vanadates, the isolated XO_4^{3-} ions do not provide fundamentals at sufficiently short wavelengths, so their overtone or combination frequencies are not intense enough to be detected in the NIR. The features indicated in amblygonite are due to motions involving the P-O-H group. Berry (1968) determined by deuteration techniques that bands near 3.39, 4.22, and 5.88 μm do indeed involve the P-O-H vibrations. Combinations of these features account for the bands in calcium phosphate monohydrate in equivalent positions to those in the amblygonite spectrum.

The features in the spectrum of colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) can be ascribed to overtones of the BO_3^{3-} ion just as similar features were explained in the carbonate spectra by the CO_3^{2-} vibrations. Although the molecular structure of metal borates is generally not well understood, the assignment of the features in the spectra of some well characterized borates with aragonite and calcite structures have been made (Steele and Decius, 1956; Weir and Lipencott, 1961).

SPECTRAL SIGNATURE DIAGRAM

All the identified spectral feature information contained in the previous figures is combined and displayed in Figure 10. This figure serves to locate and identify the origin of all the electronic and vibrational features commonly encountered in the VNIR spectra of particulate minerals.

Figure 10 is divided into two main areas, the smaller area at the lower right contains the location of features of a vibrational origin; the rest of the figure presents those features having an electronic origin. Because there are several quite different electronic processes that produce features in the VNIR, this area is further subdivided and the specific processes identified.

Although the spectra of the minerals selected for illustrative purposes typically display several features, only those are shown that are due to the specific process and the specific ion or group indicated. For example, the beryl spectrum displays multiple sharp features due to vibrations of water in several sites and features due to electronic processes involving the

Fe^{2+} ion, but only the features due to crystal field transition of the ferrous ions in the 6-fold octahedral site are identified; other features are illustrated in different parts of the diagram using different minerals.

The usefulness of this diagram is that it provides an explanation for a band at a specific location in the spectrum.

Bands due to vibrational processes can be distinguished from those having an electronic origin on the basis of resolution—the vibrational features are much sharper, and because typically vibrational features occur as multiples whereas electronic features are broad single or double bands. Naturally, if several bands occur on the diagram, before any one of these can be identified, then all features must be present in the spectrum. For example, because five features occur in the carbonate spectra, all five must be apparent before any one can be assigned to vibrations of the CO_3^{2-} ion.

An atmospheric transmission spectrum is included at the bottom of Figure 10. This defines, to a large extent, those spectral ranges where data may be collected in terrestrial remote sensing applications.

ACKNOWLEDGMENT

The body of data that forms the basis of this paper was published jointly with Dr. John W. Salisbury in a series of articles that appeared in *Modern Geology*. His contributions, which made this paper possible, are gratefully acknowledged.

REFERENCES

- Adams, J. B., and McCord, T. B., 1972, Electronic spectra of pyroxenes and interpretation of telescopic spectral reflectivity curves of the moon: Proc. 3rd Lunar Sci. Conf., D. R. Criswell, ed., v. 3, p. 3021.
- Adams, J. W., 1965, The visible region absorption spectra of rare earth minerals: Am. Mineral., v. 50, p. 356.
- Bailey, P. C., 1960, Absorption and refractivity measurements on some rare earth garnets and $\alpha\text{-Fe}_2\text{O}_3$: J. Appl. Phys., v. 31, p. 395.
- Berry, E. E., 1968, The infrared spectrum of monocalcium phosphate monohydrate: Spectrochim. Acta., v. 24A, p. 1727.
- Burns, R. G., 1968, Optical absorption in silicates, in *The application of modern physics to the earth and planetary interiors*: New York, John Wiley and Sons.
- 1970a, Crystal field spectra and evidence of cation ordering in olivine minerals: Am. Mineral., v. 55, p. 1608.
- 1970b, *Mineralogical application of crystal field theory*: Cambridge Univ. Press.
- 1974, The polarized spectra of iron in silicates: Olivine: A discussion of neglected contributions from Fe^{2+} ions in M(1) sites: Am. Mineral., v. 59, p. 625.
- Burns, R. G., Abu-Eid, R. M., and Huggins, F. E., 1972, Crystal field spectra of lunar pyroxenes: Proc. 3rd Lunar Sci. Conf., D. R. Criswell, ed., v. 3, p. 533.
- Burns, R. G., and Fyfe, W. S., 1967, Crystal field theory and geochemistry of transition elements: Res. Geochim., v. 2, p. 259.
- Burns, R. G., absorption of light by olivine: A discussion: Can. J. Earth Sci., v. 1, p. 1039.
- Clark, J. R., Pyroxenes and spinel: Petrology: N.Y., McGraw-Hill, p. 108.
- Clark, M. B., of Cu^{2+} and Ba^{2+} in Si_4O_{10} : J. Geophys. Res., v. 77, p. 1039.
- Clark, S. P., The visible and infrared spectra of Allende meteorites: J. Geophys. Res., v. 77, p. 1039.
- Dviri, M., and I. optical spectra: J. Geophys. Res., v. 77, p. 1039.
- Faye, G. H., Infrared spectra of iron in corundum: Can. J. Earth Sci., v. 1, p. 1039.
- 1972, Infrared parameters of iron in corundum bearing minerals: J. Geophys. Res., v. 77, p. 1039.
- Fowler, W. B., Academic Press, London, 1968.
- Griffith, W. P., Nature, v. 226, p. 453.
- Grum-Grzhimailo, R. K., Sukhanov, V. V., Absorption spectra of Mg^{2+} in olivine: Sov. Phys. Solid State, v. 13, p. 299.
- Holmes, O. G., of hydrated ions: J. Geophys. Res., v. 77, p. 1039.
- Huguenin, R. L., netite, I. King, Geophys. Res., v. 77, p. 1039.
- Hunt, G. R., and infrared spectra of olivine: Mod. Geology, v. 1, p. 1039.
- 1971, Visible and infrared spectra of olivine and rocks. II: Calcined olivine: J. Geophys. Res., v. 77, p. 1039.
- Hunt, G. R., Salinity and infrared spectra of olivine: III. Oxides and rocks: J. Geophys. Res., v. 77, p. 1039.
- 1971b, Visible and infrared spectra of olivine and rocks. IV: Olivine and rocks: J. Geophys. Res., v. 77, p. 1039.
- 1972, Visible and infrared spectra of olivine and rocks. V: Olivine and rocks: J. Geophys. Res., v. 77, p. 1039.
- 1973, Visible and infrared spectra of olivine and rocks. VI: Olivine and rocks: J. Geophys. Res., v. 77, p. 1039.
- Lehmann, G., and infrared spectra of olivine and trivalent iron: J. Geophys. Res., v. 77, p. 1039.
- Manning, P. G., The infrared spectra of olivine and some structural significance: Can. J. Earth Sci., v. 1, p. 1039.
- 1967b, The infrared spectra of olivine and the identification of octahedrally bonded iron: J. Geophys. Res., v. 77, p. 1039.

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- Huggins, F. E., 1972,
es: Proc. 3rd Lunar
3, p. 533.
- Crystal field theory
nts: Res. Geochem.,
- Burns, R. G., and Huggins, F. E., 1973, Visible-region absorption of a Ti³⁺ fassaite from the Allende meteorite: A discussion: Am. Mineral., v. 58, p. 955.
- Clark, J. R., Appleman, D. E., and Papike, J. J., 1969, Pyroxenes and amphiboles: Crystal chemistry and phase petrology: Mineral Soc. Am., Spec. paper, v. 2., p. 31.
- Clark, M. B., and Burns, R. G., 1967, Electronic spectra of Cu²⁺ and Fe²⁺ square planar coordinated by oxygen in Ba_xSi₄O₁₀: J. Chem. Soc., p. 1034.
- Clark, S. P., 1957, Absorption spectra of some silicates in the visible and near infrared: Am. Mineral., v. 42, p. 732.
- Dowty, E., and Clark, J. R., 1973, Crystal structure refinement and optical properties of a Ti³⁺ fassaite from the Allende meteorite: Am. Mineral., v. 58, p. 230.
- Dvir, M., and Low, W., 1960, Paramagnetic resonance and optical spectrum of iron in beryl: Phys. Rev., v. 119, p. 1587.
- Fay, G. H., 1968, The optical absorption spectra of certain metal ions in muscovite, lepidolite, and fuchsite: Can. J. Earth Sci., v. 5, p. 31.
- 1971, On the optical spectra of di- and trivalent iron in corundum—A discussion: Am. Mineral. Min. Notes, v. 56, p. 344.
- 1972, Relationship between crystal-field splittings parameters "ΔVI" and M host-O. Bond distance as an aid in the interpretation of absorption spectra of Fe²⁺ bearing materials: Can. Mineral., v. 11, p. 473.
- Fowler, W. B., 1968, Physics of color centers: New York, Academic Press.
- Griffith, W. P., 1969, Raman spectroscopy of minerals: Nature, v. 224, p. 264.
- Grum-Grzhimailo, S. V., Brilliantov, N. A., Sviridova, R. K., Sukhanova, O. N., and Kapitonova, M. M., 1962, Absorption spectra of iron-colored beryls at temperatures from 29° to 1.7° K: Opt. Spectros., v. 13, p. 133.
- Holmes, O. G., and McClure, D. S., 1957, Optical spectra of hydrated ions of the transition metals: J. Chem. Phys., v. 26, p. 1686.
- Huguenin, R. L., 1973, Photostimulated oxidation of magnetite. I. Kinetics and alteration phase identification: J. Geophys. Res., v. 78, p. 8481.
- Hunt, G. R., and Salisbury, J. W., 1970, Visible and near infrared spectra of minerals and rocks. I. Silicate minerals: Mod. Geology, v. 1, p. 283–300.
- 1971, Visible and near infrared spectra of minerals and rocks. II. Carbonates: Mod. Geology, v. 2, p. 23–30.
- Hunt, G. R., Salisbury, J. W., and Lenhoff, C. J., 1971a, Visible and near infrared spectra of minerals and rocks. III. Oxides and hydroxides: Mod. Geology, v. 2, p. 195–205.
- 1971b, Visible and near infrared spectra of minerals and rocks. IV. Sulphides and sulphates: Mod. Geology, v. 3, p. 1–14.
- 1972, Visible and near infrared spectra of minerals and rocks. V. Halides, arsenates, vanadates and borates: Mod. Geology, v. 3, p. 121–132.
- 1973, Visible and near infrared spectra of minerals and rocks. VI. Additional silicates: Mod. Geology, v. 4, p. 85–106.
- Lehmann, G., and Harder, H., 1970, Optical spectra of di- and trivalent iron in corundum: Am. Mineral., v. 55, p. 98.
- Manning, P. G., 1967a, The optical absorption spectra of the garnets almandine-pyrope, pyrope, and spessartine and some structural interpretations of mineralogical significance: Can. Mineral., v. 9, p. 237.
- 1967b, The optical absorption of some andradites and the identification of the 6B, 4A, 4E(G) transition in octahedrally bonded Fe³⁺: Can. J. Earth Sci., v. 4, p. 1039.
- 1968, Optical absorption studies of grossularite, andradite, and uvarovite: Can. Mineral., v. 9, p. 723.
- 1970a, Racah parameters and their relationship to lengths and covalencies of Mn²⁺- and Fe³⁺-oxygen bonds in silicates: Can. Mineral., v. 10, p. 677.
- 1970b, Is the diffuse interstellar absorption band at 4430 Å caused by trivalent iron?: Nature, v. 226, p. 829.
- 1971, Presence of two Fe³⁺ bearing minerals in interstellar dust: Nature, v. 230, p. 131.
- Manning, P. G., and Nickel, E. H., 1969, Optical absorption and electron microprobe studies of some high Ti-andradites: Can. Mineral., v. 10, p. 71.
- Mao, H. K., and Bell, P. M., 1973, Crystal field spectra: Carnegie Inst. Wash., Yearbook, v. 72, p. 629.
- McClure, D. S., 1957, The distribution of transition metal cations in spinels: J. Phys. Chem. Solids, v. 3, p. 311.
- 1959, Electronic spectra of molecules and ions in crystals. Part II. Spectra of ions in crystals: Solid State Phys., v. 9, p. 399.
- McGlynn, S. P., Smith, J. R., and Neely, W. C., 1961, Electronic structure, spectra, and magnetic properties of oxyacetylenes. III. Ligation effects on the infrared spectrum of the uranyl ion: J. Chem. Phys., v. 35, p. 105.
- Menis, O., Rains, T. C., and Dean, J. A., 1958, A study of the flame emission characteristics of lanthanum in an aqueous-alcohol medium: Anal. Chem. Acta, v. 19, p. 183.
- Poole, C. P., and Itzel, J. F., 1963, Optical reflection spectra of chromia-alumina: J. Chem. Phys., v. 39, p. 3445.
- Prewitt, C. T., Shannon, R. D., and White, W. B., 1972, Synthesis of a pyroxene containing trivalent titanium: Contrib. Mineral. Petrol., v. 35, p. 77.
- Przibaum, K., 1956, Irradiation colors and luminescence: London, Pergamon Press.
- Runciman, W. A., Sengupta, D., and Gourley, J. T., 1973, The polarized spectra of iron in silicates. II. Olivine: Am. Mineral., v. 58, p. 481.
- 1974, The polarized spectra of iron in silicates. II. Olivine: A reply: Am. Mineral., v. 59, p. 630.
- Spedding, F. H., and Doane, A. H., 1959, The rare earths: New York, John Wiley and Son, p. 605.
- Steele, W. C., and Decius, J. C., 1956, Infrared absorption of lanthanum, scandium and indium borate and the force constants of the borate ion: J. Chem. Phys., v. 25, p. 1184.
- Tandon, S. P., and Gupta, J. P., 1970, Diffuse reflectance spectrum of ferric oxide: Spectros. Letters, v. 3, p. 297.
- Tossel, J. A., Vaughan, D. J., and Johnson, K. H., 1973, Electronic structure of ferric iron octahedrally coordinated to oxygen: Nature, v. 244, p. 42.
- Vedder, W., 1964, Correlations between infrared spectrum and chemical composition of mica: Am. Mineral., v. 49, p. 736.
- Weir, C. E., and Lippencott, E. R., 1961, Infrared studies of aragonite, calcite, and vaterite structures in borates, carbonates and nitrates: J. Res. of N.B.S.A. Phys. and Chem., v. 65A, p. 173.
- White, W. B., and Keester, K. L., 1966, Optical absorption spectra of iron in the rock forming silicates: Am. Mineral., v. 51, p. 774.
- 1967, Selection rules and assignments for the spectra of ferrous iron in pyroxenes: Am. Mineral., v. 52, p. 508.
- Wickersheim, K. A., and Lefever, R. A., 1961, Absorption spectra of ferric ion containing oxides: J. Chem. Phys., v. 36, p. 844.
- Wood, D. L., and Nassau, K., 1968, The characterization of beryl and emerald by visible and infrared absorption spectroscopy: Am. Mineral., v. 53, p. 577.