THE VISIBLE REGION ABSORPTION SPECTRA OF RARE-EARTH MINERALS[1]

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ABSTRACT

Certain rare-earth elements, notably neodymium, praseodymium, erbium, and holmium, produce absorption bands in the visible region of the spectrum when present as trivalent ions in solutions or compounds.

In crystalline minerals these bands may be almost line-like and have a distribution pattern that is influenced by structure, composition, and optical direction.

Bands of neodymium and praseodymium characterize cerium group minerals whereas bands of erbium and holmium commonly predominate in yttrium group minerals. Detection of the bands with a microspectroscope is invaluable for the recognition of minerals containing rare earths, but the variability of lanthanide content may preclude use of these bands for identification of individual species.

In metamict minerals that show absorption spectra the bands are broad and diffuse but sharpen noticeably after heating. Absorption spectra can be obtained from some minerals only after fusion with a suitable flux.

INTRODUCTION

One of the interesting properties of the rare-earth elements is the absorption effect produced when light is transmitted through a compound or solution in which certain of these elements are present in their trivalent state. Several members of the group show this effect in the visible region of the spectrum (Fig. 1), and as a result when a compound or solution in which they are present is examined with the spectroscope, the absorption of certain wavelengths of the transmitted light is represented by dark line-like bands in an otherwise continuous spectrum.

Since its discovery by Gladstone (1858) over a century ago, the effect has been investigated extensively. Most of the research however has been concerned with the determination of the energy level changes which produce the lines, the behavior of the lines at reduced temperatures and in strong magnetic fields, and their application in analytical methods. For the most part, these investigations were made with synthetic rare-earth compounds or solutions so that the reports have not been generally of specific interest to mineralogists. A notable exception is the work of Henri Becquerel (1888), who studied the absorption spectra of several rare-earth-bearing minerals including monazite, parisite, xenotime, scheelite, and apatite, and recorded these both in the form of wavelength measurements and beautifully executed drawings. Later, Wherry (1915, 1929) in a series of papers attempted to revive interest in the use of absorption spectra for determinative mineralogy by publishing the results of his own observations and those of other investigators. Use of the ab-

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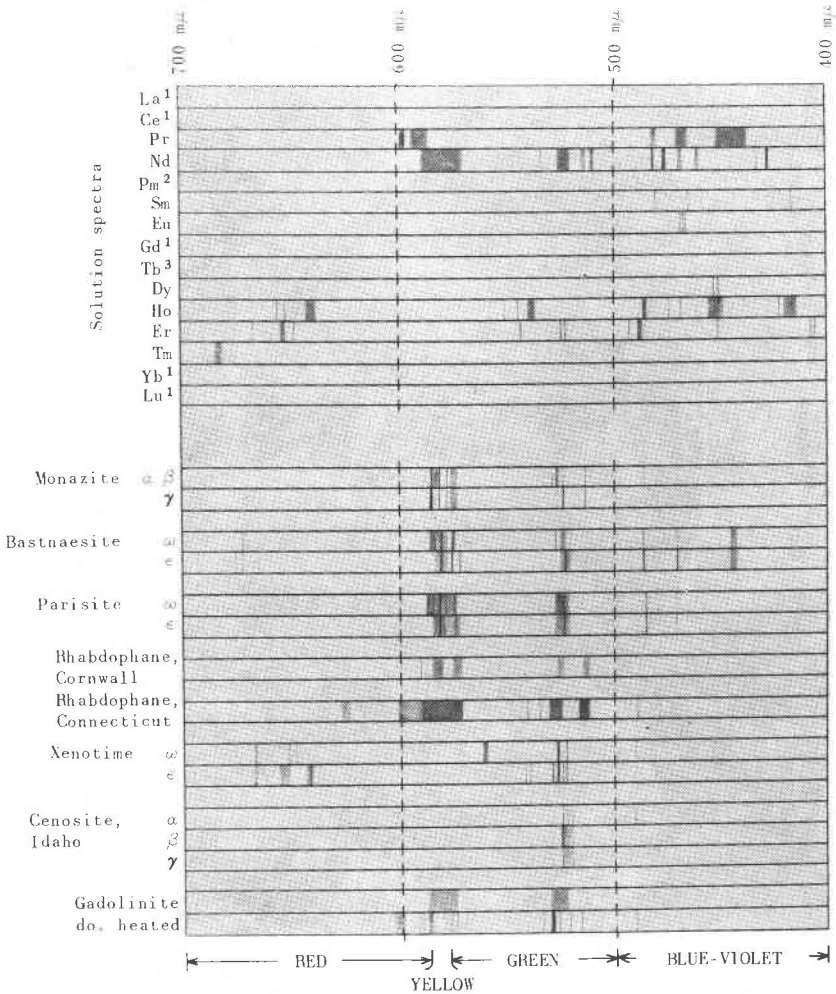[1] Publication authorized by the Director, U. S. Geological Survey.

FIG. 1. Visible region absorption bands of rare-earth ions in solution compared with those of some rare-earth minerals.

[1] No absorption bands in visible region.
[2] Shows strong absorption in visible region, but comparable data not available.
[3] Absorption bands in visible region at higher concentrations.

sorption spectra in the identification of small grains of rare-earth minerals was advocated by Corin (1931), Sandréa (1953), and Hering and Zimmerle (1963), and its field application for the recognition of monazite and xenotime in placer deposits was stressed by Mertie (1954).

The absorption characteristics of rare-earth minerals have, however,

been of little interest to most mineralogists and are rarely discussed in mineralogy textbooks and articles in the current literature. Such lack of enthusiasm is not without basis in view of the rather limited number of species that show the effect, the inconsistency in the recorded wavelengths of the absorption lines of the few minerals that have been studied, and the rarity of microspectroscopes in mineralogical laboratories. In spite of these detractions, absorption spectra afford a simple and effective qualitative test for rare-earth elements in minerals, and, as an adjunct to other techniques, can be of great value in the discovery, isolation, and identification of minerals containing these elements.

Origin of the Absorption Spectra of the Rare Earths

The absorption effects shown by rare-earth elements have their origin in their electronic configuration, which differs appreciably from that of any element preceding them in the periodic table. Throughout the table, the progression from an element of atomic number Z to that of atomic number $Z+1$ is accompanied by the addition of an electron to the next vacant position with the lowest energy requirement. For elements of low atomic number, the energy requirement of the various electron-bearing levels, or subshells, decreases regularly with distance outward from the nucleus. Thus as the orbitals in the subshells are filled, additional electrons will occupy sites in the next outermost level. This behavior pattern is followed as far as argon $(Z=18)$; for heavier elements the energy requirements of the electron sites become anomalous to the extent that certain subshells may be left temporarily vacant while others more remote from the nucleus are being populated. Whenever the energy requirements are such that the vacant subshell becomes the preferred site for additional electrons, populating of the outermost subshell is recessed until the inner level has been filled. Addition of electrons to inner subshells (backfilling) takes place several times throughout the periodic table and gives rise to elements of somewhat different properties than those with completely filled or empty inner levels. The backfilling of a subshell near the surface of an atom results in the so-called "transition" series of elements, such as the group from scandium $(Z=21)$ to nickel $(Z=28)$, in which electrons are added to the 3d subshell lying just below the outer 4s level. Backfilling of deeper sites characterizes the "inner transition" elements such as the rare earth (lanthanide) series and the transuranian (actinide) series. In the lanthanide series, electrons are added to the long-vacant 4f subshell; an analogous 5f subshell is later backfilled by the heavier actinide series.

Studies by many investigators have established that the line-like absorption bands in the visible region that are produced by trivalent

lanthanide ions most probably originate in the 4f energy level, and that the 5f level is involved in corresponding effects shown by some actinide ions, notably those of uranium, neptunium and americium (Freed and Leitz, 1949). The exact nature of the changes in the energy states of the electrons that produce the absorption is still incompletely known, but evidence supports the view that transitions largely between two energy states of the same 4f configuration are involved (Yost *et al.*, 1947; Moeller, 1963). This conclusion implies an anomalous or "forbidden" type of transition in which the electron undergoes a change in energy state without leaving the 4f subshell. The transition is made at the expense of a photon of light energy of appropriate wavelength, which is itself absorbed and hence disappears from the spectrum.

Figure 1 shows the general appearance of the absorption spectrum of trivalent ions of the lanthanide elements in the visible region. The figure was prepared from data of Prandtl and Scheiner (1934), and represents the effects produced when light is transmitted through 50 mm of solution containing one-eighth gram atoms per liter of the various rare earths as chlorides. This concentration was selected arbitrarily to show diagnostic bands and might only fortuitously correspond to the concentration of the element in a particular mineral. With concentrations greater than that selected for illustration additional bands may become visible, and wide bands develop by the coalescence of neighboring narrow ones. In lower concentrations only the more prominent bands are visible. The trivalent ions of lanthanum, cerium, gadolinium, ytterbium, and lutetium do not show absorption in the visible region, and in other valence states lanthanide ions show only broad diffuse bands (Yost *et al.*, 1947).

An important feature of the absorption bands with which we are concerned is that their wavelengths, unlike those of emission lines, are not fixed, but may be shifted slightly owing to the effect of neighboring ions on the absorbing ions. This variability is at a minimum in the spectra shown by aqueous solutions of simple salts of the rare earths, so measurements of the wavelength and intensity of absorption bands obtained from such solutions afford the basic pattern of the absorption spectra of the individual elements that produce absorption in minerals. The diagrams shown on Fig. 1 should be sufficient for the recognition of these patterns, but a more detailed representation is given by Prandtl and Scheiner (1934) and is reproduced in Yost *et al.* (1947) and in Pascal (1959). The spectrophotometer curves of rare-earth absorption of Stewart and Kato (1958) are also a useful source of data for the mineralogist.

The absorption spectra exhibited by crystalline substances are more complex than would be expected theoretically from the fundamental transitions involved. The additional line-like bands that appear are

ascribed to splitting of the original bands by the electrical field of the crystal, the degree of splitting being determined in part by the symmetry of the crystal structure (Yost *et al.*, 1947) and in part by the nature of the other ions with which the absorbing ion is associated (Spedding, *in* Spedding and Daane, 1961).

The absorption spectra produced by rare-earth ions in crystalline substances therefore differ somewhat from those produced by the same ions in aqueous solutions, but the general distribution pattern of the absorption bands still remains essentially the same.

The Absorption Spectra in Minerals

Minerals containing the rare-earth elements may conveniently be divided, on the basis of their lanthanide assemblage, into three types. The first type, which contains the greatest number of species showing absorption spectra, consists of minerals in which the cerium group elements predominate. This type, of which monazite and bastnaesite are examples, is characterized by the absorption spectra of neodymium, and to a lesser degree by that of praseodymium. The distribution of the rare earths in nature closely follows the Oddo-Harkins rule whereby the element of even atomic number is more abundant than its odd-numbered neighbors in the periodic table. Neodymium ($Z=60$) is almost invariably in higher concentration in minerals than is praseodymium ($Z=59$), with the result that the absorption spectrum of neodymium is more intense, and indeed may be the only one that can be recognized. In low concentrations neodymium produces only a darkening of the yellow region of the spectrum; in high concentrations the yellow region will contain distinct bands, and other bands will appear in the green and blue regions so that the spectrum may become quite complex as shown by cerium group minerals in Fig. 1.

The second type consists of minerals whose rare-earth assemblage contains dominantly yttrium group elements, the so-called "heavy" rare earths. Xenotime is the only relatively common species of this type that is sufficiently transparent to show absorption effects. Yttrium group minerals are characterized by the absorption bands of erbium and holmium. As may be noted from Fig. 1, the bands produced by these elements lie chiefly in the red, green, and blue-violet regions of the spectrum. Erbium, the even-atomic-numbered member of the pair, is likely to be in greater concentration than holmium, and its absorption bands in the green region at approximately 522 and 525 mμ are the ones most commonly observed. As these bands are essentially coincident with bands due to neodymium, their identity can only be certain in the absence of the characteristic neodymium absorption in the yellow region.

With a diffraction grating microspectroscope, some bands may be seen in the red region. One at approximately 640 mµ is due apparently to holmium, others of longer wavelength to erbium.

Both Wherry (1929, p. 305) and Sandréa (1953, p. 297) ascribe lines in the absorption spectrum of xenotime to samarium; this correlation appears questionable because of the low content of samarium found in xenotime (Semenov and Barinskii, 1958; Jefford, 1962) and the absence of strong absorption bands of the reported wavelengths in the solution spectrum of samarium.

The third type of rare-earth mineral is that containing both cerium and yttrium group elements and lacking extreme selectivity for either group. In such minerals, of which gadolinite is an example, the strong absorption spectrum of neodymium is likely to predominate and prevent the recognition of the weaker erbium bands.

In addition to minerals in which the rare earths are essential constituents, several mineral species may contain these elements as vicarious constituents. Although the concentration of absorbing ions may be low in these minerals, absorption effects can be observed if the minerals are transparent in thick sections. As the substitution involved is commonly that of cerium group elements for calcium, the absorption of neodymium is the one shown by some specimens of apatite, calcite, scheelite, and fluorite. The effect is well demonstrated by crystals of yellow apatite from Durango, Mexico, and by violet-colored zones in calcite from the Tri-State mining district.

Appreciable changes in the absorption spectrum are shown by anisotropic minerals in transmitted polarized light. These changes, first described by Becquerel (1887), may be demonstrated readily by observing the absorption spectrum of a randomly oriented grain of a rare-earth mineral, such as bastnaesite, on the stage of a petrographic microscope. The absorption spectrum is seen to differ in appearance on rotation of the stage. Certain strong bands may become weak and finally disappear, to be replaced in the same area of the spectrum by one or more bands of different wavelength; other bands may remain virtually unchanged. Positions for maximum and minimum intensity for the variable bands shown by uniaxial minerals are coincident with the two optical directions of the crystal; that these differences are quite pronounced will be noted from the ω and ε spectra of bastnaesite and xenotime shown in Fig. 1.

For biaxial crystals three contrasting absorption spectra are possible, as Becqueral (1888) has shown for monazite. With the microspectroscope used by the present writer, no difference could be noted between the spectra of monazite corresponding to the alpha and beta positions; hence these spectra are shown as a single pattern in the figure. In cenosite, how-

ever, three different patterns could be observed (Fig. 1), even though in this mineral, which is opposite in sign to monazite, the beta and gamma spectra are very similar.

Although there is no simple explanation for the effects of orientation on the spectrum, they are probably related basically to the bonding relationships between the absorbing ions and the other ions in the crystal lattice (Sandréa, 1953). Thus with changes in transmission direction, the interaction of the light photon with the absorbing ion takes place under varying fields of influence determined by the configuration of the ions in the lattice, which in turn is related to the crystallographic and optical directions of the crystal.

The extent to which the absorption spectrum of a mineral may be used as a criteria for its identification is problematical. Variations between the position and intensity of lines shown by crystals of the same species from different localities were reported by Wherry (1929) and are evident in the values given by Corin (1931) for the absorption spectra of several xenotime crystals. These variations, which have led to rather confusing data, are understandable in view of the differences that have been found in the distribution of the individual lanthanide elements within a single mineral species (Murata *et al.*, 1957; Semenov and Barinskii, 1958; Jefford, 1962). Thus, not only the concentrations, but also the relative proportions of the absorbing ions, neodymium, praseodymium, erbium, and holmium are subject to change which may preclude a strictly diagnostic absorption pattern for any particular species. This is illustrated in the absorption patterns of two rhabdophane samples, one of the type material from Cornwall, the other cerium-deficient rhabdophane from Salisbury, Connecticut (Hildebrand *et al.*, 1957). The Connecticut material shows the effect of a higher neodymium-praseodymium concentration by broader bands in the yellow region and by appearance of other bands not present in the spectrum of the Cornwall material.

Preliminary work by the writer suggests that structural differences may have a greater effect on the details of the absorption spectrum than do minor differences in composition. This structural influence is indicated by (1) the general similarity between the absorption patterns shown by the minerals bastnaesite and parisite (hexagonal), and (2) the marked difference between their patterns and that of monazite (monoclinic) (Fig. 1).

Further difficulties in correlating absorption spectra of mineral species result from differences in thickness and transparency of the material used, and from the inherent inaccuracy of wavelength measurements made with a microspectroscope.

Application

The absorption spectra of minerals may be observed with instrumentation no more elaborate than a hand spectroscope and a strong source of white light. The light source may be a tungsten filament lamp, a zirconium arc, or even sunlight, though sunlight has the disadvantage of introducing the Fraunhofer absorption lines into the spectrum. For the examination of small mineral grains, such as placer concentrates, a microspectroscope should be used. The instrument can be the conventional type described by Chamot and Mason (1938, p. 179–182) or one made by adapting a hand spectroscope to replace the microscope ocular (Adams, 1954). The instrument currently used by the writer is a hand diffraction spectroscope with 34° dispersion and fitted with a graduated drum. Scale units on the drum are converted to wavelengths in mμ's from a graph prepared by plotting observed scale readings against the wavelength of a number of familiar bright spectral lines. An adapter, made to hold the slit end of the spectroscope, fits into the microscope tube and converts the instrument into a microspectroscope with which wavelength measurements can be made to within ± 1 mμ. When one ocular of a binocular microscope is replaced with the microspectroscope, mineral grains can be conveniently selected and examined using incident light focused as sharply as possible on the subject. Smaller grains are best examined by transmitted light with the microspectroscope fitted to a petrographic microscope. Illumination, which should be unfiltered, is concentrated on the grain by the substage condenser. The writer has found it very convenient to use a spindle stage (Wilcox, 1959) for orienting mineral grains to obtain spectra corresponding with optical directions.

The extent to which light is absorbed is dependent on both the concentration of absorbing ions and the distance which the light travels through the absorbing medium. In the standard thin section this distance is inadequate for absorption to be detected in minerals in which the concentration of absorbing ions is low, but in minerals of high lanthanide content, such as monazite or xenotime, the effect may be noticeable particularly if the mineral grain is of sufficient size to fill virtually the entire field.

Absorption effects are not commonly shown by the rare-earth-bearing multiple oxide minerals, many of which are so dark in color as to be nearly opaque. Wherry (1929, p. 304–306) listed a few exceptions, reporting neodymium-praseodymium absorption in pyrochlore and samarskite, and erbium-samarium absorption in fergusonite and yttrotantalite. The present writer has not investigated many members of this

group, but inconsistent results are expectable in view of the variability in their lanthanide content, permitting neodymium or erbium to predominate in various samples of the same species. This behavior was shown in the absorption spectra of five fergusonite samples, all from different localities. Three of these showed a readily discernible band in the green region (521–526 mμ) due to erbium; one showed this band together with weak neodymium absorption in the yellow region, and another had dominant bands of neodymium. Analyses of fergusonites by Butler and Hall (1960) indicate that erbium is commonly, but not always, in excess over neodymium.

Most multiple oxides and other radioactive rare-earth-bearing species are in a wholly or partially metamict state. In metamict minerals showing absorption, the bands commonly are broad and diffuse, resembling those from solution spectra and reflecting the disorder within the crystal. Heating in air over a Meker burner for one-half hour changes the absorption pattern appreciably, the broad bands being replaced by sharp line-like bands characteristic of crystalline material. Patterns of gadolinite, before and after heating, are shown in Fig. 1. A somewhat similar effect has been observed (Anderson, 1963) on heating metamict zircon, in which the absorption bands are probably due to uranium.

Absorption bands indicative of the rare-earth assemblage of some minerals can be obtained after solution of the minerals in a bead of a suitable flux such as sodium ammonium phosphate (salt of phosphorus) or borax. A bead about 2 mm in diameter is made on a platinum loop and as much as possible of the powdered mineral added without making the bead opaque. The cold bead is then removed from the wire and examined in transmitted light with the microspectroscope. By use of the bead, distinct absorption spectra may be obtained from euxenite and allanite, neither of which otherwise shows appreciable absorption.

The ingenious method devised by Murata and Bastron (1956) for the detection of cerium group minerals can be very useful in conjunction with the microspectroscope. This method involves examining the sample with a short-wave ultraviolet lamp from which the filter has been removed. Visible radiation from this source consists largely of two almost monochromatic components, one in the green region, the other in the yellow. On transmission through certain minerals containing the absorbing ions of the cerium group elements, much of the yellow component is absorbed and the mineral appears emerald green. In practice, a somewhat similar green color may be developed in other minerals that absorb yellow light, consequently final confirmation should be made in white light with the microspectroscope. This use of the ultraviolet lamp is particularly con-

venient for examining placer sands for monazite, or for scanning mineral separates from which rare-earth minerals are to be isolated.

Conclusions

Absorption effects provide the mineralogist with a convenient method for the detection of the rare earths in many different minerals, either in the field or in the laboratory.

By this method, small inconspicuous grains of rare-earth minerals may be found in rock assemblages or heavy-mineral fractions and in many instances their identity as a cerium or ytterium group mineral will be apparent. The technique has the advantage of being nondestructive, and minerals can commonly be tested without removal from their matrix.

Further work may show that in spite of the inherent variability in lanthanide content found in many rare-earth-bearing species, the absorption spectra of some species are sufficiently diagnostic for at least tentative identification.

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