

ABSORPTION OF INFRARED RADIATION BY POWDERED SILICA MINERALS

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ABSTRACT

The absorption of infrared radiation over the range 2.0 to 15.0 microns by pulverized (suspended in Nujol) quartz from various localities and origins was measured in a Beckman Infrared Spectrometer. The characteristic absorption of quartz is compared to those of chalcedony, opal, alpha cristobalite, and fused silica. The effects of crystal structure apparently predominate over those of the silica molecule in the infrared absorption by pulverized silica minerals. Absorption by a single oriented plate of quartz or muscovite is dissimilar in fine detail to that of random powder.

INTRODUCTION

During a study of the absorption of infrared radiation by clay minerals (Keller, 1948) the need for information on the infrared absorption characteristics of the building units of clay minerals (silica tetrahedra, alumina and magnesia octahedra, water and OH groups) was early recognized. Although the absorption of the infrared by water and OH groups has been studied extensively by organic chemists, comparatively fewer measurements have been published on the infrared absorption by quartz, gibbsite, and brucite (see bibliography in "Infrared Spectroscopy" by Barnes, Gore, Liddel and Williams, 1944). No measurements especially on pulverized minerals were reported in the literature, but these are essential for comparisons with those of clays which must be studied in the pulverized form. Consequently before resuming work on clays, the infrared absorption by several of the silica minerals in powdered form was measured. This paper is concerned with their absorption of the infrared spectrum between 2.0 and 15.0 microns in wave length.

It will be recalled that the atoms which comprise molecules do not remain at rest but are continuously in vibration. The frequencies of their vibrations, for example those of O—H, C—O, C=O, C—H, N—H, etc., fall within the range of 10^{13} to 10^{14} cycles per second, which is the same order of magnitude as the frequencies of infrared radiation. Then if molecules of a substance whose vibrations are accompanied by a change of dipole moment are irradiated by a succession of monochromatic bands of infrared, those radiated frequencies which correspond to the intramolecular vibrational frequencies may be absorbed wholly or in part. If the per cent of radiation which is absorbed by a substance is plotted against the incident wave length (or frequency), the ensuing

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graph may be interpreted in terms of the intramolecular vibration. Hence certain molecules may be determined by their characteristic absorption, and may be "finger printed" by characteristic absorption graphs. A high degree of success has been achieved in the analysis of organic chemical compounds by chemists using infrared absorption as an analytical tool. To what extent the technique may be useful in mineralogy and related fields is relatively unexplored.

It is apparent at the outset that a knowledge of the absorption frequency of the molecules under study is essential. For simple or highly symmetrical molecules the approximate absorption frequency can be calculated by the equation:

$$N = \frac{1}{2\pi c} \sqrt{\frac{k}{u}}$$

Where N is the frequency in cm.^{-1} , c is the velocity of light, u is the reduced mass of the vibrating atoms, and k is the force constant which exists between the atoms. The formula has been simplified by reduction of the constants, and typical interatomic characteristics shown by Barnes et al.

A second approach to the derivation of absorption characteristics is empirical. Barnes et al. (p. 14), summarize the situation as follows:

Although the mathematical approach has been of great value when applied to simple or highly symmetrical molecules, most of the information derived from infrared spectra is obtained by the application of the empirical method. This method consists of comparing the spectra of the largest obtainable number of different molecules having a common atomic group. By a process of elimination, it is often possible to find an absorption band whose frequency remains constant throughout the series. The presence, in an unknown, of an absorption at this frequency may reasonably form the basis for a guess that the particular atomic group is present. Confidence in this method can be obtained only by successful applications in a large number of cases.

Although mathematically derived characteristics may be tidier to the scientific purist, an empirical study may produce additional and valuable information. Even the massive lattice vibrations of crystals may absorb radiation (see second paragraph of next quotation). Hence, the empirical approach was used in evaluating the graphs shown in the subject study. A further quotation from Barnes, et al., is pertinent.

It must not be assumed from this discussion that it is, or will be, possible to ascribe every observed absorption to a specific atomic group. Indeed, if this were true it would make more difficult the possibility of differentiating clearly between isomeric compounds. Actually only a few of the observed bands can usually be correlated in this manner. The majority of observed bands arise from normal modes of vibration which are characteristic of the molecule as a whole. These general absorption bands are very sensitive to structural changes, and so furnish us with a "fingerprint" of the molecule. They also make possible the analysis of isomeric mixtures and provide the basis for quantitative analyses of other closely related compounds.

The normal vibrations of a molecule do not account for all of the absorption bands observed in its infrared spectrum. For example, in the far infrared there are absorptions caused by the slower rotations of the molecules or the massive lattice vibrations of crystals. Moreover, throughout the whole infrared region absorptions frequently occur at integral multiples (overtone bands) of the fundamentals, or at frequencies which are equal to the sum or difference (combination bands) of fundamentals. These bands in general absorb very much less strongly than do the fundamentals and consequently must be studied with thicker samples. Since they are so sensitive to the overall molecular structure, they can sometimes be used more for successfully accurate fingerprinting of molecules and for the analysis of mixtures than the fundamental absorptions.

It is evident from the preceding discussion that absorption "peaks" or depressions are tell-tale characteristics of a positive nature of the irradiated compound. High transmission bands may be characteristic of certain compounds, but they constitute evidence of a negative type.

APPARATUS AND TECHNIQUE

The apparatus used in this investigation is a Beckman Model IR-2 infrared spectrometer. Briefly, infrared radiation from a rich source is dispersed by a rock salt prism into a spectrum from which relatively narrow wave length bands are selected and transmitted along a path to a sensitive thermocouple. The intensity of the radiation transmitted is measured with the sample, and without it, in the absorption chamber, and the per cent transmission obtained thereby. High sensitivity of the instrument is achieved by suitable electronic amplification. The current infrared spectrometers embody highly advanced improvements over the apparatus which was available only a few years ago. Many of the older measurements of infrared absorption have been revised.

In this study, from 5 to 10 milligrams of the finely pulverized mineral was stirred and dispersed in 2 drops of Nujol (medicinal mineral oil) which filled the absorption chamber. The latter consists of rock salt plates which are separated by shims of variable and selected thicknesses, and held together by a metal frame. Nujol has been used as a suspending medium because it has a satisfactory viscosity, because its index of refraction lessens the scattering reflectance from the mineral particles, and because its own absorption spectrum is relatively simple. It should be recognized that the indices of refraction of both Nujol and a dispersed mineral may be radically different in the infrared range than they are in the visible spectrum. Regarding the absorption spectrum of the suspending medium, it has been suggested that a single pure substance which could be purified chemically and reproduced closely might be preferred as a suspending medium to one like Nujol which is a complex mixture. Theoretically this is correct, but practically no pure liquid is known which

has a simple absorption spectrum and also possesses the other properties which are desired for the infrared work. Because Nujol is a mixture, many tiny absorption peaks of individual constituents are averaged out, and the curve is flat enough that absorptions occurring within the suspended mineral show up.

About four hours are required to make a run and plot it.

EXPERIMENTAL RESULTS

An absorption graph of Nujol alone in the specimen chamber is shown in Fig. 1. Along the base of the abscissa is plotted the wave length of the

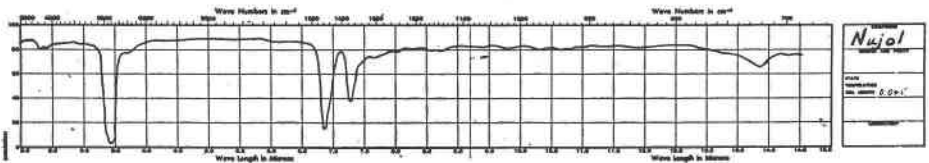


FIG. 1. Infrared spectrogram of Nujol.

radiation in microns, 2 to 15 microns at 0.5 micron intervals, and along the top is the corresponding frequency in wave numbers or reciprocal centimeter. Transmission of radiation in per cent is plotted on the ordinate. Nujol is relatively transparent to most infrared radiation, transmitting from 80 to 90 per cent over most of the spectrum. A light absorption occurs at approximately 2.3 and 2.4 microns, and almost complete absorption (opacity) for a band at about 3.43 microns in wave length. Lesser absorption occurs from 3.6 to 3.72 microns and pronounced absorption at 6.86 and 7.28 microns. Numerous slight absorptions extend over wave lengths to about 11.0 microns and another prominent peak occurs at 13.86 microns. This "background" of absorption is unavoidably present in every measurement where a mineral was immersed in Nujol. It may be "subtracted" from the mineral graph to obtain the absorption characteristics of the mineral.

QUARTZ

In Fig. 2 are shown representative absorption spectra of varieties of quartz which were finely pulverized and suspended in Nujol. Specimen No. 86 is of a clear crystal of quartz from Brazil. Omitting the absorption peaks due to Nujol, it is observed that quartz powder absorbs infrared radiation at 5.0 and 5.3 microns, and with lesser intensity at 5.93 and 6.21 microns. The second decimal figures of the latter two absorptions are taken from another measurement. A gradual increase in absorption is shown from about 4.5 microns to about 6.5 microns. Upward in wave

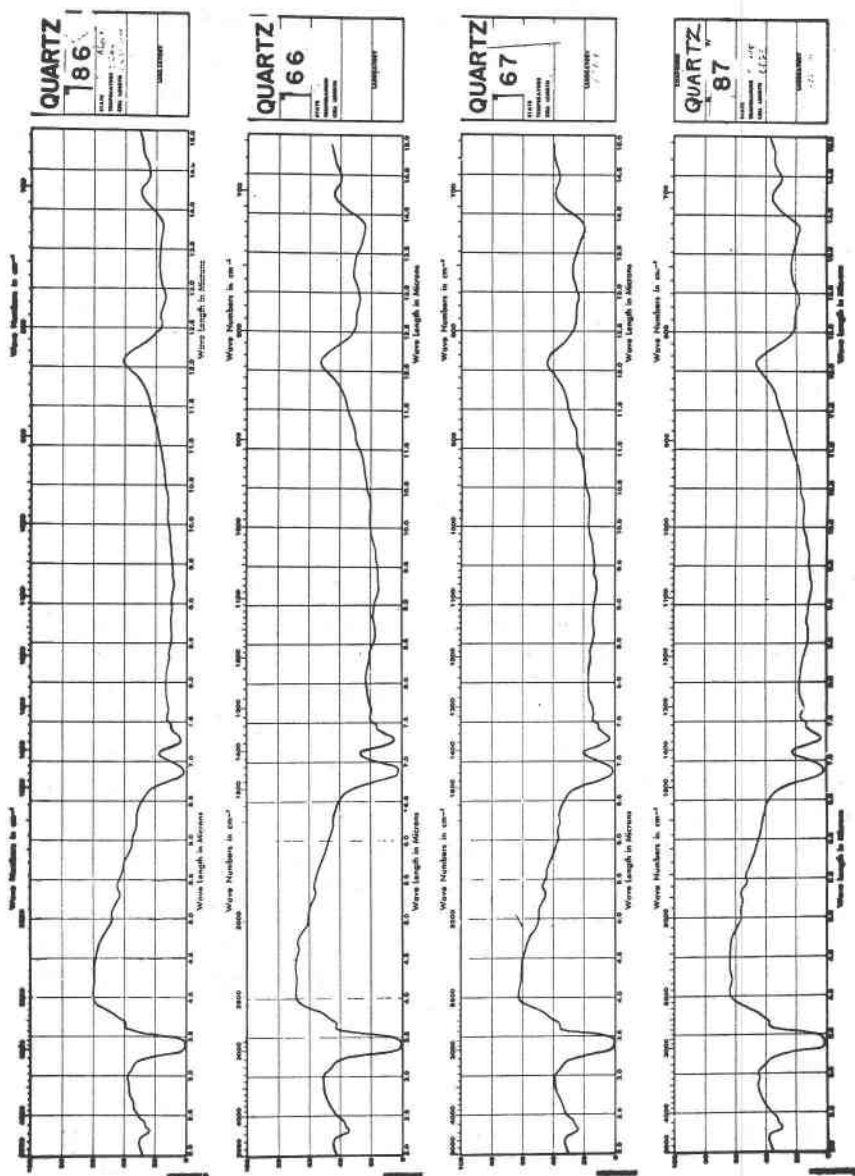


Fig. 2. Infrared spectrograms of quartz.

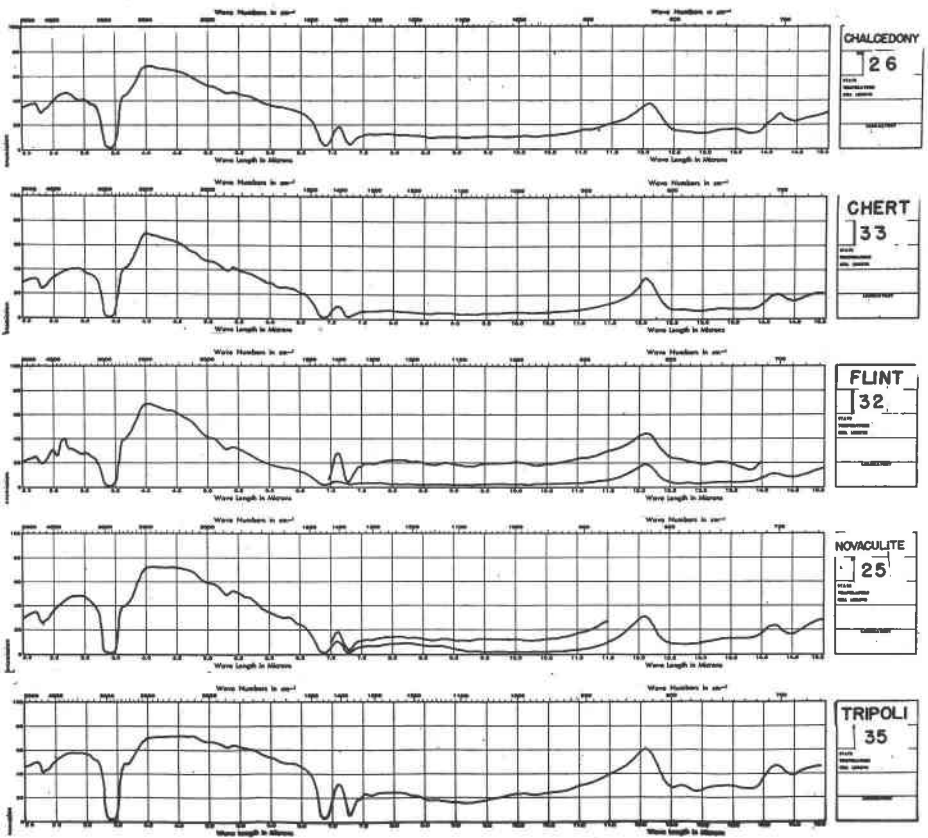


FIG. 3. Infrared spectrograms of chalcedony, chert, flint, novaculite, and tripoli.

length from the Nujol absorption at 7.9 microns the quartz powder absorbs uniformly strongly until about 9.9 microns where a gradual decrease in absorption begins and culminates at a peak of high transmission at about 12.08 microns. The transmission peak (at 12.08) is a negative measure, but it occurs so consistently with quartz powder that it has some secondary value in recognizing a quartz curve. Other absorptions occur at about 12.54 and 12.9 microns, and more strongly at 14.46 microns. The 14.46 micron absorption band appears to be highly characteristic of extended quartz-like structure. Its absence in alpha-critobalite and fused silica, which are discussed later, indicates that the absorption is a function of the quartz-type crystal structure.

Specimen No. 66, pulverized quartz from coarse-grained Missouri granite shows a graph similar to No. 86, plus an additional slight absorp-

tion at 4.64 microns. Metamorphic quartz from the Baraboo quartzite, No. 67, closely parallels the Brazil quartz. The familiar rose quartz from Custer, South Dakota, No. 87, shows absorption similar to the others previously figured.

CHALCEDONY, CHERT AND TRIPOLI

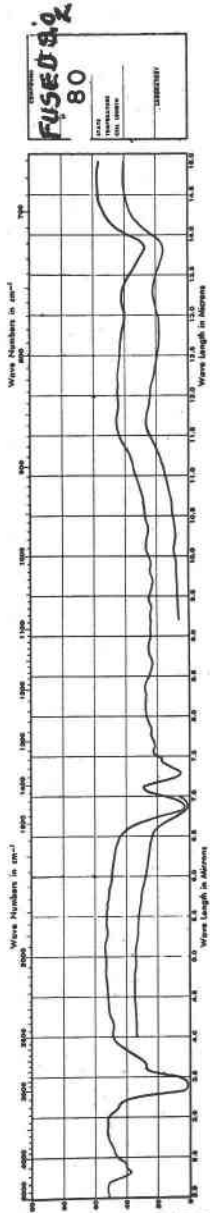
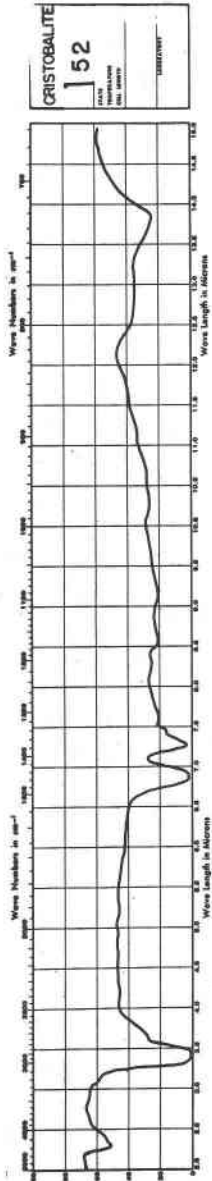
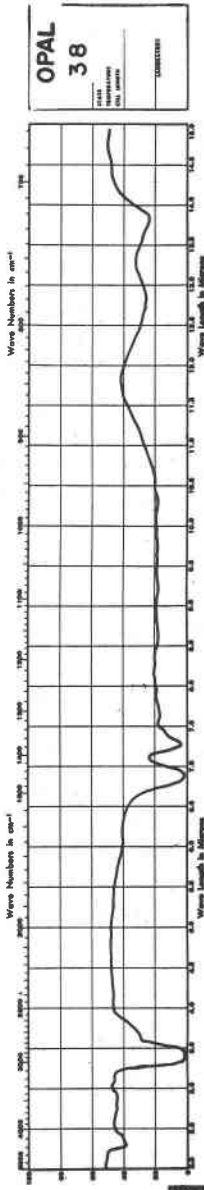
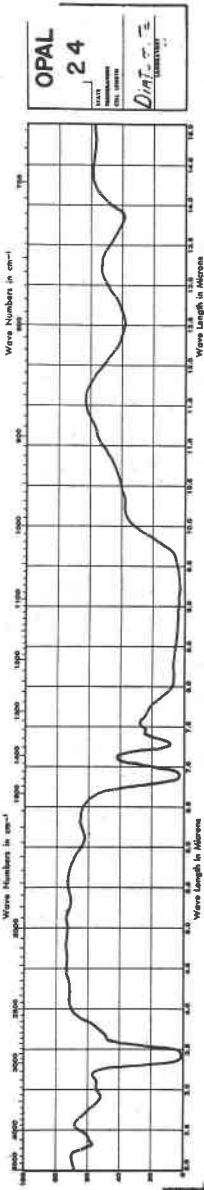
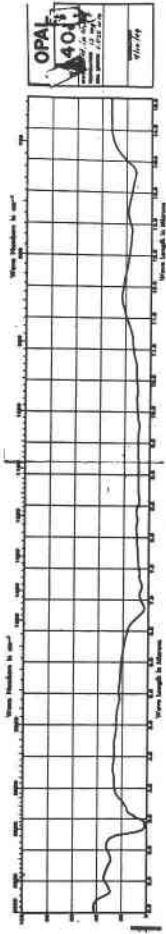
A specimen of chalcedony, typically fibrous and waxy when powdered, gives the absorption graph No. 26. The curve is smoother than those of quartz and the peaks are slightly subdued. An x -ray diffraction pattern run on this sample and compared with a pattern run on Arkansas crystal quartz, No. 54, showed peaks of slightly lower intensity and more subdued vertices than those of quartz.

Crystalline chert (pulverized), which may be composed of varying amounts of microcrystalline quartz, chalcedony and opal, is represented by absorption spectra No. 33, 32, and 25, which are respectively of chert from the Mississippian limestone near Seneca, Missouri (tripoli region), of very dark gray flint from the chalk at Dover, England, and of translucent novaculite from a hone stone quarry near Hot Springs, Arkansas. All three crystalline cherts give typical chalcedony-quartz absorption patterns. No. 32 shows extra absorption at 2.56, 2.75 and 2.95 microns. The last two are probably due to OH groups. Tripoli, No. 35, which occurs in the Seneca, Missouri, tripoli producing region has about the same absorption characteristics as the chert of that region. No. 33.

OPAL

Opal collected from different sources shows somewhat different absorptions. A specimen of water-clear hyalite opal, No. 40, from Guanaquato, Mexico, exhibits relatively featureless differential absorption. Some water in OH absorption is shown by the small peaks at 2.7 microns ("unbound OH") and at 2.86 microns ("bound OH"). At longer wave lengths there is no particularly characteristic absorption. Opal No. 40 has low birefringence and shows weak undulatory extinction. The index of refraction varies a little, ranging from 1.456 to 1.458. The water lost upon calcination (actually total ignition loss) was 2.7 per cent.

Relative to the nature of "unbound and bound OH," it may be pertinent to recall here that chemists have found OH groups absorb at different wave lengths between 2.7 and 3.1 microns depending upon the degree of hydrogen bonding of these groups with each other or with other O atoms in the lattice. Where OH groups are situated independently, monomeric, within a crystal lattice the absorption is at about 2.75 microns (2.72 in the kaolin group). Where two or more OH groups are sufficiently close together, the hydrogen of the OH groups may assume a



more or less fixed position between two oxygen atoms with the formation of a resonating bond between both oxygen atoms simultaneously, the so-called hydrogen bond. The dimeric groups absorb at about 2.85 microns and polymeric groups at about 2.95 microns. Free water, H_2O , absorbs in the 6.0 to 6.1 micron band as shown in the spectrum of opal No. 24. Preliminary work on clays and other hydrated minerals indicates that the nature of their hydration merits additional research using infrared absorption. This work is in progress by the writers.

Diatomite (opal) from a Tertiary lake deposit near Quincy, Washington, gave an absorption curve shown in No. 24. The presence of bonded OH is indicated by absorption at 2.92 microns and free water at 6.1 microns. Strong absorption occurs from 8.0 to 9.6 microns, with weaker absorption from 10.2 to 10.4 microns and in a broad peak at 12.53 microns. High transmission occurs from 11.5 to 11.64 microns. Because this absorption curve differed so much from the other silica curves a check was re-run with duplicate results. The index of refraction of opal No. 24 is about 1.418. Total loss on ignition was 15.3 per cent.

A third variety of opal, opaline chert from the Monterrey formation of California,³ absorbed infrared as shown in No. 38.

Again the absorption by OH was scanty. Strong absorption extends from 7.5 to 10.6 microns, followed by high transmission at 11.84 and a broad absorption peak centering at 12.84 microns. Obviously the several opal spectrograms are noticeably different. The absorption by the water in two opals is weaker than was expected. Taliaferro found an unexpected relationship between water in opal and densities and indices of refraction of the latter. Further research on the role of water in opal and its internal architecture is being planned. X-ray diffraction patterns of the diatomite and hyalite showed no well defined crystal structure.

Obviously the lattice organization of anhydrous silica in quartz and in crystalline chert⁴ exerts a mass crystal effect different from the water-silica system in opal.

CRISTOBALITE AND FUSED SILICA

Artificially prepared cristobalite,⁵ No. 52, deviated noticeable from quartz in its infrared absorption spectrum. In general, cristobalite lacks

³ Furnished through the courtesy of M. N. Bramlette. Sample came from specimen shown in Plate 7B in *U.S.G.S. Prof. Paper 212*, "Monterrey formation of California and origin of its siliceous rocks."

⁴ A chert from the Franciscan formation of California (furnished by M. N. Bramlette) showed typical quartz absorption, as did the cherts previously described.

⁵ Prepared through the courtesy of the A. P. Green Fire Brick Company, Mexico, Missouri. Arkansas crystal quartz was heated in a brick testing furnace and held at approxi-

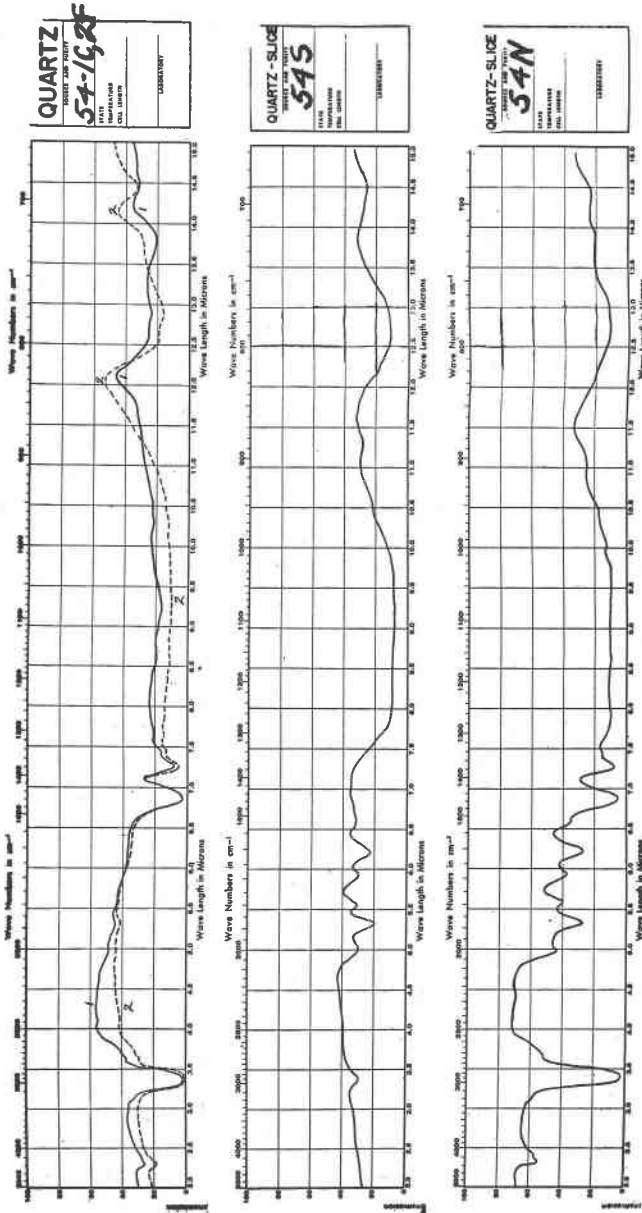


FIG. 5. Infrared spectrophotograms of coarse pulverized quartz, 54-1C, fine pulverized quartz, 54-2F, quartz slice in air, 54S, and the quartz slice immersed in Nujol, 54 N. Arkansas quartz.

the increasing absorption in the 4.0 to 6.5 micron range, is less absorbent of wave lengths in the range 8 to 11 microns, and specifically lacks the absorption peaks which quartz shows at 12.54, 12.9, and 14.46 microns.

The differences in absorption must be a function of crystal structure rather than characteristics of the silica molecule.

The absorption of pulverized fused silica⁶ is shown in No. 80. A partial re-run of the sample for check purposes is plotted on the same graph. The absorption by fused silica resembles that of hyalite opal, but is probably more pronounced in the region 7.5 to 10.5 microns. Presumably the similar random structure of both accounts for their similar absorptions.

EFFECT OF PARTICLE SIZE

If the diameter of essentially all the particles and the wave length of the radiation were the same size the result would be strong selective scattering of this radiation. Radiation of other wave lengths would be scattered to a smaller extent. The per cent transmission would thus be lower wherever wave length and particle size are similar, giving rise to apparent absorption maxima qualitatively similar to those characteristic of the various atomic groupings present in the sample. A broad range of particle sizes in the sample would cause only a very broad general scattering, perhaps extending for many microns. This is more likely to be the case for the present samples, where a wide range of sizes exists. Nevertheless it was judged advisable to check the influence of particle size in several ways.

Sodium chloride is quite transparent to infrared radiation between 2 and 15 microns. A sample of it was powdered in a manner similar to that of the silica minerals and its absorption measured in this region. It showed no evidence of selective scattering.

A portion of No. 54, Arkansas crystal quartz, was separated by sieving and washing in alcohol into two size fractions, predominating in sizes ranging from 30 to 75 microns, 54-1C, and about 15 microns in diameter, 54-2F. Their absorption spectrograms show some differences, but these are in degree and not in kind. In the absence of any drastic differences in the spectrograms due to variation in particle size, this factor appears to have only secondary importance in affecting measurements.

mately 1650° C. for five hours and allowed to cool slowly (the reheat test cycle for super-duty refractories), this being repeated for a total of 6 cycles. An *x*-ray diffraction pattern gave the lines of alpha cristobalite. The indices of refraction of the material are: omega, 1.486; epsilon, 1.484.

⁶ Donated by the A. P. Green Fire Brick Company. The index of refraction of this fused silica ranges from 1.458 to 1.461. An *x*-ray diffraction pattern showed no lines indicative of crystalline structure.

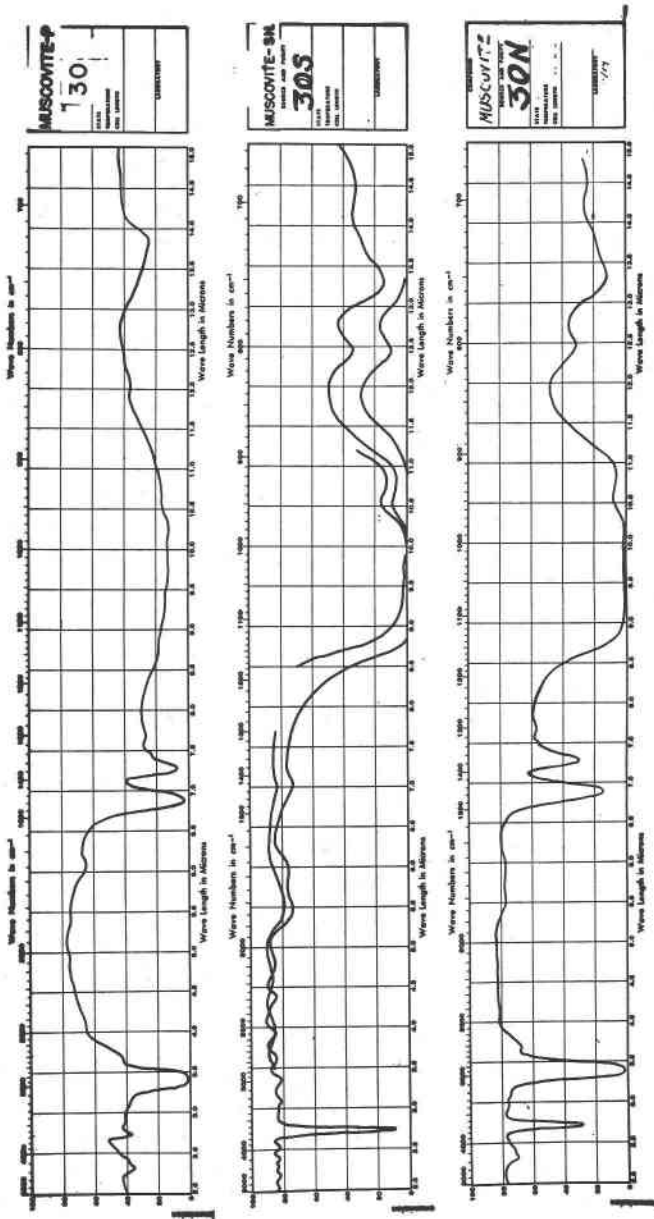


FIG. 6. Infrared spectrograms of pulverized muscovite in Nujol, No. 3, sheet muscovite in air, No. 30 S, and the same sheet immersed in Nujol, No. 30 N. Muscovite from Jackson, N. Car.

Since this paper went to press, the Carter Oil Company laboratory at Tulsa has shown notably sharper resolution in *IR* spectrograms of mineral particles whose diameter is smaller than the wave length of the incident radiation. (Personal communication, Mr. Parke Dickey, October, 1949).

POWDER AND SINGLE CRYSTAL MEASUREMENTS

Conventionally, infrared absorptions have been measured on single-piece solids, as on glass plates or on slices of large crystals. However, powders were measured in this study to provide a basis of comparison with clays which are being measured and which obviously are not available in large crystals. In order to relate the measurements between powders and plates two minerals, quartz and muscovite, were tested in both forms. As an extra control the mineral slices were re-measured while immersed in Nujol. Curves 54-1C and 54-2F which were described immediately above; 54-S, a slice of Arkansas crystal quartz cut with the *c*-axis lying in the plane of the slice; and 54-N, which is 54-S immersed in Nujol, show the variations on material all coming from the same crystal source. (Fig. 5)

Considerable deviation in details is found between powder and wafer absorption. In 54-S, the dry slice, and in 54-N, the immersed slice, details of absorption between 4.7 and 6.6 microns are shown which are much subdued in the powder. The characteristic high transmission at about 12.1 microns for the powder is not present in the slices which show a gentler transmission peak at 11.5 to 11.6 microns. Powder and slices show common absorption in the 12.7 to 12.9 micron region. The 13.8 micron absorption of the powder is not found with the slices.

A parallel series was run with muscovite, Fig. 6, using a cleavage flake of mica for the mineral slice, 30-S. Curves 30 and 30-N show the result run on the powder and on the slice immersed in Nujol, respectively. The high absorption at 2.72 to 2.74 microns is due to the unbound OH group. The strong absorption in the region 9.0 to 11.0 microns and at 12.48 and 13.3 microns with the sheet mica is subdued in the powder. We are uncertain whether the pronounced details of absorption which are shown in the single mineral plate, as contrasted to the powder, are due primarily to the physical difference in size, or to the single orientation of the slice and random orientation of the powder. Certainly the polarizing and crystallographic properties of the mineral crystal should play some part in the absorption.

On the basis of the differences in infrared absorption shown by slice and powder of quartz and muscovite, it is concluded that fine details of

the infrared absorption characteristics of the two forms of minerals cannot be predicted one from the other.

SUMMARY

Pulverized quartz absorbs characteristically certain bands of radiation in the infrared range of 2.0 to 15.0 microns. Igneous, vein, sedimentary, and metamorphosed quartz absorb similarly. Specific absorptions occur at 5.0, 5.3, 5.93 and 6.21 microns. High, fairly uniform absorption occurs from about 7.9 to 9.9 microns from where it decreases with longer wave lengths until it reaches a minimum at about 12.08 microns. At still longer wave lengths it absorbs at 12.54, 12.9 microns, and more intensely at 14.46 microns.

Chalcedony absorption curves are slightly more subdued than those of quartz.

Hyalite opal from Guanajuato, Mexico, shows almost no differential absorption. Diatomite from Quincy, Washington, and opaline chert from the Monterrey formation of California show some absorption bands which suggest departures from hyalite. Fused silica absorbs much like opal. Artificially prepared alpha cristobalite shows fewer absorption bands than does quartz. It is concluded from the differences in infrared absorption by the different silica minerals that the absorption must be a function of crystal structure rather than of the silica molecule.

All of the observations summarized above were made on pulverized materials suspended in Nujol. Variation in particle size distribution from less than 15 to about 75 microns in cross section affects infrared absorption in degree, but not in kind.

Comparison measurements made on plates of quartz and muscovite mounted dry, also immersed in Nujol, and in powder form suspended in Nujol, show notably more detail on the plates than on the powder. Results cannot be predicted for one form from the other. Probably the differences should be attributed to differences in mineral orientation.

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REFERENCES

- BARNES, R., BOWLING, GORE, ROBERT C., LIDDEL, URNER, AND WILLIAMS, VAN ZANDT, Infrared spectroscopy, Industrial applications and bibliography, Reinhold Pub. Co. (1944).
- KELLER, W. D., Absorption of infrared radiation by clay minerals (abstract): *Bull. Geol. Soc. Am.*, **59**, 1332 (1948).
- TALIAFERRO, N. L., Some properties of opal: *Am. Jour. Sci.*, 5th ser., **30**, No. 179, 450-474 (1935).