

blende and the anthophyllite-cummingtonite series); replacement of OH^- by O^{2-} (the oxy-hornblende reaction) or the presence of an atomic substitution not considered in Sundius's scheme. The relative significance of these possibilities together with a way of recognizing them will be considered in a later publication. The diagram is presented at this time because of the hope that it will prove of help (especially to students) in visualizing the broad compositional variations of amphiboles.

The assistance obtained from a National Science Foundation grant is gratefully acknowledged.

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THE AMERICAN MINERALOGIST, VOL. 44, MARCH-APRIL, 1959

THE NEAR INFRARED SPECTRUM OF BERYL

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Several references to the Raman and infrared absorption bands of beryl in the 2.7 micron (3700 cm.^{-1}) region have appeared in the literature during the past twenty-six years. Nisi (1) observed a Raman band at 3607 cm.^{-1} using as a sample a clear, light green, hexagonal prism of beryl. No attempt was made to account for this frequency. Later Matossi and Bronder (2) reported the infrared spectrum of a sample of aquamarine taken with an instrument of low resolving power. Two strong bands were observed near 3600 and 3700 cm.^{-1} . In addition weaker clusters of bands were observed in the 5000 and 7000 cm.^{-1} regions. Matossi and Bronder felt that these bands were too intense to be due to a water impurity in the beryl, arguing that a 1 per cent impurity would be possible, but that the intensity of the bands would indicate a 5 to 10 per cent impurity. They suggested that the bands could be due to a hydroxyl impurity and to multiple combinations of silicate frequencies.

Lyon and Kinsey (3) studied a narrow region of the spectrum in the vicinity of 3700 cm.^{-1} under higher resolution using a grating spectrometer and a sample of beryl 0.2 mm. thick. They found two intense bands whose centers were estimated to be 3598 and 3690 cm.^{-1} plus a weak shoulder on the high frequency side of the second band. They identified these bands with envelopes of certain rotation branches of the sym-

metric and antisymmetric stretching frequencies of the water molecule and accounted for the freedom required for rotation by means of an interesting hypothesis. They suggested that the water occurred as a monomeric impurity in the large open channels of the beryl crystal.

Eitel (4) also refers to the possible occurrence in these channels of molecular impurities. Among the impurities he names water and several alkali hydroxides.

Wilmarth, Warner, Hosler and Cameron (5) state that "alkalis and alkaline earths, principally soda, constitute as much as 4 per cent of many beryls, and constitutional water up to 2.7 per cent." These authors suggest the possibility of the occurrence of hydroxyl ions substituted for oxygens in the silicate rings of the crystal itself.

The articles referred to above suggest three possible explanations for the near infrared absorption bands of beryl. The bands may be (1) due to water molecules either free or weakly bound in the channels, (2) due to alkali or alkaline earth hydroxide molecules in the channels, or (3) due to hydroxyl groups incorporated into the beryl structure through substitution for oxygen.

Because of their frequencies there seems to be little doubt but that the fundamentals observed in the 3700 cm.^{-1} region arise from OH stretching vibrations associated with hydroxyl or water impurities. The work to be reported here represents an attempt to see what further information could be obtained from a purely spectroscopic study of beryl. Several different samples of beryl were studied to determine whether the impurities varied from sample to sample. Polarized radiation was employed to determine the degree of orientation of the impurities relative to the crystallographic axes. And all spectra were taken under high resolution over a much wider region than that observed by Lyon and Kinsey.

The grating spectrometer used in this study was the same one used by Lyon and Kinsey (3) but with its range extended and modified to operate with an AC detection system. A selenium film polarizer was mounted just in front of the sample at the exit slit of the instrument. The spectral slit width of the spectrometer varied from 3 cm.^{-1} at 3 microns to about 10 cm.^{-1} at 1 micron. All band centers quoted in this article are believed to be accurate to within 3 cm.^{-1} .

The beryl samples were selected from gem lots provided by the O'Brien Lapidary Equipment Company of Los Angeles. These lots were labeled only as to national origin. Sample 1 was a clear, medium blue, hexagonal prism 15 mm. long and 5 mm. in diameter from Madagascar. Samples 2, 3 and 4 were all rough fragments from Brazil and were respectively pale blue, medium pink and colorless. All samples were clear except Sample 2 which had fibrous inclusions.

Sample plates were cut from each specimen of beryl using standard faceting techniques and equipment. These plates were thinned in steps with absorption spectra being taken at each step.

The polarized absorption spectra obtained from the four pieces of beryl are shown in Fig. 1. Certain facts are immediately evident from the spectra. The frequencies of absorption are not the same in all samples. For example in the spectrum of Sample 3 no absorption bands agree with the bands of any other sample. On the other hand, where identical absorption bands do occur in different samples their intensities sometimes differ strikingly for similar sample thicknesses. And the relative intensities of the bands within a spectrum sometimes differ from sample to sample. These effects indicate that more than one type of molecular impurity can occur in beryl and that the concentration of each type of impurity can vary considerably.

Another obvious fact is the high degree of orientation of the absorbing entities relative to the c axis of the crystal as indicated by the strong dichroism of the bands. This would seem to rule out the occurrence of free molecular rotation within the crystal.

Let us consider for the moment the spectra of Samples 1, 2 and 4, since these show distinct similarities to one another while the spectrum of Sample 3 is completely dissimilar. The three strongest bands observed in these samples are centered at 3598 and 3700 cm^{-1} (both polarized parallel to the c axis) and at 3663 cm^{-1} (polarized perpendicular to the c axis). The first two bands are apparently those observed by Matossi and Bronder and by Lyon and Kinsey. The two stretching fundamentals of the water molecule should be polarized at right angles to one another. Thus the first two bands mentioned above cannot both be associated with the two water stretching vibrations. As further evidence for this statement we note that in Sample 1 the band at 3700 cm^{-1} is distinctly stronger than the band at 3598 cm^{-1} while in Sample 4 the band at 3598 cm^{-1} is the stronger of the two. It would appear that these two bands arise from entirely different impurities.

We might however relate the antisymmetric stretching frequency of the water molecule to the 3700 cm^{-1} band and the symmetric stretching frequency to the 3663 cm^{-1} band. First and second overtones of these two fundamentals appear in the 7100 and 10,400 cm^{-1} regions. In addition strong combinations of these fundamentals and overtones with a frequency of 1540 to 1600 cm^{-1} (or a multiple thereof) occur, giving rise to bands in the 5300, 6800 and 8700 cm^{-1} regions. The water molecule possesses a third (bending) mode of vibration, the fundamental frequency of which falls in the vicinity of 1600 cm^{-1} . The appearance of strong combinations involving such a frequency is probably the best evidence that it is water which gives rise to the 3663 and 3700 cm^{-1} fundamentals.

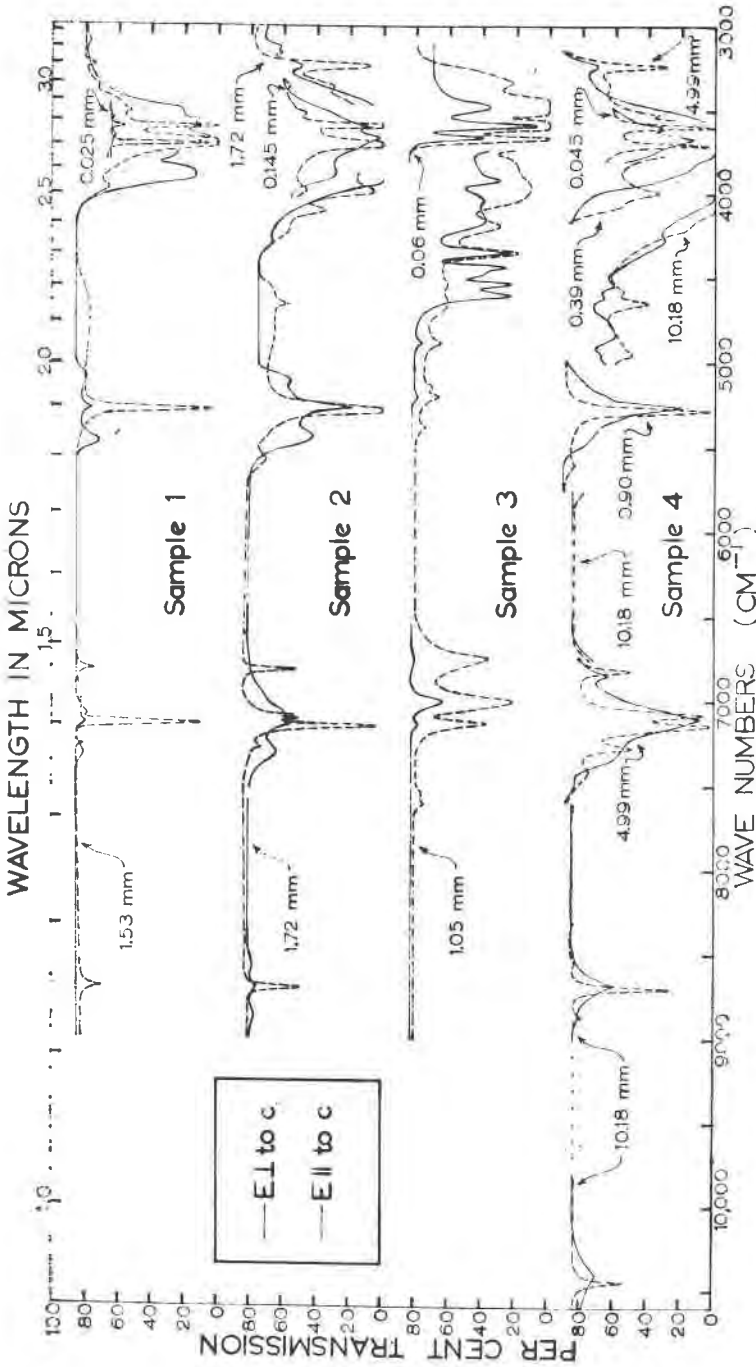


FIG. 1. Absorption spectra of four different samples of beryl.

The high frequency of these fundamentals and the narrowness of the bands would seem to indicate that the water molecules are monomeric and at most only weakly bound to the lattice. On the other hand, the strong polarization of the bands would imply that the water molecules are strongly oriented with their H—H distances parallel to the c axis of the crystal. It seems most likely then that the water molecules occur singly in the channels with the above-mentioned orientation.

The fundamental at 3598 cm.^{-1} is also polarized parallel to the c axis of the crystal. This band comes the nearest of any of the strong fundamentals to agreeing with the Raman band observed by Nisi at 3607 cm.^{-1} . The strong orientation of this band, its high frequency and narrowness and its apparent independence of other bands in this region combine to suggest that it belongs to an alkali or alkaline earth hydroxide molecule lying lengthwise in the beryl channels.

Numerous weaker bands are found in the regions immediately adjoining the strong fundamentals mentioned above. Some of these bands appear to be low frequency combinations with the fundamentals. For example at 170 cm.^{-1} the frequency appears to combine to produce both summation and difference bands with the 3700 cm.^{-1} fundamental and with its overtones and combinations. This 170 cm.^{-1} frequency could correspond to a weakly hindered rotation of the water molecule.

On the other hand many of the weaker bands seem to be unrelated to any of the fundamentals previously mentioned. These bands may be fundamentals in their own right arising from weaker impurities, or they may be combinations and overtones of lower, unobserved vibration frequencies.

The spectrum of Sample 3 is very different from the spectra of the other samples. There are three fundamentals, all imperfectly polarized but strongest parallel to the c axis, with centers at 3479 , 3583 and 3653 cm.^{-1} . First overtones of these fundamentals are found at 6745 , 6997 and 7138 cm.^{-1} . A complex set of weaker absorption bands appears on the high frequency side of the three fundamentals. The fundamentals of Sample 3 show less dichroism and are somewhat broader than the fundamentals of Samples 1, 2 and 4. Thus if any of the samples of beryl contain bound hydroxyl groups substituting for oxygen, Sample 3 is the most likely prospect.

It is clear that this study has not solved the entire problem. In order to relate the spectra to specific impurities it would be best to correlate the spectroscopic study with a program of controlled synthesis of beryl. The idea of such a synthesis with controlled impurities is appealing from the standpoint of the physicist or chemist since it contains the possibility of isolating and orienting for spectroscopic study a variety of small

molecules in the beryl channels. On the other hand, assuming that a detailed identification of absorption bands can eventually be made, the infrared spectrum of beryl should be useful to the mineralogist in the identification of impurities and in the determination of their concentrations.

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THE AMERICAN MINERALOGIST, VOL. 44, MARCH-APRIL, 1959

THE SYNTHESIS OF UVAROVITE

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As part of another investigation, we recently attempted the preparation of the garnet $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$. The direct synthesis of this garnet has been reported by Hummel (1) whose results we have corroborated only in part.

The largest amount of garnet phase was produced by heating the pressed mixture of reactants ($3\text{CaO} + \text{Cr}_2\text{O}_3 + 3\text{SiO}_2$) at 1400°C . for 2 hrs. The extra phases present were $\alpha\text{-CaSiO}_3$ and Cr_2O_3 . Three samples heated at 1200°C . for 47, 125 and 192 hrs. gave only very small amounts of garnet phase and large amounts of the $\alpha\text{-CaSiO}_3$ and Cr_2O_3 .

The powder data for the garnet phase are given in Table 1. The lattice constant of the synthetic uvarovite is $12.00 \pm 0.02 \text{ \AA}$.

Menzer (2) has reported a lattice constant of $11.974 \pm 0.003 \text{ \AA}$ for an uvarovite specimen from Sysmä, Finland. The chemical analysis of this sample indicated the presence of 1.93% Al_2O_3 , 0.41% Fe_2O_3 and 0.50% MgO impurities. A sample from Bissersk in the Urals reported by Menzer had a lattice constant of $11.969 \pm 0.013 \text{ \AA}$ but larger amounts of Al_2O_3 (5.8%) and MgO ($\sim 1.3\%$). This sample also had larger amounts of iron, probably 2.0% in terms of Fe_2O_3 , than did the sample from Finland.

We have obtained two samples of natural uvarovite of which the lattice constants have been measured but no chemical analyses made. One, obtained from Ward's Natural Science Establishment, originally found in Orford, Quebec, was crystallized on tremolite. The crystals were