THE AMERICAN MINERALOGIST, VOL. 53, MAY-JUNE, 1968

AN EXAMINATION OF RED BERYL FROM UTAH

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ABSTRACT

The color of red beryl from Topaz Mountain, Thomas Range, Utah, is due to several absorptions peaking in the 0.48 to 0.55 μ region and is probably caused by Mn^{2+}. The lattice constants are $a=9.23637\pm4$ Å, $c=9.1972\pm1$ Å. The unusual complete absence of water is probably due to growth at a very low pressure and high temperature.

INTRODUCTION

At Topaz Mountain, Thomas Range, Utah, a red beryl[1,2] occurs in gas cavities (lithophysae) in rhyolite (Hillebrand, 1905; Montgomery, 1934, 1935; Palache, 1934). The color of this beryl has been termed rich raspberry red (Hillebrand, 1905), cherry red (Montgomery, 1934) and rose red (Palache, 1934). The beryl is intergrown with quartz, topaz, and bixbyite, other associated minerals being spessartite garnet, tridymite, hematite, ilmenite, and pseudo-brookite; calcite, fluorite, and hyalite are late minerals.

The occurrence of beryl in a lava is most unusual and an exeptionally high temperature of formation has been inferred. There appears to be no discussion of the water content or of the origin of the color of this beryl other than the Hillebrand (1905) suggestion that manganese causes the color; he also states that an approximate analysis confirmed beryl and indicated the presence of an appreciable amount of manganese, but gave no quantitative data.

EXPERIMENTAL

Samples were obtained from the Smithsonian Institution and Harvard University collections by the courtesy of J. S. White, Jr., and C. Frondel, respectively.

The crystals are flat hexagonal prisms, up to 7 mm across and 4 mm thick. The prism faces were determined to be {100} by X-ray diffraction. The raspberry red color is not uniform, with lighter regions adjacent to the basal faces. In thin sections the color resembles that of morganite. Many tiny included quartz grains occur, particularly at the centers of the prisms, and there are occasional attached topaz grains and small dark pseudo-brookite needles.

A Debye-Scherer diffraction pattern of a crushed specimen was taken with filtered Cr $K\alpha$ radiation in a 114.6 mm. diameter camera. This showed only lines due to beryl and quartz, confirming the identity. Indexing of the beryl lines gave the unit cell parameters $a=9.24_2$ Å, $c=9.19_4$ Å; the accompanying quartz indexed with $a=4.91_5$ Å, $c=5.40_0$ Å. Precision

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[1] A specimen of similar appearance in the Harvard collection is said to have come from an unknown locality in Durango, Mexico (Montgomery, 1967), but the similarities in color banding, quartz intergrowth, *etc.*, make it unlikely that a second locality is involved.

[2] The name bixbite (Eppler, 1912) has been suggested for this variety of beryl, but does not seem to be in common usage.

measurements (Barns, 1967) using reflections from the faces of a large crystal gave $a = 9.23637 \pm 0.00004$ Å, $c = 9.1972 \pm 0.0001$ Å, $c/a = 0.9958$, and $V = 679.50$ Å^3.

Since only a limited amount of material was available and the regions of clear red beryl free of quartz were small, a major component analysis could not be attempted. Since the density is so close to that of quartz, it was necessary to use hand picking of crushed specimens to provide clear red material for the qualitative and quantitative emission spectroscopic analyses shown in Table 1. The alkali content is quite low, as had been inferred from the low density of 2.67 g/cm^3 and the refractive indexes of $\omega = 1.576$ and $\epsilon = 1.570$ (Palache, 1934).

Slices were cut parallel to prism faces and examined with polarized radiation as previously described (Wood and Nassau, 1967, 1968). The transmission curves obtained are shown in Figure 1.

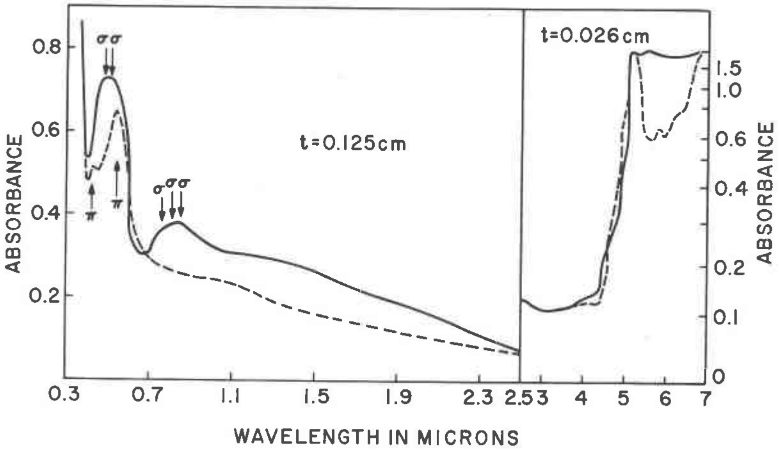

FIG. 1. The absorption spectrum of red beryl from Utah. Full curve ordinary ray (location of absorption peaks marked "σ"), dashed curve extraordinary ray (peaks marked "π").

DISCUSSION

Absence of water. The region of optical transmission of Figure 1 from about 0.3 to 7 μ is the same as that observed in the natural and synthetic beryls previously examined (Wood and Nassau, 1967, 1968). The striking difference is the complete lack of any molecular impurity absorption lines in the region above 1 micron. Every one of the 62 naturally occurring beryls in our previous study (Wood and Nassau, 1968) showed pronounced water absorptions, as do all published natural beryl spectra; analyses usually indicate 0.3 to 3 percent H_2O. Based on an absorption coefficient of about 200 cm^{-1} for the 3 μ water line, it is possible to place an upper limit of 0.002 percent on the water present in our sample. From the absence of its absorption band, carbon dioxide is also indicated to be absent (less than 0.002%). This lack of molecular species also contributes to the low density.

Several possible factors may have contributed to produce the absence of water in this beryl and the inferred low water activity (concentration) in the growth medium. In view of the formation in rhyolite close to the surface, the hydrothermal (pneumatolytic) growth must have occurred at a rather low pressure. Growth is still plausible in view of the very high temperature suggested by Montgomery (pers. comm.). The presence of tridymite as an associated mineral (Frondel, pers. comm.) is indicative of a formation temperature between 870° and 1470°C, if growth occurred under equilibrium conditions (Frondel, 1962). An additional factor may have been the presence of sufficient HF in the growth medium to further dilute the water present. In this connection it may be noted that the topaz associated with the beryl has unusually high fluorine (20.37%) and low water (0.19%) contents (Deer *et al.*, 1962). If appreciable amounts of HF were present, however, the possibility of HF molecules entering the beryl channel arises. The HF molecule is small enough to fit into the channels, but it would also be expected to give molecular absorptions in the same region as H_2O and CO_2. Based on their absence, one may estimate that less than 0.002 percent HF can be present. An additional check was made by mixing a sample with $CaCO_3$ and examining its emission spectrum for the CaF_2 molecular band head. The results indicated less than 0.5 percent F in the beryl.

The possibility that water was present in the beryl originally but was subsequently lost can be ruled out on the basis of experiments attempting to alter the molecular spectra (Wood and Nassau, 1968). Of the three factors, high temperature, low pressure, and high HF content, the low pressure is probably the most important factor leading to the absence of water in this beryl.

Cause of the Red Color. In the chromophoric (color forming) region of the spectra a number of absorptions occur. The ω spectrum shows absorptions at 0.48, 0.51, 0.78, 0.81, and 0.84 μ, and the ϵ spectrum at 0.425 and 0.545 μ. These absorptions are quite intense. From the analysis one need only consider Fe, Ti, and Mn as possibilities as chromophores since the other ions in Table I above the 0.00X% level do not ordinarily absorb radiation in the visible region of the spectrum.

Titanium is not chromophoric in the common tetravalent state, but for the trivalent state in octahedral coordination in corundum it exhibits a single broad absorption band near 0.51 μ (McClure, 1962). The tetrahedral Ti^{3+} is not commonly found. The absorption in Al_2O_3 appears exceedingly weak, however, probably because of the strong pref-

TABLE 1. ANALYSES OF RED BERYL FROM TOPAZ MT., UTAH (Wt. %)

A. Quantitative Spectroscopic:	
K	0.17
Cs	0.10
Na	0.03
Li	0.01
F	<0.5
Fe	0.7
Mg	0.23
Ti	0.09
Mn	0.08
B. Qualitative Spectroscopic:	
>1.0	Al, Be, Si
0.X	Fe
0.0X (high)	Cs, K, Mg, Mn, Ti
0.0X	Ca, Li, Na, Zn
0.00X	Cu, Ni, Rb, Zr
0.000X	Pb, Sn
C. Optical Absorption:	
$F<0.002$	
$H_2O<0.002$	
$CO_2<0.002$	

erence for the tetravalent state, allowing only a few ions to be present in the trivalent state. We believe that the titanium is present in the Utah beryl in the tetravalent non-chromophoric form and that the absorption bands observed are not due to this ion.

We have shown previously (Wood and Nassau, 1968) that the broad peaks in the vicinity of 0.8 μ are due to Fe^{2+} ions in several different site locations. The intensity of this band group in the Utah beryl is not as high as one would expect on the basis of the analysis if all the iron were present as the divalent ion. For example, a golden beryl (#448) containing a low 0.X% Fe had $\alpha=3.2$ cm^{-1} near 0.8 μ (Wood and Nassau, 1968) compared with $\alpha=0.42$ cm^{-1} over the background for 0.X% Fe in the present case ($\alpha=A/t$ where A is the absorbance and t the sample thickness in cm). This means that an appreciable fraction of the Fe ions are in the trivalent state and are probably the cause of the rising absorption below 0.5 μ and the line at 0.425 μ (Wood and Nassau, 1968).

The red color, however, is caused by the multiple peaks between 0.48 μ and 0.545 μ which absorb visible light except at the red end of the spectrum. This is the same absorption region as that of the pink beryl morganite, but the details of the absorption are different. For example, morganite has absorptions at 0.495 (ω), 0.54 (ω), and 0.555 μ (ϵ) as compared with 0.48 (ω), 0.51 (ω) and 0.545 μ(ϵ) for the Utah red beryl. There certainly is a strong similarity between the two spectra even if there is not an exact coincidence. In the case of morganite we attributed the color to the divalent Mn^{2+} ion (Wood and Nassau, 1968), and eliminated the trivalent ion as a possibility. The same arguments eliminate the Mn^{3+} ion here, and we accept the Mn^{2+} ion as a valid possibility. This ion has a spectrum which is difficult to analyze, since different coordinations do not give such qualitatively different absorption as do the other transition metal ions. In the case of beryl there is also the additional complication of the channel sites where still different chromophoric Mn^{2+} ion species may be possible. We therefore have not been able to account for each individual line in the spectrum as we did in the case of Cr^{3+} in emerald, for example, on the basis of modern crystal field theory. On the other hand, the intensity of the absorption near 0.5 μ supports the assignment of Mn^{2+} as the chromophore responsible for the color in both pink morganite and the red Utah beryl. In the red Utah beryl $\alpha = 2$ cm^{-1} above the background near 0.5 μ, while in morganite it is of the order of 20 times less. The Mn concentration in the morganite samples which we have analyzed is also almost 20 times less (morganite sample #490: Mn$<$0.005 wt% by spectroscopic analysis), lending support to our assignment. It should be understood, however, that until the spectra can be analyzed in full detail this assignment of the color to Mn^{2+} must be treated as only tentative.

The only other red or manganese-containing beryl noted in the literature is pale rose red rosterite (vorobyeveite) from the Island of Elba (Zambonini, 1928). This was reported to contain 0.74 percent MnO, and is also an abnormal beryl, having an exceptionally high alkali content (Na_2O 4.22, Li_2O 0.43, K_2O 2.25, and Cs_2O 0.91%) but a normal water content of 0.84 percent. The spectral characteristics of this material have not been reported, and we have been unable to obtain specimens of this or of any other high-Mn-containing beryl for optical absorption studies.

ACKNOWLEDGMENTS

We wish to thank Miss B. E. Prescott and W. E. Burke for technical assistance, and R. L. Barns for the precision X-ray measurements. We are particularly grateful to Prof. C. Frondel for making quantities of the material available. We wish to thank Prof. Frondel and Dr. A. Montgomery for helpful discussions.

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Manuscript received, October 20, 1967; accepted for publication, January 5, 1968.