THE COLOR OF AMETHYST, ROSE, AND BLUE VARIETIES OF QUARTZ.

By Thomas L. Watson and R. E. Beard, Of the University of Virginia.

INTRODUCTION.

There is a surprising lack of exact information on the cause of color in minerals, even in many of the common varieties. This is especially true of minerals possessing exotic color in contradistinction to those having natural color, dependent on chemical composition. The literature is largely a foreign one, is comparatively small but scattered, and much of the earlier work is of doubtful value. Again, there is an almost entire lack of reliable analyses involving accurate determinations of the minute quantities of colorative substances (pigments) diffused through minerals which exhibit exotic color.

Decided progress, however, has been made in recent years in the study of cause of color in dispersely colored minerals, many of which are known to be very sensitive to high temperatures and in some cases even to daylight. The chemical nature of the coloring substances is less well known and opinion on the subject is divided. Heating tests for destroying color and its restoration on exposure to the emanations of Roentgen, cathode, or radium rays are used to distinguish between colorative substances of organic and inorganic nature. Also by the use of the ultramicroscope and the application of the principles of colloid chemistry the nature and composition of the substances causing color may be determined.

The present paper gives the results of some experiments recently completed by the writers on the color of several varieties of quartz, and a brief summary and discussion of the work by others on the same varieties of the mineral. There is included on page 559 a note by George Steiger, Chemist to the United States Geological Survey, of some quantitative determinations made of manganous oxide (MnO) in rose quartz from Creede, Colorado, and in amethyst from an unknown locality. Especial attention is directed to the analyses of amethyst and rose quartz from many different localities tabulated on page 554.

The writers are indebted to Dr. Edgar T. Wherry, of the United States National Museum, for helpful suggestions offered on reading the manuscript.
ANALYSES.

Preparation of samples.—Twelve thoroughly clean and fresh representative samples, eight of rose quartz and four of amethyst, from different localities were selected for analysis. Each sample was crushed without grinding in a steel mortar and passed through silk gauze having 13 meshes to the millimeter. The powder was placed in a porcelain dish and dilute hydrochloric acid added and allowed to stand for about 10 minutes, when it was diluted with water, allowed to settle, and the liquid decanted off. This treatment with dilute hydrochloric acid and washing with water was repeated seven or eight times, after which the liquid gave no indication of the presence of iron. The samples were then dried on the water bath and used for analysis.

Methods of analysis.—From 4 to 5 grams of the sample, prepared as outlined above, were accurately weighed into a platinum crucible and treated with a few drops of sulphuric acid and hydrofluoric acid and heated until all silica was volatilized. The residue was fused with sodium carbonate and the melt dissolved in nitric acid. The resulting solution was examined for iron, manganese, titanium, and cobalt, according to the methods outlined by Hillebrand.1

Iron was determined by titrating with potassium permanganate solution, 1 cc. of which was equivalent to 0.00067 gram of ferric oxide. Manganese and titanium were determined colorimetrically. The precipitate of cobalt sulphide was so small that it was not feasible to handle it gravimetrically, so that the filter containing it was ignited and the total residue taken up in a borax bead. The color of the beads varied from a faint blue to a clear and distinct blue, but in no case was the bead highly colored.

The results obtained on analysis follow in tabular form:

Partial analyses of amethyst and rose quartz.

[R. E. Beard, analyst.]

<table>
<thead>
<tr>
<th>No.</th>
<th>Variety</th>
<th>Constituents determined.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TiO₂</td>
</tr>
<tr>
<td>I</td>
<td>Amethyst</td>
<td>0.0199</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>0.0166</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>0.0145</td>
</tr>
<tr>
<td>IV</td>
<td></td>
<td>0.0031</td>
</tr>
<tr>
<td>V</td>
<td>Rose</td>
<td>0.0032</td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td>0.0063</td>
</tr>
<tr>
<td>VII</td>
<td></td>
<td>0.0029</td>
</tr>
<tr>
<td>VIII</td>
<td></td>
<td>0.0028</td>
</tr>
<tr>
<td>IX</td>
<td></td>
<td>0.0028</td>
</tr>
<tr>
<td>X</td>
<td></td>
<td>0.0043</td>
</tr>
<tr>
<td>XI</td>
<td></td>
<td>0.0029</td>
</tr>
<tr>
<td>XII</td>
<td></td>
<td>0.0028</td>
</tr>
<tr>
<td>XIII</td>
<td></td>
<td>0.0090</td>
</tr>
</tbody>
</table>

2 Precipitate of cobalt sulphide was too small to handle gravimetrically but was ignited and taken up in a borax bead with the color results shown in table.
3 Same as II, except more deeply colored and a single large crystal was used for analysis.
4 Bead was colored a deeper blue than for any other of the 12 samples analyzed.
5 *Analyses by Robert Robertson. The Virginias, 1885, vol. 6, p. 2.
The MnO.

I. Prince Edward County, Virginia. Collected by William M. Thornton, Jr. Furnished by Prof. F. P. Dunnington, University of Virginia.

II. Madison County, Montana. Furnished by Foote Mineral Company.

III. Madison County, Montana. Furnished by Foote Mineral Company.

IV. Brazil, South America. Furnished by Foote Mineral Company.

V. Amazon claim, 3 miles north of Texas Creek, Colorado. Furnished by D. B. Sterrett through United States National Museum.

VI. South Dakota. Furnished by United States National Museum. Specimen without number.


IX. South Dakota. Furnished by United States National Museum. No number.


XIII. Rutile district, Nelson County, Virginia.

As tabulated the figures disclose rather marked variation in each of the constituents for both the amethyst and rose varieties of quartz. When individual analyses are considered, it is observed that amethyst contains the highest percentage each of manganous oxide (MnO) and ferric oxide (Fe₂O₃), while rose quartz shows the highest percentage of titanium dioxide (TiO₂) and the lowest percentage each of manganous oxide (MnO) and ferric oxide (Fe₂O₃). The average percentages of the individual constituents determined for the two varieties of quartz are as follows:

<table>
<thead>
<tr>
<th></th>
<th>TiO₂</th>
<th>MnO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amethyst quartz</td>
<td>0.002577</td>
<td>0.000565</td>
<td>0.000420</td>
</tr>
<tr>
<td>Rose quartz</td>
<td>0.003185</td>
<td>0.00423</td>
<td>0.002735</td>
</tr>
</tbody>
</table>

PETROGRAPHY.

A thin section was cut from each of the 12 specimens analyzed (eight of rose quartz and four of amethyst) and studied microscopically. In each thin section the quartz was colorless and exhibited the features common to vein quartz in general. Three of the sections of rose quartz and one of amethyst exhibited slight to distinct wavy extinction, with optical disturbance not noted in either of the other eight slides. Inclusions of varying nature, chiefly mineral (solid) but sometimes liquid, were developed in each slide and in several they were fairly abundant. Their distribution was usually irregular but at times they were partly arranged in lines.

The identity of most of the mineral inclusions could not be definitely established. With only one exception (amethyst), rutile in the form of needle-like inclusions was definitely determined as being present. The rutile inclusions were more abundant in the rose quartz and were only sparingly present in three and entirely absent from one of the amethyst from Brazil (IV in table of analyses, page 554) purchased from the Foote Mineral Company. The larger average titanium content in the rose quartz is shown in the table of chemical analyses on page 555. The minute, dark-colored, dust-like inclusions in both varieties of the quartz were indeterminate as
to composition. They may possibly represent some form of iron oxide or manganese oxide or both.

The evidence gained from microscopic study of the thin sections strongly indicates that the color of the two varieties of quartz can not be ascribed to microscopically visible inclusions, since in general character and abundance the inclusions were apparently not different from those frequently found in ordinary colorless quartz.

HEATING TESTS.

The color of many dispersely colored minerals has been shown to be very sensitive to high temperatures, and in some cases even to sunlight. Such minerals include halite, fluorite, amethyst, smoky quartz, topaz, zircon, tourmaline, etc. To this list should be added rose quartz and green feldspar (amazon stone). Upon testing it is very likely that other minerals will be shown to decolorize on heating.

Previous work.—In 1883 Becquerel\(^1\) showed that the color of the decolorized fluorite and halite was restored on exposure to the cathode rays. More recently Berthelot\(^2\) (1906) and Simon\(^3\) (1908) showed that the color of some of the decolorized minerals is restored on exposure to radium rays, while that of others was not restored by these radiations. From these experiments the conclusion was reached that for the minerals studied (zircon, amethyst, smoky quartz, red tourmaline, and Brazilian topaz by Simon), the color was due to inorganic and not to organic compounds, since exposure to radium rays restored the minerals to their original condition. Berthelot concluded that the coloring substance of smoky quartz, green fluorite, and emerald was organic, since the color of these minerals was not restored on exposure to radium rays after being decolorized by heating. Simon, however, was successful in restoring the color of smoky quartz after it was destroyed by heat, hence excepted to Berthelot’s conclusion regarding the nature of the coloring substance of this mineral.

The action of Roentgen, cathode, and radium rays on minerals has been extensively investigated by Kunz and Baskerville.\(^4\)

Work of the writers.—Heating tests were carried out by the writers on fairly large size fragments chipped from hand specimens of amethyst, rose quartz, blue quartz, green feldspar (amazon stone), and green and purple fluorite. The tests were made under uniform conditions in a closed platinum crucible heated in each case for 10


minutes in the flame of a No. 4 Meker burner, which yields a temperature of 1,120–1,140° C. Exact measurement of the temperature to which the minerals were subjected was not made, but it was probably around 1,100° C.

The results of these tests were that the original color of four specimens of amethyst, eight of rose quartz, and one each of green and purple fluorite and green feldspar (amazon stone) was completely destroyed. The minerals were completely decolorized on heating, with the single exception of the deep green feldspar from Amelia County, Virginia, which assumed a faint pinkish color after cooling, due probably to the presence of ferric oxide. The luster on the cleavage surfaces of the feldspar was not affected by the heating.

The color of the deep blue quartz from Nelson County, Virginia, was unaffected after heating for two periods of 10 minutes each, except that a pronounced red color developed along original fracture lines in the mineral on cooling. No change in the original color for other portions of the mineral was observed. Robertson noted that after fusing a fragment of the blue quartz from the same locality before the hot-blast blowpipe flame, the mineral retained its color.

From the results obtained by others it is probable that the color of the minerals tested by the writers would have been destroyed at a lower temperature and in a shorter period of heating. After an exposure for seven months to daylight there is slight indication of the return of the original color in the decolorized specimens of amethyst and fluorite, but not in the rose quartz, blue quartz, or green feldspar.

DISCUSSION OF RESULTS.

Amethyst.—The amethystine color of the amethyst variety of quartz has been attributed to the presence of a variety of substances by different investigators, but it has been generally assumed to be due to the presence of manganese oxide dissolved and diffused through the quartz. Manganic oxide, titanic oxide, sodium ferrate, iron sulphocyanate, and organic matter are substances that have been reported by different writers as the cause of amethystine color in quartz.

Nabl suggested in 1899–1900 that the coloring matter of amethyst is due to the presence of iron sulphocyanate, because the absorption spectrum of amethyst seemed to him to be about the same as that of this compound in ether solution; and he believed that he established this further by analyses showing the presence of sulphur and nitrogen. The more recent work of Berthelot and Simon, briefly summarized below, does not bear out this suggestion.

1 The Virginias, 1885, vol. 6, p. 2.
In 1904 Wherry\(^1\) suggested that the variety of amethyst quartz found in Delaware County, Pennsylvania, was probably colored by a titanium compound, since the microscope showed the presence of rutile inclusions. This might well be questioned in light of the investigations by the senior writer and others on blue quartz, which is discussed below.

In 1906 Berthelot\(^2\) showed that when amethyst is decolorized by heating it regains its violet color on exposure to radium rays. He found that quartz and glass containing small amounts of manganese behaved similarly; hence the color of amethyst was referred by him to a slight manganese content.

The investigation by Simon\(^3\) in 1908 represents the most important contribution thus far made on the color of minerals. By destroying the color of a number of dispersely colored minerals in oxidizing (oxygen), reducing (hydrogen), and when necessary neutral gases, and examination of the chemical character of the resulting gases or distillates, Simon concluded that the colors of the five minerals investigated by him (zircon, amethyst, smoky quartz, tourmaline, and Brazilian topaz) were produced by unstable inorganic compounds. He states that these unstable inorganic compounds are simply rearranged at elevated temperatures but not destroyed, since exposure to radium rays or even to sunlight will restore them to their original condition. According to Simon, the exact nature and constitution of the coloring substances are not known.

The work of the present writers eliminates, it is believed, the probability of inclusions of foreign substances of visible microscopic size as a cause of amethystine color in quartz. While minute inclusions of varying solid and liquid substances were present in the thin sections of amethyst examined microscopically, they were of such character as regards distribution and quantity as not to be seriously considered as a cause of color. In the absence of ultra-microscopic study, the existence of foreign substances of submicroscopic size can neither be denied nor affirmed.

The analyses made of amethyst from different localities and tabulated on page 554 are important in showing appreciable quantities of the iron, manganese, and titanium oxides—metallic oxides which are known to affect the color of minerals. Also the cobalt oxide, a highly colorative substance even in small quantity, was found in each of the four analyses of amethyst in quantity sufficient to impart a distinct blue color when taken up in a borax bead. Examination of the analytical results discloses the fact that both iron and titanium oxides exceed in amount several times that of manganese oxide.

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\(^1\) The Mineral Collector, 1904, vol. 11, p. 88.
However, in light of some recent quantitative work on amethyst carried out by George Steiger in the chemical laboratories of the United States Geological Survey, there is proof that the amount of manganous oxide reported in the analysis below is sufficient to produce the depth of color shown in the mineral which he analyzed. The mode of combination of the manganese is not necessarily the same. The amount of manganous oxide found by Steiger is less than that determined by the writers in the four specimens tabulated on page 554.

The results of the investigation by Steiger as prepared by him are published below with his permission.

A. Rose quartz from Creede, Colorado.
B. Clear, fairly dark colored crystals of amethyst, locality unknown.

\[
\begin{array}{c|c|c}
\text{MnO.} & \text{A} & \text{B} \\
& 0.0002 \text{ per cent.} & 0.00012 \text{ per cent.} \\
\end{array}
\]

The minerals were finely powdered, 30 gms. of each were decomposed with sulphuric and hydrofluoric acids and evaporated, the heat being continued until the fluorine had been completely expelled, diluted with water, and filtered.

Silver nitrate was added to the filtrate, manganese oxidized with ammonium persulphate, and determined by comparison of the color of this solution with a standard solution of manganese.

In preparing the first samples a steel block was used in powdering. It was thought manganese might have been introduced through small fragments of steel, and accordingly a second set of ground samples were prepared, this time using an agate mortar in their preparation. Determinations in the second set checked with the first as closely as could be expected.

The following experiment is interesting in showing that such colors as are observed in these minerals can easily be accounted for by the quantities of manganese present.

To 12 cc. of water (this amount roughly representing the bulk of 30 gms. of quartz) was added one-tenth cc. of permanganate solution containing 0.0006 gms. of MnO per cubic centimeter. This solution contained an equivalent amount of manganese per unit volume as the rose quartz; the color produced was of a much darker shade than that of the mineral. A similar experiment was carried out, using an equivalent amount of manganese to that found in the amethyst, and in this case the color of the solution was about that of the mineral.

It is probable that the percentage amount of either of the three metallic oxides found on analysis (table of analyses, p. 554) is sufficient to produce disperse color in quartz. From the known chemical behavior of these substances when small portions are taken up on heating by other bodies, such as borax, salt of phosphorus, glass, etc., manganese produces more exactly the color of amethyst than either the oxide of iron or titanium. In the bead tests with borax and salt of phosphorus, manganese oxide yields amethystine color only when heated in the oxidizing flame, becoming colorless when heated in the reducing flame. The usual explanation for these reactions is that in the former case manganese is converted into a higher form of oxidation and in the latter it is changed by reduction to a lower form—MnO. From the carefully conducted
experiments by Simon on amethyst, the color, if due to manganese—and we believe that it is—seems to be independent of the processes of oxidation and reduction, since he found it was destroyed by heating the mineral in either an oxidizing or a reducing atmosphere, and likewise could be restored on exposure to radium rays in an atmosphere of either oxygen or hydrogen.

From the investigations thus far made into the cause of color of amethyst the following conclusions seem to be warranted: (1) That since the color can be destroyed in an atmosphere of either oxygen or hydrogen and restored in an atmosphere of either, it is independent of the processes of oxidation and reduction, which definitely eliminate organic substances as a cause of the color; (2) that it is due to some inorganic substance whose nature and constitution are yet to be definitely determined; (3) that of the metallic oxides shown to be present in amethyst by chemical analysis, manganese seems to be the most likely one to produce the amethystine color; (4) that the analyses of the mineral show a sufficient quantity of manganous oxide present to produce the color; and (5) that colloidal particles of submicroscopic size, probably manganese oxide, will be found upon ultramicroscopic study to be the cause of the color.

**Rose quartz.**—A larger number of thin sections of rose quartz from different localities were studied microscopically than of amethyst, but with practically the same results. Irregularly distributed inclusions of the same nature and approximate quantity were observed as in the amethyst, and are not regarded by the writers as having any effect in producing the color.

Eight partial analyses of rose quartz from as many different localities were made, with the results shown in table on page 554. The same metallic oxides (TiO₂, MnO, Fe₂O₃, and CoO) were found as in the amethyst, with somewhat similar variations in each constituent noted when individual analyses are compared. (See p. 559 of this paper determination of manganous oxide in rose quartz from Creede, Colorado, by George Steiger.) Titanium dioxide (TiO₂) averages higher, while manganous oxide (MnO) and ferric oxide (Fe₂O₃) average lower for rose quartz than for amethyst. The color of the borax bead imparted by the very slight amount of cobalt oxide (CoO) present ranged from distinct blue to very pale blue; but on the whole the bead tests indicated probably a smaller content of cobalt oxide (CoO) than for amethyst.

In every case the mineral was completely decolorized on heating, which was to be expected, since it is well known that the color of rose quartz fades on exposure to daylight. The writers did not carry out any tests to determine the restoration of color of the decolorized specimens, but Doelter¹ points out the lack of restoration.

¹ Das Radium und die Farben, 1910, pp. 21 and 78.
of color destroyed by heat in the case of rose quartz, which proves that the color is due to organic and not to inorganic substances.¹

Dana² quotes Fuchs as stating that the color is due to titanium, since he found 1 to 1.5 per cent in specimens from Rabenstein, near Bodenmais, and the former (Dana) then remarks that it may come in part from manganese.

From the chemical nature of the metallic substances determined on analysis to be present in rose quartz, the character of inclusions found on microscopic study of thin sections, the complete absence of the slightest indication of the original color being restored in the decolorized specimens on heating after exposure of seven months to daylight, and the lack of restoration of color destroyed by heat on exposure to radium rays by Doelter, the writers conclude that the color of rose quartz can not be attributed to an inorganic substance.

Blue quartz.—By way of contrast it may be of interest here to briefly summarize the results of the investigations into the cause of blue color in some quartz. The occurrence in quantity of beautiful deep sky-blue opalescent quartz in quartzose igneous rocks and at times in metamorphosed sediments derived from them, is known in many localities both in this country and abroad, and has been the subject of investigation in a number. This variety of quartz is by no means uncommon in the Southern Appalachians, and is particularly characteristic of some rock types of the Blue Ridge Mountains and its outliers in Virginia.

The senior writer has examined microscopically many thin sections of blue quartz from different localities in the southeast Atlantic States, and in every case the substance of the quartz was found to be crowded with hairlike inclusions of rutile, which were frequently arranged with more or less crystallographic regularity. On the other hand, quartz of light color or colorless to dark smoky often shows inclusions of rutile needles, with no indication whatever of blue color.

The blue color of the quartz was apparent in thin sections as well as in hand specimens. There is no evidence, however, that the included crystals of rutile observed in the quartz are blue in themselves, although Dana records among the varieties of color for rutile bluish and violet shades. Of the well-known laboratory tests for titanium, two impart a violet color (1) to the salt of phosphorus bead in the reducing flame when cold and (2) to a hydrochloric acid solution when boiled with metallic tin, but neither compound of titanium (Ti₂O₃ and TiCl₃), supposed to produce the color, is known to occur in nature.

¹See p. 559 of this paper for amount of manganous oxide (MnO) found by George Stegler in rose quartz from Creede, Colorado, and description of laboratory experiment.
²A System of Mineralogy, 1892, p. 187.
From a chemical and microscopical examination into the cause of the blue color of quartz in Nelson County, Virginia, Robertson\(^1\) concluded that "in view of the color of some of the varieties of titanic oxide, when seen by reflected light, it appears possible that the partial reflection of light by the surfaces of these microscopic crystals occasions the color in question, or the latter may be in a measure due to the interference of light occasioned by these crystals."

Blue quartz occurs as a constituent of the quartz members of the charnockite rock series of India. On microscopic examination Holland found the blue quartz to be crowded with minute hairlike inclusions, presumably rutile, arranged with crystallographic regularity. Concerning the cause of the blue color of the quartz he says: "I conclude that the hairlike inclusions, to which probably the blue color of the quartz is due, are arranged with crystallographic regularity."\(^2\)

In his studies of the quartz-feldspar porphyry in which are developed phenocrysts of sky-blue opalescent quartz from Llano County, Texas, Iddings\(^3\) states that the blue color of the quartz "is undoubtedly due to the reflections of blue light waves from the minute colorless prisms, whose width is a fraction of the length of light waves. It is similar to the blue color of the sky. It is probable, however, that there is also blue light produced by interference of the light reflected from both sides of the minute tabular crystals whose width is also of the order of a fraction of a light-wave length; so that both kinds of phenomena occur within these quartzes."

In the comagmatic area of titanium-bearing rocks of Amherst and Nelson Counties, Virginia, deep blue opalescent quartz both in minute grains and in large masses is an abundant constituent. The blue color of the quartz is pronounced even in thin section, and pressure effects are exhibited chiefly in granulation, fractures, and wavy extinction. The most pronounced microscopic character of the quartz is the presence of abundant closely crowded, minute hairlike inclusions of rutile, which are distributed rather unevenly through each grain. After a detailed study of the quartz from this area by Watson and Taber,\(^4\) the following conclusion as to color was stated: "It seems probable that the blue color of the quartz characterizing the rocks of the Amherst-Nelson Counties area is to be attributed to the multitude of hairlike inclusions as explained by Robertson, Iddings, and Holland."

A different cause of the color of the constantly present blue quartz in the Milford granite of Massachusetts and Rhode Island has been

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\(^1\) The Virginia, 1883, vol. 6, pp. 2-3.
\(^2\) Memoirs, Geol. Surv. of India, 1903, vol. 28, pt. 2, pp. 138-139.
\(^3\) Journ. of Geology, 1901, vol. 12, p. 227.
suggested by Emerson and Perry,¹ who state that "a state of strain has probably produced the blue color." They say: "Most of this quartz is blue, and this color appears also in the contact zones and even in the secondary quartz that is found in fragments of schist which are inclosed in the granite and which have been greatly altered by it. The fractured grains of quartz show with polarized light the strongest undulatory extinction, which indicates a state of strain has probably produced the color." The authors do not mention at this place (p. 46) the occurrence in the quartz of rutile inclusions, but that they do occur is shown in a previous statement, where the contact effect of the Milford granite on schists is described. They say: "These grains are often full of rutile needles, like true granite quartz." ²

The blue quartz of the Virginia rutile area is generally characterized macroscopically by fractures and microscopically in thin sections by undulatory extinction, but the senior writer attributes the blue color of the mineral to the behavior of light on the minute rutile inclusions and not to any state of strain. This view is strengthened by the fact that heating does not destroy the blue color of the quartz.

¹ Bull. 311, U. S. Geol. Survey, 1907, p. 46.
² Idem, 1907, p. 32.