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THE CAUSE OF COLOR IN ROSE QUARTZ (CONCLUDED)

EDWARD F. HOLDEN, *University of Michigan*
(Continued from page 88)

VI. THE ABSORPTION SPECTRUM OF ROSE QUARTZ

The absorption of light by rose quartz is slight, as might be expected, because of the small amount of pigment present. Wherry,¹ using a microspectroscope, found no absorption for this mineral beyond a shortening of both ends of the visible spectrum. But using a strong arc as the source of light, concentrating the light by a lens, and passing it through sections of rose quartz the writer was able to observe some selective absorption. The results are given in Table V.

TABLE V. THE ABSORPTION OF LIGHT BY ROSE QUARTZ

Spec. no.	Color class	Path of light	Thickness of section	Type of surfaces	Lower limit of transmission	Region of slight absorption	Upper limit of transmission
12a	ii	Transmitted	1.0 cm.	Ground	0.43+ μ	0.47-0.51 μ	0.72- μ
12a	ii	Transmitted	2.1	Unground	.43+	.47- .52	.72-
20	v	Transmitted	1.7	Ground	.43+	.47- .51	.71-
20	v	Reflected	1.7	Ground	.43+	.47- .51	.71-
14	vii	Transmitted	3.7	Unground	.43+	.47- 52	.72-
11	viii	Transmitted	0.9	Ground	.41+	none	.76-
10	ix	Transmitted	3.2	Unground	.43+	.47-51	.72-

In all cases there was some shortening of the visible spectrum, and in all but one section, the thinnest one employed and of a pale color, there was observed a region of slight absorption from 0.47-0.52 μ , in the blue and blue green.

This result, while in itself alone not conclusive, is confirmative of the evidence of the analyses that the color is due to manganese. It excludes from consideration several other metals, and agrees with the spectrum of Mn⁺⁺⁺ compounds. From the character of the absorption Cr, Nd, Co,² and colloidal gold, the only metal

¹ Edgar T. Wherry. *Smithsonian Misc. Coll.*, 65, No. 5, (1915).

² While Co solutions absorb in the blue and green, with a maximum at 0.51 μ , they almost always have other absorption bands not shown by rose quartz.

whose colloidal solutions approximate the color of rose quartz,³ would be eliminated.

Of the manganese compounds, permanganates and manganates are excluded because of their instability and non-occurrence in nature, as well as their unfavorable absorption spectrum. Mn^{IV} ($MnCl_4$) solutions transmit only in the orange and red.⁴ Mn^{II} compounds are extremely weak pigments and need not be considered. Rhodochrosite and rhodonite, with 62 and 54% MnO , respectively, are not as deep a pink as many of the rose quartz specimens, which contain less than 1/50,000th as much MnO . Many chemists consider that the Mn^{II} salts owe their color to traces of a compound of Mn in a higher state of valence.

Violet or pink manganese glasses which have been shown by Scholes⁵ to be colored by a Mn^{III} compound, have an absorption spectrum very similar to that of rose quartz. They absorb in the yellow, green, and blue, with a maximum at about 0.49μ . The greater width of the band in these glasses may well be due to their higher Mn content. The maximum absorption is in exactly the same position in the rose quartz (0.49 - 0.495μ). Furthermore, the absorption of Mn^{III} compounds in solutions, as described by Jaeschke and Meyer,⁶ is similar to that of rose quartz. The absorption varies with the acid radicle, that of $MnPO_4$ being the nearest to that in rose quartz. A $MnPO_4$ solution, which contained 0.56% MnO , in a thickness of 1.0 cm. absorbed light from 0.46 to 0.58μ ; one with 0.011% in a thickness of 20cm. absorbed from the ultraviolet up to 0.51μ . Therefore the absorption of rose quartz likewise points to coloring by a compound of manganese, probably of Mn^{III} .

VII. THE DICHROISM OF ROSE QUARTZ

The clear transparent specimens of rose quartz, when examined with the dichroscope, show distinct dichroism. They evidently

³ In *Koll. Z.*, 4, 188, (1909), C. Doelter describes a successful experiment in producing a rose quartz colored by colloidal gold. At a temperature of 900° - 1000° , he passed an electric current through a gilded plate of quartz, cut perpendicular to *c*. Enough colloidal gold was carried into the mineral to color it rose. But he remarks that he should hardly attribute the color of rose quartz in general to colloidal gold.

⁴ W. Jaeschke and J. Meyer. *Z. physik. Chem.*, 88, 281-9, (1913).

⁵ S. R. Scholes. *J. Ind. Eng. Chem.*, 7, 1037, (1915).

⁶ *Op. cit.*

contain large areas in which a crystallographic orientation prevails. The thickness necessary for distinct dichroism to be noted is about 10 cm. in the palest specimens, and only 1 cm. in the more deeply colored ones. In one direction the color is a pronounced pink, in the other almost colorless, with a slight yellowish tinge. When both of the spots seen through the dichroscope are of the same color, they are pink, which indicates the color transmitted by light passing through the specimen in a direction parallel to the vertical axis. The absorption, then, is ω (pink) $>$ ϵ (nearly colorless). This was verified on a thick section of the deepest colored specimen (30), so cut by trial that its faces were parallel to and perpendicular to the optic axis.

The character of the dichroism is another bit of evidence that rose quartz is colored by a Mn⁺⁺⁺ compound. It is exactly the same as that observed in other pink minerals known to contain Mn⁺⁺⁺ in appreciable quantities, to which they owe their color. The following table presents the pleochroism of these minerals. In all of them there are two principal colors: rose to violet, and colorless to yellow.

TABLE VI. PLEOCHROISM OF MINERALS COLORED BY Mn⁺⁺⁺ COMPOUNDS

Mineral	Approx. % Mn ₂ O ₃	Pleochroism
Rose quartz*	0.000x	Pink (ω). Nearly colorless, yellowish tinge (ϵ)
Pink beryl*	0.0x	Pink (ϵ). Colorless (ω)
Kunzite*	0.1	Amethystine to pink (X and Y). Colorless (Z)
Rubellite	0.x-2	Pink (ω). Nearly colorless (ϵ)
Thulite	0.x	Rose (X and Y). Yellow (Z)
Pink andalusite	0.x-7	Rose red (X). Colorless or very pale yellow (Y,Z)
Piedmontite	6-19	Amethyst violet (Y). Bright red (Z). Lemon to orange yellow (X)

* In thick section

VIII. THE LOSS OF COLOR ON HEATING

The color of rose quartz is known to be unstable at a moderate temperature. The results of tests made by Dr. Lind and the writer show that the color disappears when a temperature of about 575°C. (in air) is reached, although there was found no relation between the loss of color and the inversion of α to β quartz, which occurs near the same temperature. The close agreement of

the temperatures is apparently only a coincidence. Hermann⁷ and Simon⁸ have investigated the effects on color caused by heating minerals in various gases. However their work on quartz was chiefly with other varieties than rose quartz.

The writer subjected a number of specimens to four heats at temperatures from 160° to 400°, as follows: (1) 16 specimens were heated to 160°-170° for a continuous period of 81 hrs. (2) 10 specimens were heated to $265 \pm 10^\circ$ for 6 1/2 hrs., in 3 periods. (3) 16 specimens to $345 \pm 10^\circ$ for 3 periods totalling 6 hrs. (4) 16 specimens to 400° (approximately) for one period of 3 1/2 hrs. In none of these heat treatments was the color of any of the specimens visibly diminished. The heating was carried on in air.

Dr. Lind then tried similar experiments, in air, at higher temperatures. (Dr. Bardwell tested specimen No. 30.) Table VII gives the data he obtained. The original color of each specimen, and the class to which its color had dropped after each heating, are given.

Dr. Lind came to these conclusions: "The decolorization is certainly a time reaction and I see no evidence from the experiments that there is any sharp change in the rate around the transition temperature of 575°, though the change appears to set in just below or in the neighborhood of this temperature; but the third heating makes it very evident that merely passing the transition temperature does not hasten decolorization any more than would be expected merely from a rise in temperature. There was certainly a tendency of some of the specimens to be decolorized more rapidly than others. This tendency does not appear to depend upon the amount of color originally present. . . . The color reduction seems to be a true one of kind, that is, in no case did the color go off to any other one, but gradually reduced the depth of the rose color."

How do these results agree with the theory that the color of rose quartz is due to a compound of Mn^{'''}? Manganese compounds readily change their state of oxidation under conditions of rising temperature, and the loss of the rose color at or near 575° is certainly not opposed to a coloring by Mn^{'''}, especially since the Mn compound in rose quartz must be in a very finely divided state, and would be therefore likely to be more than usually susceptible

⁷ W. Hermann. *Z. anorg. Chem.*, **60**, 369-404, (1908).

⁸ K. Simon. *Neues Jahrb. Mineral.*, Beil.-Bd. **26**, 249-95, (1908).

TABLE VII. THE DECOLORIZATION OF ROSE QUARTZ BY HEATING IN AIR

1st heating: 2 1/2 hrs. at 530°. 2nd heating: 2 hrs. at 560°-590°.
 3rd heating: 3 hrs. at 575-630°.

Color class original	Spec. no.	Result of		
		1st heating	2nd heating	3rd heating
i	30	_____	(ix) ⁹	(xi) ¹⁰
ii	12a	no change	vi	xi
iii	1	"	x	xi
iii	9	"	vi	xi
iv	8	"	vi	xi
v	20	slight reduction	xii	xiii
v	21a	some reduction	xiii	xiv
vi	16	no change	ix	xi
vi	7	"	ix	xii
vi	28	"	xii	xiii
vii	14	_____	_____	xiv
viii	11	no change	xiii	xiv
ix	18	_____	_____	xii
ix	10	_____	_____	xi
ix	17	_____	_____	xiii
ix	13	_____	_____	xii
x	19	_____	_____	xii
x	24	_____	_____	xiii
xi	2	_____	_____	xiv
xii	23	_____	_____	(xiv) ¹¹
xiii	27	_____	_____	xiv
xiii	6	_____	_____	xiv
xiii	21b	_____	_____	xiv
xiii	12b	_____	_____	xiv
xiv	This is the color of class xiii after heating.			

⁹ Result of special heating, 2 hrs. at 600°.

¹⁰ Result of special heating, 2 hrs. at 675°.

¹¹ Owing to decrepitation in heat 2, this specimen was given a special heating of 19 1/4 hrs. at 600°-590°, with the result noted.

TEMPERATURE RECORDS. Heat No. 1. In at 9.30 A.M., temp. 530°; 10.15, 530°; 11.00, 530°; out at 12.00 M., 538°. Heat No. 2. In at 1.00 P.M., 560°; 1.30, 560°; 2.00, 570°; 2.30, 580°; out at 3.00 P.M., 590°. Heat No. 3. In at 9.00 A.M., 575°; 9.30, 610°; 10.00, 620°; 10.30, 622°; 11.00, 623°; 11.30, 630°; out at 12.00 M., 631°. Special heat for specimen No. 23: In at 2.00 P.M., 600°; 3.00, 600°; 5.00, 600°; 8.00, 600°; out at 9.15 A.M., 590°.

to temperature changes. Either a reduction to MnO or oxidation to MnO_2 , would discharge the color. Whatever the mechanism of the loss of color, it is certainly one that can be undergone by Mn_2O_3 , for the dried silica gel colored by Mn''' , described in part IX of this paper, loses its color on heating even more readily than does the rose quartz. This is probably because the gel is more porous.

It might be added that Bamberger and Grengg¹² state that rose quartz does not suffer any change in color when cooled to -190° .

IX. SIMULATION OF ROSE QUARTZ

Since from several points of view a compound of trivalent Mn is suggested as the pigment of rose quartz, an endeavor was made to reproduce the color synthetically with Mn''' . In a borax fusion, 0.01% MnO produced a color equivalent to that of rose quartz of color class v. Manganese in such fusions is trivalent. Of more significance is the fact that it was possible to duplicate the color by means of a Mn''' compound in silica gel. The gel was prepared by the addition of a phosphoric acid solution to a solution of sodium silicate, "water glass." A Mn''' borate was prepared by fusing Mn in borax. The gel, when firm, was broken up and covered with a solution of the Mn''' borate in phosphoric acid. This was absorbed by the gel, giving it a rose color. By very slow drying at about 70° a glassy hydrated silica, colored by a trivalent Mn compound, was obtained. In composition it differed from rose quartz only in containing more water. Its resemblance to that mineral was practically perfect. Material so prepared, which was of a much deeper color than any of the rose quartz, contained 0.02% MnO . This experiment is a strong indication, in connection with the results previously described in this paper, that it is to a compound of trivalent manganese that rose quartz owes its color.

It was necessary to use 0.01% MnO to reproduce the color of the deepest rose quartz in the laboratory, while in nature, as the analyses indicate, much less suffices. But it was noted that on drying the gel containing Mn''' its color deepened. It is probable that the action of heat and mineralizers in nature is such as to bring out a deeper color, with a given amount of Mn, than was

¹² M. Bamberger and A. Grengg. *Centr. Mineral.*, 65-74, (1921).

possible in the laboratory. This is not surprising, when it is considered that 2.5% Cr_2O_3 is necessary to give artificial ruby the color caused by traces of that element in the natural mineral.

The rose colored silica gels lost their color at a temperature even lower than that at which rose quartz is decolorized. At this temperature the gel structure did not break down, so that the loss of color is not an apparent loss caused by a structural disintegration of the gel, but is due to some change in the Mn compound. Dr. Bardwell, who carried out tests upon three samples of these rose colored gels, reports that a heat treatment of 30 minutes at 200° caused the loss of color in two, while the third retained a slight pink. At 330° a 15 minutes treatment completely decolorized all three, and caused them to become translucent. This establishes the fact that a moderate temperature may cause the loss of colors which are due to the presence of small amounts of compounds of trivalent manganese.

Dr. Bardwell exposed three samples of each of the three gels to β and γ radiations from 230 mg. Ra for 78 days; for each gel some of the original fragments, some of the fragments which had been heated to 200° for 30 minutes, and some which had been heated to 330° for 15 minutes. In no case was any change of color caused by the radiation, although in the same period a specimen of dark rose quartz (No. 30) changed to a very dark smoky color. Either the artificial products do not contain whatever substance is responsible for the production of the smoky color in radiated rose quartz or the difference is one of state.¹³ These experiments indicate conclusively that the radium-induced smoky color has no connection with the rose color, caused by manganese.

X. SUMMARY AND CONCLUSIONS

Since the research here described dealt with a large number of specimens of rose quartz, the results may be generalized to apply to all occurrences of that variety. Rose quartz is always massive, and occurs in association with granitic rocks. Its color can not be due to the action of radioactive substances on white quartz, since

¹³ Dr. Bardwell says in this connection, in a communication: "It seems to me that in terms of our (Lind and Bardwell, *this journal*, 8, 178, 1923) theory of the coloring of stones by radiation that the difference between natural rose quartz and the silica gels is one of state. These silica gels can probably not be considered true solids, and therefore the displacement of electrons by radiation is not permanent, because they are not held in their displaced positions but can return."

it is impossible to reproduce the color on heat decolorized specimens, or to strengthen the color, by means of strong radium preparations. In every case the color so obtained was that of smoky quartz. The analyses show that the color can not be due to compounds of Ti or Fe, or to hydrocarbons. Ti is accounted for by the universally present rutile inclusions, and Fe is derived chiefly from limonite stains. But Mn varies regularly in amount with the depth of color, and there are no inclusions to which it is due. Rose quartz is decolorized in air near 575°C., and if formed above that temperature quartz will be white even though it may contain enough manganese to have colored it at a lower temperature. The absorption spectrum agrees with that of Mn⁺⁺⁺ glasses and solutions. Its pleochroism is exactly like that of other minerals which owe their color to Mn⁺⁺⁺. The loss of color on heating is accounted for by a change in the valence of the manganese. Rose quartz was very closely simulated in amorphous hydrated silica, colored by only 0.01% MnO. This silica gel was even more easily decolorized by heat than was the natural rose quartz.

There is, therefore, a strong convergence of different lines of evidence leading to the conclusion that rose quartz owes its color to the presence of trivalent manganese.

THE PROPERTIES OF SCAPOLITE

A. N. WINCHELL, *University of Wisconsin*

The chief constituent molecules of scapolite were first recognized by Tschermak¹ fifty years ago. This made it possible for Lacroix² to show that, in general, the refringence and birefringence increase with increase of calcium. About fifteen years ago Himmelbauer³ investigated the matter in more detail and prepared diagrams showing the relations between variations in composition and in the length of the vertical axis, the specific gravity, the refringence and the birefringence. He assumed rectilinear variations in all cases. Discrepancies were not small in all cases, but were attributed to impurities.

¹ *Sitz. Akad. Wiss. Wien.*, LXXXVIII, I, 1154, (1883).

² *Bull. Soc. Fr. Min.*, XII, 356, (1889).

³ *Sitz. Akad. Wiss. Wien.*, CXIX, I, (1910).