

A NEW PROPERTY OF MATTER: REVERSIBLE
PHOTOSENSITIVITY IN HACKMANITE
FROM BANCROFT, ONTARIO

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ABSTRACT

Hackmanite from near Bancroft, Ontario, undergoes a remarkable color intensification following brief exposure to a suitable source of ultra violet light, including the argon bulb, iron spark, carbon arc with cored carbons and quartz tube mercury vapor lamp, changing from colorless or pale pink to a raspberry shade or deep violet. With the argon bulb, however, a much longer exposure is required. By means of selective filters, the exciting radiation has been determined as being not longer than about 4800 A.U., and extending down to about 2250 A.U., and perhaps lower. The induced color slowly fades in darkness to a bright red violet, but fades rapidly and nearly completely on exposure to strong light, the radiation responsible for the reversal phenomenon having a peak in the visible region in wave lengths shorter than yellow, although extending to 7500 A.U. Longer wave lengths up to 39000 A.U. having no effect.

The intensification and reversal may be repeated indefinitely, and is suspected of being connected with the known presence of a trace of manganese, spectrographic analysis disclosing 0.001% of this element. However, the presence of the extraneous elements Li, Ga, Pb and Nd, was also revealed, as well as traces of Be, Ba, Sr, and perhaps P, some of which may also be involved in either its photosensitivity or luminescent properties, or both. The pink sodalite thus exhibiting color intensification and reversal, fluoresces a salmon color when viewed with the aid of a Corning Red Purple Corex A No. 986 filter, and phosphoresces sky blue, but colorless undetermined associated minerals may phosphoresce bluish, yellowish, greenish, orange, or not at all. It is suggested that both the partial recovery of color in darkness following reversal, and the partial reversal in darkness following excitation, are both due to concomitant phosphorescence having compound radiations. Some reversibly photosensitive and thermosensitive substances of related interest are discussed.

INTRODUCTION

Several years ago while examining miscellaneous minerals for evidence of fluorescence and phosphorescence with an ultra violet lamp of the iron spark type, a specimen of hackmanite, a member of the sodalite group, from near Bancroft, Ontario, was tested. The specimen was a very poor one, and no particular fluorescence or phosphorescence was noted, but in the light the impression was obtained that violet red spots had appeared as a result of the exposure to ultra violet light, which had not previously been present. However, as the spots appeared to be permanent, and the original appearance of the mineral had not been carefully noted, the matter was not then further investigated. Recently, however, through the kindness of Dr. T. L. Walker, Director of the Royal Ontario Museum of Mineralogy, Toronto, Canada, a far superior specimen of hackmanite from the same locality was received. It was well tinted in patches of pink, not unlike that of rose quartz, and was described by the sender as being of much better color than was available

until recently, but as not losing its color in such a spectacular way, sometimes within a few seconds after being exposed to light. Dr. Walker interpreted this to mean that this recent material contained considerable more of the pink mineral than the original lot described by him some years ago,¹ and expressed the belief that it would lose practically all its color after a few days exposure to light, as has been previously recorded by himself and others. The mineral associates from this locality are nepheline, cancrinite, calcite, plagioclase, essonite, diopside and vesuvianite. The fact that hackmanite, formerly known as pink sodalite, fades on exposure to light, has been known for almost a hundred years, although apparently the alleged phenomenon was regarded with some scepticism by mineralogists until the twentieth century.

The original pink sodalite collected by Giesecke between 1806 and 1808 in Greenland, is thus described by Allan:² "Its color is green unless freshly fractured, when it presents a brilliant pink tinge, but this on exposure to light goes off in a few hours."

Vredenburg³ in describing certain rocks containing sodalite and nepheline from Kishengarh State in Rajputana, refers to a peculiar sodalite as follows: "Moreover, some of the sodalite exhibits an extraordinary phenomenon hitherto unrecorded in any mineral. While some of the specimens are of a bright blue color similar to that of the mineral from many other localities, others appear under ordinary conditions transparent and colourless. But some of these colourless fragments when kept in the dark for a fortnight or three weeks assume a pink color which disappears rapidly on exposure to bright daylight, and almost instantaneously in direct sunshine.

"The phenomenon is particularly brilliant when the rock is first broken in the field, and the large blocks of elaeolite (some of which are over a yard wide) appear, on fracture, as if suffused with blood. The colour seems to re-appear more completely in some specimens than in others, for while the disappearance of the colour is very rapid, its re-appearance which constitutes the most remarkable feature of the change, is very slow. The precise nature and cause of this peculiar phenomenon are at present unknown."

It is evident that Vredenburg observed not only a striking fading (reversal) of the original color, but likewise noted a slow and inexplicable color recovery in darkness.

Borgström⁴ described this variety of sodalite from the nepheline rock called tawite in the Lujaur-Urt on the Kola Peninsula, as hackmanite, and remarked that it was bright red violet in color, bleached rapidly in daylight, and contained 0.39% of sulfur equivalent to 6.23% of ultramarine.

Finally, Walker and Parsons¹ recorded the following of the hackmanite from Dungannon Township near Bancroft, Hastings Co., Ontario: "On freshly-broken surfaces of the rock—one frequently observes spots of fine pink colour, which for the most part disappears completely in direct sunshine in from ten to thirty seconds. When placed in the dark the colour gradually returns, but according to our observation it never becomes as bright as at first, even after being protected from light for one week."

Their analysis gives also "Mn trace" but no sulfur (difference from Borgström's hackmanite), and they conclude with respect to the color changes: "Nothing of a fundamental nature has as yet been determined in regard to the colour change, except that it is due to some part of the visible spectrum. Exposure to *x*-ray fails to bring about the change in colour." They regarded the occurrences in Greenland, Kola, Kishengarh and Bancroft as being closely related.

EFFECT OF ULTRA VIOLET LIGHT FROM THE IRON SPARK

The new specimen was accordingly subjected in darkness to intense excitation from the iron spark discharge, being held close (2 cm.) to the gap for ten seconds. A reddish violet coloration was noted but attributed to fluorescence. This was followed by a general, distinct and rather persistent bluish phosphorescence described by Brown.⁵ On turning on the light, however, the author was amazed at the change which had come over the mineral. It was splashed with broad patches, streaks and spots of a rich and beautiful raspberry-red color, the acquired hue having little in common with the original pink color still visible on the unexposed areas of the specimen. This color appeared to be well retained in darkness, although it was of lessened intensity after being kept thus overnight, and given time, presumably would slowly fade to deep pink. In light of ordinary intensity indoors, the acquired color was found sufficiently permanent to admit of prolonged examination. In this way, it was determined that the areas of the original pink mineral coincided with those acquiring the permanganate color under ultra violet radiation, and likewise exhibiting a bright blue phosphorescence, similar in color, although not in intensity, to that of the remarkable phosphorescent manganiferous calcite from the Chisos Mountains, Brewster County, Texas.* However, there was an over-all fainter bluish phosphorescence throughout the whole area exposed, which may arise from invisible deeper areas. On holding the mineral close to an ordinary frosted (60 watt) electric lamp for a brief interval (30 seconds), the deep induced

* Following excitation in the dark with the iron spark for 10 seconds at 2 cm., the phosphorescence of this calcite suffices to read news type for five seconds.

color rapidly faded until the original appearance was restored, when the process could be repeated. So far as the writer knows, this is the first instance of induced reversible photosensitivity in a mineral, the general behavior indicating that the color is intensified by exposure to certain frequencies in the ultra violet, and the induced color is in turn reversed by the higher frequencies in the visible spectrum.

Brown⁵ also tested the fluorescence of this Ontario hackmanite under ultra violet (as well as under red (heat)) radiation, using a quartz-mercury lamp provided with a filter of Wood's glass to cut off visible light, only 3000–4000 A.U. being transmitted. However, he failed to note any visible change other than a "pink" fluorescence and a "white" phosphorescence induced by heating below red heat in a dark room. This latter effect was photographed and appears to be similar or identical to the general phosphorescence excited by ultra violet radiation.

EFFECT OF CORNING RED PURPLE COREX A No. 986 FILTER

The visible light from the iron spark was cut off through the interposition of a Corning Red Purple Corex A No. 986 filter, and the mineral again tested. A very beautiful general fluorescence was seen whose color is best described as salmon. In addition, large areas colored cobalt blue were observed, as well as other areas having a rich purple color. The blue areas are doubtless identical with the sodalite from Bancroft, mentioned by Brown⁵ as fluorescing in that color, while the purple patches may be in part due to some other non-fluorescent white mineral colored by the transmitted light. Phosphorescence was perceptible but very noticeably weaker, and the same was true of color intensification. Further testing demonstrated that the mineral fluorescing in blue lacked any visible power of phosphorescence or of color intensification.

EXCITATION UNDER THE CARBON ARC

The hackmanite was tested by exposure at 18 cm. to an ultra violet "Health" lamp rated at 1000 watts, using "Eveready" (cored), "Super Tan" carbons at 9 amperes. The characteristic color was rapidly developed, any reversing effect due to the abundant light evidently being more than compensated for by the high intensity of the ultra violet emitted. Consequently, interposition of the Corning Red Purple Corex A No. 986 filter made little perceptible difference.

EXCITATION UNDER THE ARGON BULB

Preliminary experiments with this source of excitation were negative, but it was found that by sufficiently extending the time of exposure, very

satisfactory results could be achieved. The following tabulated results were achieved in a dark room with the specimen in contact with the bulb, the usual fluorescence being noted:

<i>Time of exposure in minutes</i>	<i>Degree of intensification</i>
2	Very faintly colored
4	Slightly colored
8	Well colored
16	Strongly colored
32	Very deeply colored

It is not certain whether this reluctance is due to the low relative intensity of the argon bulb,⁶ to the inability of the glass to transmit short waves less than 3000 A.U.,⁶ or to both these factors.

EXCITATION UNDER QUARTZ TUBE MERCURY VAPOR LAMP

This was made with a Hanovia lamp having a 6'' tube and rated at 1000 watts, protected by a lead shield. The hackmanite was placed 23 cm. below the lamp and pronounced color intensification readily occurred. The Corning Red Purple Corex A No. 986 filter visibly interfered with excitation, however. This was demonstrated by exposure after covering part of the specimen with the filter, the difference in color intensity being readily apparent. Color intensification was (almost) completely inhibited by interposition of ordinary window glass.

Although Brown⁵ utilized this source of ultra violet illumination, he failed to note any color intensification in hackmanite from this locality although the mineral earned special mention because of its unusual photo-luminescent properties. Possibly any color intensification developed was confused with the red violet color transmitted by the filter, and as over 200 specimens were examined, presumably in a dark room, the new phenomenon easily escaped observation.

EFFECT OF VARIOUS FILTERS ON REVERSAL

Following intensification by ultra violet light from the iron spark, the effect of various filters on the color reversal was studied by placing them between the excited mineral and an ordinary frosted 60 watt electric light. The only filter tested which completely inhibited reversal was a Corning Heat Transmitting No. 254, although Red Purple Corex A No. 986 and the yellow, orange and red filters visibly interfered with reversal, the effect of the last three increasing in the order stated.

TABLATION OF EXPERIMENTS ON REVERSIBLE PHOTOSENSITIVITY OF HACKMANITE INCLUSIVE OF EFFECTS OF VARIOUS FILTERS

Filter Used (C = Corning)	None inter-posed	C Clear Corex A 980 3 mm.	C Red Purple Corex A 986 2.5 mm.	C H.R. Clear Corex D 970 2 mm.	C Chemical Pyrex 2 mm.	C Clear Blue Fluores- cing 014 3 mm.	Window Glass 1.5 mm.	C Yellow Noviol C 338 3.5 mm.	C Orange 349 3.5 mm.	C Signal Red 243 3.9 mm.	C Clear Corex A Water Cell 10 mm.	C Heat Trans- mitting 254 3.5 mm.
Approximate Transmission in A.U.		2250-27000	2500-4250; 6500-10750	2650-35000	2800-35000	3200-39000	3225-39000	4800-45000	5360-45000	6170-45000	±3300-14000*	7500-39000
Quartz Tube Mercury Vapor Lamp; 10 cm.; 60 sec.	+	+	+(weaker)	+(weaker)	+(weaker)	+(much weaker)	+(very weak)	-	-	-	+	-
C Type Carbon Arc; 10 cm.; 60 sec.	+	+(weaker)	+(stronger)	+	+(weaker)	+(very weak)	+	-	-	-	+	-
Excitation with Iron Spark; peak at 2600 A.U.; weak in long U.V.; 2 cm.; 10 sec.	+	+	+(weaker)	+(weaker)	+	+(very weak)	+(very weak)	-	-	-	-	-
Argon Bulb 3000-4500 A.U.; adjacent; 16 min. in dark room	+	+	+	+	+	+	+	-	-	-	+	-
Frosted 60 watt Tungsten Lamp adjacent; 30 sec.*	+	+	+(considerably weaker)	+	+	+	+	+(slightly weaker)	+(weaker)	+(considerably weaker)	+	-

* Following excitation with Iron Spark as above. Note:—Ultra Violet: ← 4000 A. U., Visible: 4000 A. U. → 7500 A. U.

PARTIAL INTENSIFICATION IN DAYLIGHT FOLLOWING
COMPLETE REVERSAL WITH ELECTRIC LIGHT

A specimen of hackmanite which had been completely reversed by exposure to electric light until nearly colorless was observed to acquire a noticeable rosy hue after a few minutes exposure to north light on a dull and cloudy day. By partially screening the mineral and again reversing the exposed area, the difference in color was made very evident. At first, this effect was attributed to a preponderance of ultra violet light over visible light occasioned by the condition of the weather, but later it was found that the color of reversed hackmanite was equally well restored by exposure to direct sunlight. The effect is then due to the normal difference in composition between electric light and daylight.

SUMMARY OF EXPERIMENTS ON INTENSIFICATION
AND REVERSAL

The results of some of the preceding experiments, and other additional tests not specifically mentioned in the text, have been arranged for convenience in the preceding table.

RADIATION RESPONSIBLE FOR EXCITATION AND REVERSAL

From inspection of these tabulated tests, we may infer that since excitation is inhibited by any filter from Corning Yellow Noviol C up to and inclusive of Corning Heat Transmitting filter No. 254, wave lengths roughly from 4800 A.U. to 39,000 A.U. are not responsible. On the other hand, ultra violet radiation down to 2250 A.U. and perhaps lower, causes intensification of color. Insofar as reversal is concerned, however, the activating radiation appears to show a peak in the visible region in wave lengths shorter than yellow, although extending to 7500 A.U., longer wave lengths up to 39,000 A.U. having no effect.

REVERSIBLE PHOTOSENSITIVITY IN ACTIVATED
TITANIUM DIOXIDE

The only other instance of a reversibly photosensitive substance which has come under the writer's notice is that of a sample of a commercial titanium oxide which possesses the property of turning to a cream color in sunlight, or under the iron spark, which tint fades to white when the material is placed in darkness for some time. A spectrographic examination kindly made by Dr. Francis C. Wood, Director of The Institute of Cancer Research of Columbia University, disclosed the presence of traces of lead and zinc, these metals having been introduced accidentally in the process of manufacture.

REVERSIBLE THERMOSENSITIVITY

This related phenomenon is better known and examples are more numerous. Certain chemical substances change color on heating and reverse their acquired color on cooling, notably the allotropic mercuric iodide, HgI_2 , which turns yellow on heating and becomes red again on cooling.⁸ At much more elevated temperatures, the author has observed that the normal chromates of the alkaline earths of the type RCrO_4 , change from their respective shades of greenish yellow to yellow, to orange and red shades, the original colors reappearing in reverse order on cooling. CaCrO_4 , for instance, changes from a pure yellow to a brick red upon heating, and back again to yellow upon cooling. This is better demonstrated with electric heat, otherwise some of the chromate may be reduced to chromite, resulting upon cooling in a greenish shade instead of yellow. The extent of the color change increases with diminishing atomic number of the alkaline earth whose normal chromate is heated.

GILLESPIE, A REVERSIBLY THERMOSENSITIVE MINERAL

A specimen of an undetermined rose-red crystalline mineral was presented to the author some years ago through the generosity of Mr. Peter Zodac of Peekskill, New York, who stated that it had been found near Fairbanks, Alaska, by a prospector. A test for manganese was obtained, and on heating the powdered mineral, the color changed from old rose to violet blue. Upon cooling, the reverse color change occurred. This mineral was therefore reversibly thermosensitive. Although resembling piedmontite in its strong pleochroism, the mineral was quite unfamiliar to the author who submitted it to Dr. Frederick H. Pough of the Department of Mineralogy of The American Museum of Natural History, New York, for examination, and who kindly identified it as the new and very rare mineral gillespie, $\text{FeO} \cdot \text{BaO} \cdot 4\text{SiO}_2$, which has been described by Schaller⁹ and Rogers.¹⁰ It is stated to contain " Mn_2O_3 " 0.14% and to darken in a closed tube when heated, assuming a deep violet color, regaining its original red color upon cooling. The manganese found was assumed to be present in the strongly chromatic manganic state, the deep red color of the mineral being attributed to this, with possibly a small quantity of ferric iron. In the abstract of the original paper, the abstractor, Dr. Edgar T. Wherry, "does not consider it probable that any manganese could occur in the manganic state in the presence of excess ferric iron, and would prefer to class this among minerals the cause of whose color is as yet undetermined." A test of this mineral under ultra violet light from the iron spark, however, gave no visible evidence of either luminescence or photosensitivity.

Mention of these reversibly thermosensitive substances is made inas-

much as it is natural to assume that the mechanism of the phenomena involved in those substances which change color reversibly under the influence of light or heat, may well have factors in common. For instance, Tool and Stair¹¹ have shown that the ultra violet transmission of some commercial glasses lowered through solarization can be restored by suitable heat treatment, preferably somewhat above 500°C. Visible coloration accompanying artificial solarization and decrease of transmission of the shorter visible rays, apparently disappeared completely at even lower temperatures (200° or 300°C.), this disappearance being accompanied also by visible thermoluminescence. In other words, the colors excited by short wave ultra violet light were reversed by long wave radiation (heat).

RESEARCHES OF DOELTER

Changes in the color of minerals through ultra violet, *x*-ray and Ra radiation have been extensively investigated by Doelter^{12,13} who found that in general the colors were largely due to the presence of oxides of iron, chromium and manganese, and not to materials of an organic nature. The effect of radium frequently resulted in reduction, whereas ultra violet light had an oxidizing action, hence these agencies often induced opposite changes. Subsequently, he showed¹⁴ that idiochromatic minerals, i.e., those which owe their color to a normal constituent in direct combination, are rarely affected; and concluded that the mode of combination of the substance was the dominant factor in determining color, stability decreasing from a maximum with direct union, through less stable intermediate isomorphous mixtures, to a minimum with diffuse admixture. Also, he stated¹⁵ that many minerals contain two coloring matters, one labile and colloidal, the other stable and isomorphous with the mineral, the former being affected by Ra or ultra violet light, while the latter is not. In another paper,¹⁶ Doelter discussed the colloidal pigments of minerals, and shows that the color of light reflected from colloidal pigment particles having diameters of the order of the wave length of light, is of greater wave length as the diameter of the particle increases. He inferred that different colors result from the same pigmentation existing in different degrees of dispersion. Other color changes in minerals under radiation, are tabulated by Doelter¹⁷ who noted that the same species from different localities, and different samples of the same mineral from the same locality, vary in color behavior. Finally, he found¹⁸ that minerals colored by Ra frequently exhibit changes in color following storage in the dark for several years, and those that have been afterwards decolorized by heat sometime slowly regain their color.

Generalizing from his researches, one might perhaps ascribe the behavior of hackmanite as due to the presence of labile, colloidal, diffusely admixed manganese oxide, having a particle size comparable to the wave length of light, ultra violet and visible light reversibly affecting the degree of dispersion and thus the color of the light reflected.

It should be noted, however, that in Doelter's experiments on the effect of ultra violet light on the colors of minerals, exposure for several hours was made using a specially constructed arc lamp and focusing on the specimens with a quartz lens. His researches, too, appear to have been concerned largely with the mechanism of the color changes involved, and therefore confined in the main to the study of a somewhat limited number of type species adapted to his purposes. At any rate, he did not include hackmanite in the minerals examined.

EFFECT OF OXIDIZING AND REDUCING AGENTS ON THE INTENSIFIED COLOR

Doelter¹⁴ found also that those colors most readily developed in minerals by exposure to Ra were also as a rule the least stable. Certain minerals such as fluorite and some specimens of topaz may lose their acquired color spontaneously. In another instance, concentrated H_2O_2 was found to remove the color from the surface of fluorite and rose quartz after ten days treatment. An attempt was made therefore to determine whether the color change involved in the intensification of the color of hackmanite was due to oxidation or reduction. Following exposure to ultra violet light, color intensified areas of the mineral were treated respectively with 30% hydrogen peroxide and a strong solution of sodium hydrosulfite ($Na_2S_2O_4$). No visible change could be detected after allowing to stand for an hour, but this procedure would perhaps be more convincing if carried out on the finely powdered mineral for much longer periods, inasmuch as color intensification appears to extend well below the surface whereas the solutions used were only in superficial contact.

SPECTROGRAPHIC EXAMINATION OF HACKMANITE

As there was a strong likelihood that both the luminescent and photosensitive properties of hackmanite might be connected with the presence of the trace of manganese mentioned by Walker and Parsons, it became of interest to determine this element more precisely. Through the kindness of Dr. Lester W. Strock of the firm of Lucius Pitkin, New York, a quantitative spectrographic analysis of the reversibly photosensitive hackmanite for extraneous elements was made with the following interesting results:

Li	0.01%
Ga	0.01%
Pb	0.005%
Mn	0.001-0.002%
Be	tr.
Ba	tr.
Sr	tr.
Nd	evidence of line at 4303.61
P	tr.

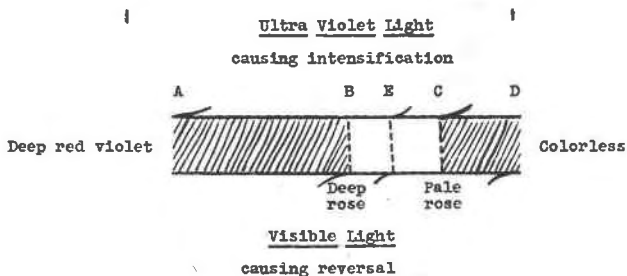
Although the concentration of manganese is lower than expected, this may be favorable to the condition postulated by Doelter in which the particle size is comparable to that of the wave lengths of light concerned. Gallium has not infrequently been reported in aluminum minerals, but the presence of some of the other unusual elements, particularly of the rare earth, may well be significant, not only in connection with the photosensitivity, but with the luminescent properties exhibited.

CONCLUSION

It is to be hoped that the remarkable induced reversible photosensitive behavior of the hackmanite described will be more exhaustively investigated from a more quantitative standpoint, particularly as it appears to be a new and unique property of matter in mineralogy. It would be particularly interesting to determine what, if any, relation exists between the photosensitivity and the luminescent properties in respect to the presence of manganese and the other unusual elements found. However, it may be pointed out that since the photosensitivity has been shown to be perfectly reversible and dependent on the ratio, intensity and time of the opposing activating radiations, and since their resultant effect is reflected in the intensity of the corresponding residual color, it is evident that both the partial recovery of color in darkness, following reversal, and the partial reversal in darkness, following excitation, represent (see diagram) simply two different phases (B and C) intermediate between the color extremes (A and D). It is suggested, therefore, that the cause in each case is the concomitant phosphorescence whose radiation, must also be of a compound nature. The time taken to attain equilibrium at B or C is indicative of the low intensities involved, but is to some degree compensated by the fact that the induced radiation occurs *in situ*. It may be that given sufficient time, B and C might become coincident at some intermediate point E, representative of final equilibrium.

Shaded areas represent partial reversal (AB), and intensification (CD), occurring in darkness and attributed to concomitant phosphorescence. E is the hypothetical equilibrium point.

DIAGRAM ILLUSTRATING VARIOUS PHASES OF REVERSIBLE PHOTOSENSITIVITY
IN HACKMANITE FROM BANCROFT, ONTARIO



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