

NOTES AND NEWS

FLUORESCENCE OF MINERALS IN ULTRA-VIOLET RAYS*

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Certain crystals of fluorspar (fluor or fluorite), especially the twinned cubes from the lead mines of Weardale in County Durham, England, display different colors when viewed from different points of view. The color as seen varies according to the relative positions of the source of light, the specimen, and the eye of the observer. When the crystal is between the source of light and the eye one color is seen, and when the eye is between the crystal and the source of light another color appears. The difference depends on whether the crystal is viewed by transmitted or by reflected (scattered) light. Holding a clear transparent crystal up to the window, the color seen may be pale shades of brown, pink, green (in some crystals a good emerald-green), or colorless; these colors being usually arranged in alternating layers parallel to the cube faces of the crystal. But when the same crystal is viewed by reflected light, with the back of the observer towards the window, a totally different color is seen. This appears, especially in direct sunlight, as a rich bluish-violet glow or shimmer diffused over the surface of the crystal, very much like the bloom on a ripe plum. When a lens is held in front of the crystal, a conical beam of sunlight inside the crystal is traced out by this color.

White light, such as sunlight, may be resolved into its component colors by various methods. Everybody knows the colors of the rainbow and the "prismatic colors" produced when light passes through a prism (such as the bevelled edge of a mirror)—red, orange, yellow, green, blue, indigo, violet. These colors are the expression of the differences in wave-length, which are successively shorter from red to violet. The spectrum of sunlight is, however, not confined to the rays visible to the eye. Beyond the red we have the infra-red, these being heat-rays of longer wave-length; and beyond the violet the ultra-violet—chemically active rays of shorter wave-length.

Now if we place a small crystal of fluorspar in the red part of the spectrum of sunlight nothing remarkable happens, but when it is moved up to the violet end it begins to glow with a bluish-violet color; and this glow becomes more intense when the crystal is moved farther on into the invisible ultra-violet. The crystal possesses the curious property of absorbing the invisible rays of shorter wave-length and giving out in their stead visible rays of longer wave-length. It is, in fact, acting as a transformer of the wave-length. Just how this happens we do not know. A learned discussion with mathematical treatment of the relation between the ether vibrations of light and the orbits of electrons would be out of place in this magazine.

* This article appeared in the *Natural History Magazine*, issued by the British Museum, October 1928, vol. 1, pp. 291-298; but as this magazine does not reach many American readers the article is reprinted in this Journal with the author's permission. Attention is especially called to the description of an exhibition case to illustrate the fluorescence of minerals in ultra-violet light which has attracted wide attention. Editor.

This interesting phenomenon, shown *par excellence* by fluorspar, was termed fluorescence (from analogy to opalescence) by Sir George Gabriel Stokes¹ in 1852. It had been first investigated by Sir David Brewster in 1834 to 1848 and by Sir John Herschel in 1845, and was also studied by Dr. John Hall Gladstone² in 1855. But it still remains a puzzle, although voluminous treatises have been written on the subject by German physicists.

An important point to bear in mind is that a fluorescing body is self-luminous and, like a glow-worm, it is a source of light. This "cold light" is the most efficient form of lighting, for there is no accompanying waste of energy in the production of unwanted heat. It is the lighting of the future.³ Now-a-days, for example, we strike a match for two totally different purposes—to shine a light or to light a fire. In one case we want light and in the other heat, so we use one and waste the other. Further, the fluorescent color emanates from the body itself; it is not a selective color depending on the nature of the outside illumination. (A rose that is red in white light will be black in green light).

Fluorescence is shown directly in ordinary light by comparatively few substances. Besides fluorspar, we have the mineral-oils (petroleum), including their separation products, paraffin-oil (kerosene) and the heavy lubricating and engine oils, which, as is well known, display blue and green colors on the surface by reflected light. It is also well shown by certain aniline dyes, such as fluorescein and eosin, and by uranium-glass. Usually, however, for most substances the fluorescence is masked by the daylight. The phenomenon is shown to the best advantage in a dark room and using only the dark ultra-violet rays to excite the new radiations. High-tension electric sparks are rich in ultra-violet rays. Sir George Stokes made use of lightning in some of his experiments on fluorescence, but he found that this was not easy to control. Striking results may be obtained with a Ruhmkorff coil or a small transformer stepping up to 4000 volts and sparking between iron terminals. But the most convenient and efficient source of ultra-violet rays is the silica-glass mercury-vapor lamp, which is now much used for the production of "artificial sunlight." A screen of a special kind of dark glass cuts out all the visible rays of light and allows only the ultra-violet rays to pass out of the apparatus.

¹ In 1892 at Cambridge I was fortunately able to attend a short course of lectures on fluorescence given by Sir George Stokes. His experiments, with the simplest and most primitive of apparatus, were performed in a beam of sunlight admitted through a slit in a shuttered window. For each experiment it was necessary to wind down the heavy shutter and each time solemnly to wind it up again. He continued to talk in his feeble voice while grinding away at the winch-handle of the creaking rack and pinion, with the result that very little was heard of his lectures. When I offered to help the feeble old man in this laborious operation I was severely told "Young man, keep your place."

² Some of Dr. Gladstone's original materials were sent to me by his daughter, Miss Florence M. Gladstone, only a fortnight before her death in July, 1928.

³ Fluorescence may be excited by several different methods. The radioactive method by mixing a radium salt with a luminous paint is much used for watch dials. The method with a mercury-vapor lamp, although very convenient for experimental purposes and for a small display, would be very wasteful economically for lighting on a large scale.

While on a visit in 1924 to the famous mineral locality of Franklin Furnace in New Jersey I was much interested in a simple method used by the New Jersey Zinc Company for the quick detection of willemite (zinc silicate), which is an abundant mineral in the zinc ores at that locality. In several of the laboratories and offices there was fixed to the wall in a dark corner a small apparatus giving a high-tension spark which could be switched on from the lighting circuit. A piece of ore held beneath the spark showed up any willemite present by a vivid green fluorescence. Some very pretty effects were obtained; for example, specks of pale green willemite embedded in snow-white calcite glowed as brilliant green spots in a crimson background. This simple test I thought might be applied to the zinc ores of Broken Hill in Northern Rhodesia. In these mines there are large quantities (over 100,000 tons) of a peculiar "yellow rock" or "yellow waste" carrying up to 33 per cent of zinc oxide, which had never been completely determined mineralogically, although in 1908 I had detected in it some obscure crystals of willemite. These minute crystals when exposed to the ultra-violet rays showed a bright yellow fluorescence, quite different from the brilliant green of the Franklin Furnace willemite. Trying willemites from other localities I found that, while some showed a bright yellow or a dull dark-green fluorescence, most of them showed none at all. Even certain types of willemite from Franklin Furnace were found to be unresponsive.

I was therefore forced to the conclusion that fluorescence in ultra-violet rays is not a sure test for willemite, and I very soon found that the same applies to other minerals. Some specimens of fluor spar show no fluorescence, and this is the case with the single specimen of the Derbyshire "blue John" that I have tried, although I have been told that this variety of fluor spar shows it to perfection. Thinking that the fluorescence might be due to traces of coloring matter present in the mineral, some small perfectly colorless and water-clear crystals of fluor spar from the iron mines of west Cumberland were tried: these displayed a very rich and deep violet fluorescence. On the other hand, some dark-colored specimens from other localities showed no fluorescence.

A set of twenty-three small crystals of diamond from British Guiana, selected to show the range in color and the inclusions in the crystals, was tested in ultra-violet rays. A yellow-green octahedron gave a brilliant fluorescence of the same color, three colorless crystals showed up a good blue, and the rest were unresponsive. Different varieties and specimens of the mineral species corundum also gave varying results. Red gem corundum (ruby) shows a wonderful scarlet glow, and the stone appears to be surrounded by a halo. Exactly the same effect is shown by the artificially made rubies, and also by red spinel of gem quality. Yellow gem corundum gives an orange-yellow fluorescence, but the blue sapphire and the amethystine, green, and colorless gem varieties of corundum are unresponsive. Opals also are capricious. Only the purest of all opals, the colorless and water-clear "hyalite," was found to respond. Specimens from Mexico and from the Kaiserstuhl in Baden gave out a soft sap-green light; but similar specimens from other localities refused to act.

These few examples serve to indicate that extremely variable results are obtained, and it is therefore not surprising that there are many contradictory statements in the literature. Many writers have remarked on the fact that they were unable to obtain the results recorded by previous observers; and indeed in

some cases the same experimenter has not always been able to repeat his own results, probably because he was not using the same materials and under exactly the same conditions. The early workers⁴ were placed at a disadvantage in having only the inconstant sunlight at their disposal. Depending on the time of day or of year, sunlight has to traverse different thicknesses of the atmosphere, and consequently the absorption of the ultra-violet varies and in foggy weather is practically complete. (For this reason a patient for ultra-violet treatment is sent to the mountains rather than to the seaside). The fluorescence of any particular substance is evidently excited by ultra-rays of a certain wave-length or over a certain range of wave-lengths; and unless just the right kind of rays are present no fluorescence is produced. Several writers have given glowing accounts of the behaviour of the mineral pectolite in the ultra-violet rays. I myself have tried various forms of pectolite from different localities, but always with negative results. Again, I read in a book that *æsculin* gives a brilliant fluorescence; but the sample that I obtained refused to act (perhaps because it was labelled "*esculine*"—indicating that it was an old preparation). However, with a new preparation of *æsculin*, obtained simply by pouring boiling water on horse-chestnut twigs, the tea-colored extract showed a beautiful turquoise-blue fluorescence in the ultra-violet.

The selection of suitable materials, or rather of individual specimens, is thus quite haphazard. The majority of my trials have been complete failures. A possible method would be to go round the Mineral Gallery on a dark night with a portable ultra-violet apparatus, and so pick out those specimens which are possessed of the whim to glow up. But quite likely by the morning they would have changed their minds and then refuse to function. Time could scarcely be a factor, but they may be influenced by light, differences of temperature, humidity of the atmosphere, or even by the countless "wireless" waves of all manner of wave-lengths that now permeate everywhere. It would indeed be interesting to find a mineral, or crystal, that fluoresces to, say, "2LO."

Almost without exception fluorescent substances are transparent or at least translucent to light. It appears to be necessary that the rays should penetrate the substance to a certain distance for the effect to be produced. The most remarkable result that I have obtained is with a black opaque specimen of zinc-blende from Tsumeb in South-West Africa. It is a piece of massive granular zinc ore looking much like a lump of coal. This was tried because it shows in a very striking manner the allied phenomenon of triboluminescence (luminescence by rubbing): when it is lightly scratched with a knife-blade it gives streaks of yellow sparks. In the ultra-violet rays it glows with a brilliant fiery yellow like a live coal. When the specimen is lightly touched with the finger the merest invisible trace of the substance is picked up, but sufficient to give a good glow. Zinc-blende is quite a common mineral, but only certain specimens from Tsumeb and a pale-colored variety from Beaver County, Utah, have been found to show the fluorescent glow.

Some substances fluoresce only in the solid state, others only in the liquid state

⁴ My own tests have been made under what I believe to be more constant conditions, using a Hanovia silica-glass mercury-vapor lamp at 1 ampère and 220 volts, with a dark glass screen passing ultra-violet rays of wave-lengths about 390 to 310 μ . These longer ultra-violet rays can pass through several layers of glass, but I have made no quantitative measurements.

or in solution, whereas the metal sodium fluoresces in the gaseous state. Other substances show up only when their solution is painted on white paper or when used as dyes on fabrics. Often also the presence of some other substance is necessary. Artificially prepared willemite (zinc silicate) shows no fluorescence when chemically pure; but the property is strongly brought out by the addition of a small amount of manganese. (This explains the fluorescence of the Franklin Furnace willemite; but why crystals of willemite found embedded in black manganese ore at the Sable Antelope mine in Northern Rhodesia fail to fluoresce, I cannot understand). The various salts of quinine display their remarkable fluorescence to advantage only in the presence of free acid, the merest trace being sufficient. Many other vegetable alkaloids give strange results, and under the right conditions it is possible to detect the presence of some of these in one part in a thousand million. The behaviour of the wide range of plant products in ultra-violet rays would no doubt afford an even more fascinating study than mere minerals. It was in the alcoholic extract from laurel leaves that Sir David Brewster first discovered in 1834 the phenomenon of fluorescence. A freshly prepared clear leaf-green solution of chlorophyll is remarkable in showing a deep blood-red fluorescence in the ultra-violet (and curiously, the same red color is seen by transmitted light through thicker layers of the solution, but this is a quite distinct phenomenon known as dichromatism).

An exhibition case to illustrate the fluorescence of minerals (and some other substances) in ultra-violet rays has been fitted up in one of the wall-cases in the corridor at the entrance to the Mineral Gallery of the Natural History Museum at South Kensington, London. This is probably the first public exhibit of the kind, and during the August Bank Holiday week it attracted thousands of visitors. Marvellous changes in color effects are produced by simply pressing a button outside the case. The specimens are first seen in ordinary light with inside electric lighting ("linolight"). When the button of the two-way switch is pressed, this changes over to ultra-violet rays, which are produced by a Hanovia "artificial sunlight" mercury-vapor lamp fitted with a dark screen to cut out all the visible light rays, allowing only the dark ultra-violet to fall on the specimens. Large groups of fluorspar crystals shine up with a wonderful bluish-violet glow, willemite and autunite with a brilliant green, zinc-blende with a golden yellow, white calcite with a rose-red, etc. When the spring-switch is released this fairyland of glowing colors suddenly vanishes.

The case has been painted with a dark grey background, care being taken to avoid a fluorescent paint. Labels for each specimen have been painted with a white fluorescent paint (zinc white) on dark grey card, and these are easily read in the two illuminations. Even in the lighted corridor the effect is very striking; but of course still better results would be obtained in a dark room, though this would be less suitable for public exhibition.

Chemically germanium is closely related to tin and Prof. Papish of Cornell University has detected this element in nearly all cassiterites examined but it is present only in traces. The search for germanium is being extended to a number of minerals occurring in pegmatites and veins. Thirty-four specimens of topaz, examined spectrographically, from twenty-seven different localities were found to contain germanium. Topaz from Schneckenstein, Saxony, and from Zinwald, Bohemia, contained only traces but the majority of specimens from other localities

showed quite a number of spectral lines of the element. Prof. Papish is now engaged in attempting a *quantitative* determination of germanium in topaz.

Dr. W. F. Foshag, of the division of mineralogy of the U. S. National Museum, has been made a corresponding member of the Sociedad Científica "Antonio Alzate" of Mexico.

The Roebing collection of the National Museum has acquired by purchase an unusual platinum nugget from the Choco district, Colombia. It weighs $17\frac{1}{4}$ troy ounces and shows associated chromite in numerous places on its surface.

PROCEEDINGS OF SOCIETIES

NEW YORK MINERALOGICAL CLUB

Minutes of the November Meeting

A regular monthly meeting of the New York Mineralogical Club was held at the American Museum of Natural History on the evening of November 21, 1928, under the chairmanship of the president, Dr. Herbert P. Whitlock. About forty-five members and visitors attended.

Messrs. William P. Hewitt, J. P. H. Marker, and Leo H. Norodny of New York City, Mr. R. C. Neuendorffer of North Tarrytown, N. Y., Col. William Boyce Thompson of Yonkers, N. Y., and Mr. E. C. Doremus of Boonton, N. J., were elected to membership.

Mr. Morton reported a successful Club excursion to the quarries at Paterson, N. J., on Election Day, Nov. 6th. Over thirty persons attended and about twenty different mineral species were found.

The Club was then addressed by Mr. Wilbur G. Valentine, of Columbia University, on *The New Ore Body at Cananea, Mexico*. This ore deposit is interesting for its peculiar crucible shape and zoned structure. The principal minerals are bornite, chalcopyrite, molybdenite, pyrite, and quartz. The deposit occurs in a quartz-porphry intrusive into volcanic rocks. It is apparently entirely unconnected with any feeder or channel of supply from below.

The origin of the ore body is very obscure. It has been ascribed to magmatic differentiation and also to deposition from solutions after the formation of the quartz-porphry. Objections to both theories were presented. Sinking of the surface has also been invoked by Locke to account for the unusual shape.

The lecture was illustrated by lantern slides and by a large number of specimens of the ore. In addition to these exhibits a specimen showing parallel crystals of rose quartz from Bedford, N. Y., was displayed by Mr. Weidhaas.

HORACE R. BLANK, *Secretary*

PHILADELPHIA MINERALOGICAL SOCIETY

Academy of Natural Sciences, November 1, 1928

A stated meeting of the Philadelphia Mineralogical Society was held on the above date with the president, Mr. Trudell, in the chair. Twenty-seven members and twenty visitors were present. The name of Mr. Charles M. B. Cadwalader was presented for active membership.