THE PHOTO-LUMINESCENCE* OF ILLINOIS FLUORITE AND CERTAIN ZINC MINERALS AND ASSOCIATED SPECIES FROM THE JOPLIN, MISSOURI, DISTRICT

E. Mitchell Gunnell

Introduction

During the course of laboratory studies made at Washington University, St. Louis, Missouri, early in 1931, the writer examined a series of minerals, among which were a number of specimens of fluorite from Hardin County, Illinois, and several zinc minerals with their associated gangue species from the Joplin, Missouri, district. The object of this study was to observe such luminescence as might be activated by ultra-violet rays. The purpose of this paper is to give the results of these tests and to briefly survey some of the previous literature on the luminescence of these particular minerals.

The apparatus used to produce the activating radiation consisted of a poly-metallic carbon arc lamp housed in an insulated light-tight box, the latter being equipped with a filter-glass window placed directly in front of the arc itself. This type of apparatus is not new to investigators, a similar arrangement having been described by Andrews[1] in 1925. Eveready Therapeutic "C" carbons,[2] a poly-metallic cored type designed to produce a maximum radiation in the upper region (between 3200 and 4000 Å. units) of the ultra-violet spectrum, were employed as electrodes. A filter glass of the Corex A, UV Transmitting Red Purple type,[3] allowing passage only to wave-lengths between 2900 and 2800 Ångstrom, was used to absorb the interfering constituents of visible light produced by the arc. This apparatus operated on alternating current and proved to be both compact and efficient.

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* By "photo-luminescence" is meant either the fluorescence or the phosphorescence excited by ultra-violet rays of the particular wave-lengths employed in these tests. This infers the possibility of a specimen that is negative to one part of the ultra-violet spectrum exhibiting luminescence when exposed to another part of the same spectrum. Few investigators appear to have taken cognizance of this possibility.

[1] Andrews, W. S., The Production of Fluorescence and Phosphorescence by Radiations from the Carbon Arc Lamp. *Gen. Elec. Rev.*, **28**, 9, 659–661, 1925.

[2] Manufactured by the National Carbon Company, Inc., of Cleveland, Ohio.

[3] Manufactured by the Corning Glass Works of Corning, New York.

THE FLUORESCENCE OF ILLINOIS FLUORITE

Fluorite of two quite distinct types is obtained in southern Illinois, the massive cleavable "vein" spar mined at and near Rosiclare, and the crystallized "blanket" spar from the Spar Mountain and Crystal Mines near Cave-in-Rock. The fluorite at the former place occurs along a nearly vertical fault plane, while that at the Cave-in-Rock mines lies in closely-grouped, nearly horizontal sheets coincident with, and evidently replacing, Mississippian limestone of Chester age.[4] While occasional well-shaped crystals are met with in the fault vein workings, the bedded deposits in particular contain abundant crystals of great size and beauty of color. Some of these rival in all respects the long-famous specimens from Durham, England, seen in most mineral cabinets.

The specimens of fluorite tested were selected from a large quantity of material collected as best exemplifying the wide range in color exhibited by the Illinois occurrences. A peculiar feature observed in many crystals from the Spar Mountain Mine was the zoning of the characteristic deep violet to purple color towards the extreme outer surfaces, the interior of such crystals being devoid of colorization. The Rosiclare specimens, generally, do not show such concentration of the purple color, but evenly distributed bands of violet hue are sometimes noted in them.

No definite relationship between the colors of the crystals and their ultra-violet luminescence was here discovered. There was noted, however, a general tendency for the lighter colored specimens—colorless, white, and green—to exhibit the brightest fluorescence. Also, specimens of a blue to bluish-violet color were strongly fluorescent, being comparable both in color and luminescence to certain specimens from Weardale, Durham, England. Crystals of a yellow color gave negative results when exposed to the ultra-violet light, although hardly enough specimens of this color were tested to justify any definite statement of the invariability of this relationship.

A peculiar fluorescence worthy of record was observed in a greenish-yellow crystal from the Spar Mountain Mine. The mass of the crystal exhibited only a weak bluish fluorescence during exposure to the ultraviolet rays, but along closely grouped planes parallel to the cube $\{100\}$ faces a most brilliant yellowish-white

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[4] For a complete geological description of the Illinois fluorite deposits, see Bain, H. F., The Fluorspar Deposits of Southern Illinois: *U. S. G. S., Bull.* **255,** 1905.

fluorescence was observed. The fluorescence of each of these planes appeared to emanate from countless minute inclusions arranged in zones within the crystal. Specimens of fluorite with petroleum inclusions have been found at several of the mines in the Rosiclare area, notably the Hillside Mine.[5] It seemed quite probable to the writer that the fluorescence of this particular crystal might be due to such inclusions of petroleum, and in order to test this conjecture several specimens containing visible petroleum inclusions were subjected to the radiation. An identical luminescence was actually observed, the petroleum inclusions showing a bright yellowish-white fluorescence. This similar behavior would appear to justify the belief that the fluorescence of the large crystal was due to inclusions of petroleum. Engelhardt[6] examined a specimen of rock salt from Starunia in thin section under a luminescence-microscope and noted that the petroleum inclusions present exhibited a very strong yellow fluorescence.

Although Engelhardt made the statement that organic compounds must be regarded as being responsible for the fluorescence of fluorite,[7] it would now appear, according to the recent investigation of Tanaka,[8] that in many instances the rare elements samarium, yttrium, thallium, and others, are the chief activating agents. Engelhardt's conclusion is probably true for certain specimens of fluorite, as for example the one just described, but the rare element theory seems to offer a better explanation for most fluorescent fluorites. The results of Tanaka's work is corroborated by the earlier work of Urbain,[9] who found that rare earth elements were responsible for the cathodo-luminescence of fluorite. Humphreys[10] in 1904 examined a large number of fluorites in order to ascertain the distribution of yttrium and ytterbium in this mineral, and observed that the three specimens richest in both elements were

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[5] Pough, F. H., The Fluorite Deposits of Southern Illinois and Kentucky: *Rocks and Minerals*, **23**, 7, 14–16, 1932.

[6] Engelhardt, E., Lumineszenzerscheinungen der Mineralien im ultra-violetten Licht: *Inaugural-Dissertation*, University of Jena, page. 37, 1912.

[7] *Ibid.*, page 34.

[8] Tanaka, T., On the Active Agents in Luminescent Fluorspars and in Corundum and Spinel. *J. Opt. Soc. Am. & Rev. Sci. Instr.*, **8**, 501–510, 1924.

[9] Urbain, G., Recherche des elements qui produisent la phosphorescence dans les mineraux. Cas de chlorophane, Variete de fluorine. *C. R. Acad. Sci.*, **143**, 825–827, 1906.

[10] Humphreys, W. J., On the Presence of Yttrium and Ytterbium in Fluor-Spar. *Astrophys. J.*, **20**, 266–272, 1904.

highly thermo-luminescent. Morse[11] in 1906 investigated the possible relationship of color in fluorites to optical properties, especially luminescence, and concluded that the organic substances, which at least in part cause the color, have nothing to do with the fluorescence and thermo-luminescence of this mineral.

THE PHOTO-LUMINESCENCE OF CERTAIN ZINC MINERALS AND ASSOCIATED SPECIES FROM THE JOPLIN, MISSOURI, DISTRICT

The materials tested were mostly from the various mineralogical collections belonging to Washington University, and included eleven specimens of sphalerite, ten of smithsonite, eleven of hemimorphite, twenty-one of calcite, and six of dolomite. All were selected to represent the range of color, structure, and texture within each species as it occurs in the Joplin area. Although all these specimens were known positively to have come from that locality, more accurate labels than simply "Joplin, Missouri" were available for only a few of them.

Since luminescent phenomena depend upon selective absorption of ultra-violet rays and their re-emission as visible light, metallic and semi-metallic minerals which are wholly or nearly opaque to such rays cannot exhibit this property. This principle automatically disposes of the more metallic varieties of sphalerite, such as "black-jack," "steel-jack," and the like. Since most of the sphalerite mined in the Joplin district is of these dark-covered types, it was considered improbable that photo-luminescence would be observed to any high degree in this mineral. However, since luminescent sphalerites are known from several other domestic and foreign localities, there was a possibility that specimens of the light red, translucent "ruby-blende," of which magnificent specimens are common in the Joplin area, might show fluorescence. These tests, however, did not reveal a single sensitive specimen of sphalerite from this locality. Tribo-luminescence has been observed in sphalerites from many places and several of these are also known to exhibit fluorescence in ultra-violet rays.[12] Regarding the cause of

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[11] Morse, H. W., Studies on Fluorite: *Proc. Am. Acad. Arts Sci.*, **41**, 585–613, 1906.

[12] Tribo-luminescent sphalerites from (1) Franklin Furnace, New Jersey, (2) Horn Silver Mine, Beaver County, Utah, (3) Mariposa County, California (phosphorescent only), and (4) Tsumeb, South West Africa. These specimens, with the exception of that from California, exhibited a brilliant orange fluorescence, while the color of the tribo-luminescence of all was an orange-red.

the luminescence of this mineral, it is well known that the white variety "cleiophane," found at Franklin Furnace, New Jersey, is generally manganiferous, and its brilliant orange-red fluorescence has been attributed to the presence of this element. Synthetic zinc sulphide has been prepared with manganese as the active ingredient, and the spectrum of its tribo-luminescence corresponded very closely with that of the natural mineral.[13] This indicates that the luminescence of certain sphalerites may be due to slight quantities of manganese, while iron—suggested as another possible active ingredient—has invariably destroyed the luminescence of synthetic zinc sulphides.[14] From the negative results of the writer's observations on the behavior of Joplin sphalerites under ultra-violet light, it would appear that the impurities present are detrimental to the production of luminescence in material from this particular area.

Smithsonite from the Joplin region proved to be in all cases except one both fluorescent and phosphorescent upon exposure to the ultra-violet light. The one inactive specimen was cavernous and highly ferruginous. The fluorescence of smithsonite was generally strong and of a white or yellow color, but in one specimen labelled "Jasper County, Missouri," it was a pale green. The phosphorescence was a pale green in all cases and while distinct, it was of very short duration. Engelhardt noted a strong greenish-white fluorescence in five specimens of smithsonite from various European localities,[15] and attributed this property to the presence of organic compounds.[16]

Hemimorphite from the Joplin district was invariably luminescent, and with only one exception—a group of white crystals from Granby—exhibited both fluorescence and phosphorescence. The fluorescence was either light yellow, bluish-white, or light green in color, and varied markedly in intensity. Specimens that fluoresced with a yellow color did so brilliantly, while the bluish-white fluorescence was invariably weak and of short duration. A white botryoidal specimen from Joplin exhibited the strongest fluorescence of any hemimorphite tested. These variations in intensity and character of fluorescence correspond quite closely with the results ob-

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[13] Nelson, D. M., Photographic Spectra of Tribo-luminescence. *J. Opt. Soc. Am. & Rev. Sci. Instr.*, **12**, 207–215, 1926.

[14] Mac Dougall, E., Stewart, A. W., and Wright, R., Phosphorescent Zinc Sulphide. *Trans. Chem. Soc. J.*, **111**, 663–683, 1917.

[15] Engelhardt, E., *op. cit.*, page 19.

[16] *Ibid.*, page 34.

tained by Engelhardt[17] on six specimens of hemimorphite from various European localities. It appears that this author includes this mineral in a series of luminescent minerals secondarily formed from aqueous solutions, the luminescence of which he believes to be due to organic impurities.

Only six of the twenty-one specimens of Joplin calcite that were tested exhibited fluorescence, two with a strong rose color, two with an intense yellow to yellowish-white, one with a very strong orange, and one with a weak green tint. No relationship was observed between the color of a crystal and its luminescence; in fact, specimens of the yellow color generally found by Headden[18] to be phosphorescent after insolation were invariably negative to the radiation here employed. A cleavage piece of deep violet color exhibited the most intense fluorescence noted in this mineral; it was of a reddish-orange hue. The phosphorescence of these luminescent calcites was always weak, and generally of a dull white tint. Headden at first believed the luminescence of the yellow calcite from Joplin to be due to contamination by a rare earth oxide of the yttrium group[19]; later he was of the opinion that such sensitivity was due primarily to a particular atomic structure.[20] His analyses failed to detect any organic coloring matter in these calcites, thus contrasting with Engelhardt's belief that the luminescence of calcite was due to the presence of organic compounds.[21] Tanaka[22] investigated the question of the activating impurities of cathodo-luminescent calcite, and stated that manganese was the chief agent, with yttrium as a less common one.

Dolomite was entirely negative. Engelhardt[23] noted a weak red fluorescence in several dolomites, a weak dark blue fluorescence in others, and a strong whitish fluorescence in specimens from Sternenberg and Mt. Vesuvius. According to Tanaka[24] manganese is the chief activating agent in cathodo-luminescent dolomite.

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[17] *Ibid.*, page 24.

[18] Headden, W. P., Some Phosphorescent Calcites from Fort Collins, Colorado, and Joplin, Missouri. *Am. J. Sci.*, **21**, 301–308, 1906.

[19] *Ibid.*, page 308.

[20] Headden, W. P., The Relation of Composition, Color, and Radiation to Luminescence in Calcites. *Proc. Colo. Sci. Soc.*, **11**, 399–434, 1923.

[21] Engelhardt, E., *op. cit.*, page 34.

[22] Tanaka, T., On the Active Agents in Luminescent Calcites, Aragonites, and Dolomites. *J. Opt. Soc. Am. & Rev. Sci. Instr.*, **8**, 411–418, 1924.

[23] Engelhardt, E., *op. cit.*, page 19.

[24] Tanaka, T., *op. cit.*, page 418.