

STUDIES IN MINERAL FLUORESCENCE

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ABSTRACT

Availability of an unusual instrument giving monochromatic radiant energy of a higher order of magnitude than hitherto possible has permitted the pursuit of this research. Specimens of forty-three minerals representing twenty-one distinct species have been examined in ultraviolet radiation and a tentative relationship between the frequency of the incident radiation and the frequency of the reradiated light has been determined.

Fluorescence in minerals has been a commonly known phenomenon for many years, and during the last five years mineralogists have had access to various sources of ultraviolet radiation, as for example the argon tube. This has resulted in the demonstration of fluorescence in an increasingly large number of the mineral species and in the awakening of wide-spread interest in this property.

To obtain a range of frequencies in the ultraviolet the practice of other workers has followed three methods. The first has been to remove the plate holder from a prism, or diffraction grating spectrograph, and to allow monochromatic radiation to fall upon the specimen. This process is subject to great calibration difficulties and with interference from scattered light of other frequencies present nearby, especially the visible lines. While this method is suitable for chemical compounds which may be spread out in a thin layer on a glass plate, it is unsatisfactory for examination of the rather rough surfaces of minerals, particularly those species which lose the characteristic fluorescent response when pulverized.

A second way to secure monochromatic radiation has been through the use of specially made glass filters which allow only certain ranges of frequencies to pass. Here one is subject to the obvious difficulty of getting a sufficiently wide assortment of frequencies having sharp cut-off limitations, although the radiation intensity is comparatively strong.

Monochromators using prisms made from natural crystals of quartz seriously limit the transmitted radiant energy because of the necessary size restriction of the cut prisms.

The type of paper usually found in the literature makes it evident that investigators have been limited in facilities for measuring fluorescent responses under a suitable range of frequencies.

The reason for the study, the results of which appear in this paper, has been the availability, through the courtesy of its designer, Mr. Frank A. Benford of the Research Laboratory of the General Electric

Company, at Schenectady, N.Y., of an unique monochromator of the following construction.

Fused quartz prisms weighing approximately seven and ten pounds each, which have optical surfaces of the order of ten and fifteen centimeters on a side respectively, turn on their axes by means of revolving tables, being actuated simultaneously. A revolving drum scale is attached permitting the setting of the instrument at the desired frequency. There are two sets of quartz collimating lenses. The light source is a mercury vapor arc in quartz operating at 150 volts and 3.6 amperes, being kept at constant temperature by a stream of air directed upon it, thus maintaining a constant energy output.

It is important to note the special design of the fused quartz prisms. They are not entirely free from bubbles and striae and therefore scattered light is present in small amounts. But by an ingenious design of their angles it has been possible to divert from the optical system much energy from those wavelengths longer than the one in use at any given time. These are naturally the wavelengths of greater energy and would be especially undesirable lest they mask the fluorescent effect when tests are made near the visible range.

The monochromator is unique primarily in that it gives radiant energy of a much greater order of magnitude than that of instruments heretofore in use, enabling the easy examination of large irregular surfaces at a given wavelength.

It was decided to make the selection of minerals as complete as possible, hence a collection of several thousand specimens was tested for fluorescence with both mercury lamp and disruptive iron spark radiations. Forty-three specimens representing twenty-one distinct species were finally chosen for study. Each mineral was examined through the range of ultraviolet frequencies available from the monochromator and the following table prepared (Table 1).

TABLE 1

Wavelength	Relative energy (% of lamp input)	Sphaerite ZnS Tsumeb, Africa	Fluorite CaF ₂ St. Lawrence, Co., N. Y.	Fluorite (brown) CaF ₂ Ohio	Fluorite (yellow) CaF ₂ Ohio	Fluorite CaF ₂ Montana	Fluorite (blue) CaF ₂ England	Fluorite (green) CaF ₂ England	Semi-opal SiO ₂ · nH ₂ O Nevada
2652Å	.0005	3 orange	0	3 brown	1 brown-green	2 blue	2 blue-violet	2 violet	6 green
2700Å	.0008	4 orange	0	3 brown	1 brown-green	2 blue	2 blue-violet	2 violet	7 green
2752Å	.0010	5 orange	0	3 brown	1 brown-green	2 blue	2 blue-violet	2 violet	7 green
2804Å	.0016	5 orange	0	3 brown	2 brown-green	2 blue	3 blue-violet	2 violet	8 green
2894Å	.0010	5 orange	0	3 brown	2 brown-green	1 blue	3 blue	3 blue	6 green
2925Å	.0005	5 orange	0	3 brown	2 brown-green	2 blue	4 blue	4 blue	6 green
2967Å	.0025	5* orange	0	4 brown	3 brown-green	3 blue	5 blue	4 blue	6 green
3024Å	.0063	5* orange	3 blue	4 brown-green	3 brown-green	4 blue	6 blue	5 blue	7 green
3128Å	.0130	6* orange	4 blue	5 brown-green	4 brown-green	4 blue	7 blue	6 blue	7 green
3341Å	.0030	6* orange	4 blue	3 brown-green	2 brown-green	5 blue	8 blue	8 blue	5 green
3650Å	.0235	8* orange	5 blue	5 brown-green	4 brown-green	7 blue	9 blue	9 blue	6 green
4047Å	.0100	6* orange	5 blue	5 brown-green	2 brown-green	?	8 blue	8 blue	5 green
4358Å	.0140	6* orange	?	?	?	?	?	?	?

* Phosphorescence.

? Response doubtful.

TABLE 1 (Continued)

Wavelength	Hyalite $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ Mexico	Hyalite $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ North Carolina	Ruby Al_2O_3 North Carolina	Brucite $\text{Mg}(\text{OH})_2$ Texas, Pa.	Brucite $\text{Mg}(\text{OH})_2$ Hoboken, N.J.	Calcite CaCO_3 Montana	Calcite CaCO_3 Chisos Mtns., Texas	Calcite CaCO_3 Imperial Co., Calif.	Calcite (green) CaCO_3 California
2652Å	8 green	8 blue-green	0	0	1 light blue	0	5* blue	0	0
2700Å	7 green	8 blue-green	0	0	1 light blue	0	2* blue	0	0
2752Å	7 green	7 blue-green	0	1 light blue	1 light blue	0	2* blue	0	0
2804Å	8 green	8 blue-green	0	1 light blue	1 light blue	0	4* blue	0	1 pink
2894Å	6 green	7 blue-green	0	1 light blue	1 light blue	0	4* blue	0	1 pink
2925Å	5 green	7 green	0	2 light blue	2 light blue	0	3* blue	0	1 pink
2967Å	6 green	7 green	0	2 light blue	2 light blue	0	5* blue	0	1 pink
3024Å	7 green	8 green	0	3 light blue	3 light blue	0	5* blue	1 red	2 red
3128Å	7 green	8 green	0	3 light blue	4 light blue	0	4* blue	2 red	3 red
3341Å	5 green	7 green	0	3 light blue	4 light blue	0	0	2 red	3 red
3650Å	6 green	7 green	4 red	6 light blue	7 light blue	1? red	7 pink	4 red	5 red
4047Å	2 green	6 green	5 red	3? light blue	3? light blue	?	4 pink	5 red	5 red
4358Å	?	?	?	?	?	?	?	?	?

* Phosphorescence.

? Response doubtful.

TABLE 1 (Continued)

Wavelength	Calcite CaCO ₃ Sterlingbush, N.Y.	Calcite CaCO ₃ Saxony	Calcite CaCO ₃ Devonshire, Eng.	Calcite CaCO ₃ Franklin Furnace, N.J.	Calcite CaCO ₃ Franklin Furnace, N.J.	Calcite CaCO ₃ Franklin Furnace, N.J.	Dolomite (Ca, Mg)CO ₃ Baden, Germany	Gay-Lussite CaCO ₃ ·Na ₂ CO ₃ ·5H ₂ O Washington	Kunzite LiAl(SiO ₃) ₂ California
2652Å	0	2 pink	1 pink	6 pink	3 pink	4 orange- pink	2 green	0	0
2700Å	0	3 pink	2 pink	6 pink	3 pink	4 orange- pink	3 green	0	0
2752Å	1 pink	4 pink	3 pink	6 pink	4 pink	6 pink	3 green	3 pink	0
2804Å	5 pink	5 pink	4 pink	8 pink	4 pink	6 pink- orange	3 green	3 pink	0
2894Å	5 orange- pink	5 pink	4 pink	7 pink	4 pink	6 pink- orange	1 green	2 pink	0
2925Å	4 orange- pink	6 pink	4 pink	7 pink	5 pink- orange	7 orange	1 green	3 pink	0
2967Å	6 orange- pink	7 pink	5 pink	7 orange- pink	5 orange	7 orange	1 green	3 pink	0
3024Å	7 orange- pink	7 pink	7 pink	8 orange	7 orange	8 orange	1 green	4 pink	0
3128Å	5 orange- pink	8 pink	8 pink	9 orange	8 orange	9 orange	0	5 pink	0
3341Å	1 orange- pink	3 pink	2 pink	7 orange	4 orange- pink	6 orange	0	4 pink	1 orange
3650Å	2 orange- pink	3 pink	4 pink	5 orange	6 orange- pink	7 pink- orange	0	4 pink	4 orange
4047Å	?	2 pink	8 pink	5 orange	7 orange- pink	7 orange- pink	0	?	4 orange
4358Å	?	?	?	?	?	?	?	?	?

* Phosphorescence.

? Response doubtful.

TABLE 1 (Continued)

Wavelength	Pectolite $\text{HNaCa}_2(\text{SiO}_3)_3$ Paterson, N.J.	Sodalite $\text{Na}_4(\text{Al, Cl})\text{Al}_2(\text{SiO}_4)_3$ Brewig, Norway	Hackmanite Complex Silicate Bancroft, Ontario	Willemite Zn_2SiO_4 Franklin Furnace, N.J.	Willemite (crystals) Zn_2SiO_4 Sterling, N.J.	Scapolite Complex Silicate Quebec	Wavellite $4\text{AlPO}_4 \cdot 2\text{Al}(\text{OH})_3 \cdot 9\text{H}_2\text{O}$ Devonshire, Eng.	Autunite $\text{Ca}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ Chesterfield, Mass.	Autunite $\text{Ca}(\text{UO}_2)_2\text{P}_2\text{O}_8 \cdot 8\text{H}_2\text{O}$ Grafton, N.H.
2652Å	0	0	0	8 green	4 green	3 yellow- orange	0	5 green	6 green
2700Å	0	0	0	8 green	4 green	4 yellow- orange	0	5 green	6 green
2752Å	0	0	0	9 green	4 green	4 yellow- orange	0	5 green	6 green
2804Å	0	0	0	9 green	4 green	5 yellow	0	6 green	7 green
2894Å	0	0	0	9 green	3 green	5 yellow	0	6 green	7 green
2925Å	0	0	0	9 green	2 green	5 yellow	0	6 green	8 green
2967Å	0	0	1 pink	9 green	2 green	6 yellow	0	7 green	8 green
3024Å	0	0	1 pink	9 green	2 green	7 yellow	1 green	7 green	9 green
3128Å	0	0	2 pink	8 green	0 green	7 yellow	1 green	7 green	9 green
3341Å	0	0	2 pink	7 green	0 green	7 yellow	1 green	4 green	8 green
3650Å	1 orange	4 pink	5 orange- pink	8 green	0 green	10 yellow	3* light green	6 green	9 green
4047Å	0	4 pink	6 orange- pink	0 green	0 green	9 yellow	1* light green	0 green	7 green
4358Å	?	?	5 orange- pink	5 green	0 green	9 yellow- orange	? green	? green	? green

* Phosphorescence.

? Response doubtful.

TABLE 1 (Continued)

Wavelength	Autunite Ca(UO ₂) ₂ P ₂ O ₇ ·8H ₂ O Autun, France	Barite BaSO ₄ Przibram, Bohemia	Barite BaSO ₄ Schemnitz, Hungary	Anglesite PbSO ₄ Phoenixville, Pa.	Gypsum CaSO ₄ ·2H ₂ O Bennett Co., S.D.	Gypsum CaSO ₄ ·2H ₂ O Chicago, Ill.	Scheelite CaWO ₄ Bohemia	Scheelite CaWO ₄ California
2652Å	7 green	1 blue	0	1 green- yellow	0	0	4 blue	8 blue
2700Å	7 green	1 blue	1 light green	1 green- yellow	1 yellow- orange	0	5 blue	7 blue
2752Å	7 green	1 blue	1 light green	2 green- yellow	1 yellow- orange	0	6 blue	7 blue
2804Å	8 green	1 blue	1 light green	2 green- yellow	1 yellow- orange	1 blue	7 blue	8 blue
2894Å	8 green	0	1 light green	2 green- yellow	1 yellow- orange	0	3 blue	6 blue
2925Å	8 green	0	1 light green	2 green- yellow	1 yellow- orange	0	1 blue	4 blue
2967Å	8 green	0	2 light green	3 green- yellow	1 yellow- orange	1 blue	1 blue	2 blue
3024Å	9 green	1 blue	2 light green	3 green- yellow	2 yellow- orange	1 blue	0	0
3128Å	9 green	2 blue- green	2 light green	4 green- yellow	3 yellow	2 blue	0	0
3341Å	8 green	1 green	1 light green	3 green- yellow	2 yellow	1 blue	0	0
3650Å	9 green	2 yellow- cream	1 light green	5 green- yellow	4 orange- yellow	2 blue- green	0	0
4047Å	8 green	0	0	2 yellow	3 orange- yellow	?	0	0
4358Å	7? green	0	0	?	?	?	?	?

* Phosphorescence.

? Response doubtful.

With reference to these observations, the subject of the intensity of fluorescent light from the specimen deserves primary consideration. For a given specimen the relationship between incident radiant energy and fluorescent light energy is not a linear one. This fact may be made evident by the simple experiment of doubling the incident energy at a given frequency and observing the increase in fluorescence. This may be appreciable but fluorescence will rarely approximate twice its former value. Therefore, large variations in the strength of a given line produce rather small changes in fluorescent light from the specimen. There is probably some phenomenon of absorption operative here. To establish this relationship is difficult. Variations of incident energy from the monochromator with each successive spectral line make it, therefore, of little avail to measure fluorescent response in absolute units. Thus, instead of using a photocell or thermopile for quantitative measurements, the table is derived from visual estimation.

A zero rating indicates no fluorescence while optimum brightness is recorded as ten units. Thus "1" indicates a barely discernible fluorescence while "5" or "6" is perhaps the average value. Color is indicated on the table for each response. Phosphorescence is shown by an appropriate symbol.

It is extremely important always to interpret the recorded intensities as dependent upon the energy of each ultraviolet wavelength.

Attention is first directed to those specimens which undergo color changes. There are nine minerals in which the change is definitely observable. They are:

<i>Minerals</i>	<i>(Incident radiation decreases in frequency)</i>
Fluorite (brown) Ohio	brown to brown-green
Fluorite (blue) England	blue-violet to blue
Fluorite (green) England	violet to blue-violet
Hyalite North Carolina	blue-green to green
Calcite Texas	blue to pink
Barite Bohemia	blue to blue-green to green to yellow-green
Anglesite Phoenixville, Pa.	green-yellow to yellow
Gypsum Chicago, Ill.	blue to blue-green

We note at once an important fact. In every instance above, the wavelength of the fluorescent color varies directly with the wavelength of the incident ultraviolet radiation. In other words, the higher the frequency of the ultraviolet radiation, the higher the frequency of the reradiated energy.

Opposed to this group is a series which tends to show the opposite effect. This is composed of:

<i>Minerals</i>	<i>(Incident radiation decreases in frequency)</i>
Calcite Sterlingbush, N.Y.	pink to orange-pink
Calcite Franklin Furnace, N.J.	pink to orange-pink
Hackmanite Bancroft, Ontario	pink to orange-pink
Scapolite Ontario	yellow-orange to yellow to yellow-orange (?)

Here it would seem as if the incident frequency and reradiated frequency varied in inverse proportion. However, the above four specimens are not clearcut examples, due to the difficulty in describing what really amounts to a slight gradation of shading. This evidence, therefore, is not given extensive consideration.

The third and largest group contains the remaining specimens, those which show no appreciable change in color under the entire range of incident frequencies. It will be noted that a specimen may show fluorescence of but one color under a certain incident frequency, yet fail to respond at all to other nearby incident frequencies which one might expect to produce adjacent spectral colors in the visible range.

Two conclusions may be made in reference to the species examined. The frequency of the fluorescent light is a discontinuous function of the frequency of the incident radiation. Further, within limited regions where specimens show that it is a continuous function, the frequency of fluorescent color varies directly as the frequency of the incident ultraviolet radiation. This mutual variation is not a direct octave relationship nor is it a linear one, for any specimen studied.