

Northwest
Micro Mineral
Study Group

MICRO PROBE



FALL, 2021

VOLUME XIII, Number 4

ALAS!!! NO MEETING SCHEDULED

We were planning to finally meet
In November, but none of the places
we have used recently were willing to
schedule anything until next year.

President's Letter

My storage area is getting full. I have been doing some trading across the US so I have acquired some interesting specimens to share. I hope all of you are also saving up and we make all the tables groan under the weight when we can meet. 🙄

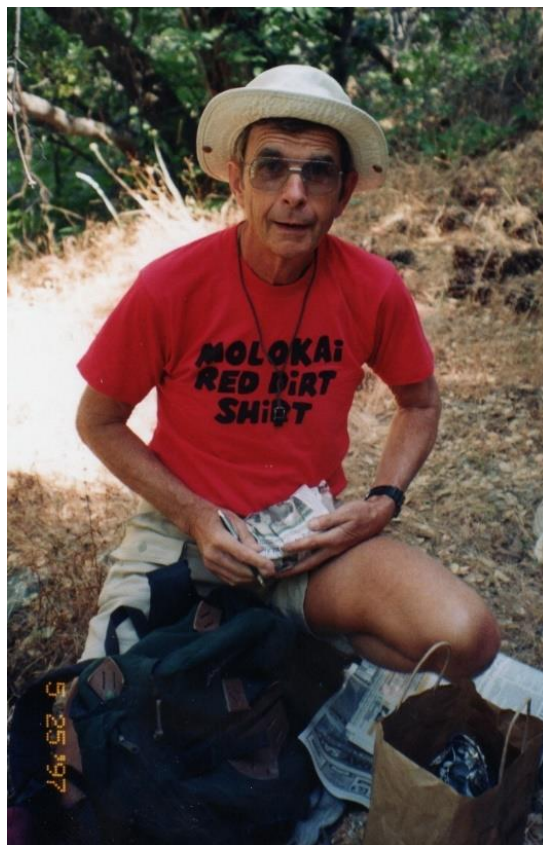
I have tried to schedule a meeting, but I just have not been successful finding a venue that is open for us. I have thought about options even to the point of meeting outside, in a park, and bringing flashlights to use to light up the specimens (I do not think we could get away with a small generator running). Or we could just have a Zoom meeting with presentations (no freebee table 😞).

If anyone has any great ideas about meeting places, please let me know (heesacker@coho.net) and I can try to pull something together for November. Otherwise, we will try again next year in May.

Maybe catch you at a club's Zoom meeting but until then happy collecting and I hope all of you are staying healthy.

Beth Heesacker, *President*

In this issue, we feature a major article about fluorescence that originally appeared in serial form in *The Conglomerate*, the monthly newsletter of the *Baltimore Mineral Society*. It has been enriched with photographs of fluorescent minerals by the editor from his personal collection. I hope you enjoy the comprehensive nature of this article.



IN MEMORY OF William Wise

It is with great sadness that I must report the passing of a great figure in West Coast mineralogy. Bill Wise lost his battle with cancer on June 29, and the mineral community lost a great asset and true friend.

Bill discovered geology and minerals as a teen-ager. He attended Stanford and Johns Hopkins Universities and accepted a faculty position at UC Santa Barbara, where he taught undergraduates and supervised graduate students for over 30 years. He was Russ Boggs' thesis advisor. He was convinced that field work was an essential part of the education of a geologist, and he loved to conduct and participate in field trips.

As a professional geologist, Bill authored numerous papers, including ones announcing new minerals. He was particularly interested in zeolites, and was a great help to Rudy Tschernich in putting together his book, *Zeolites of the World*. He served for many years on the zeolite subcommittee of the Commission on New Minerals and Mineral Names.

But at heart, Bill was a collector and micromounter. He was recognized as such by his induction into the Micromounters Hall of Fame in 1987. He was an active member of the Northern California Mineralogical Association and a regular participant and speaker at the Pacific Micromount Conference in southern California. His talks were informative and entertaining, delivered with just the right touch of humor and always aimed appropriately to the interest and understanding level of his audience.

My memories of Bill involve interacting at meetings, where he always shared interest and encouragement. He took an interest in whatever I was working on and invariably supplied useful information and suggestions. He was a delightful participant at NCMA field trips. He had many many friends, all of whom are going to miss his wisdom, humor and encouragement.

Don Howard

Fluorescence and Phosphorescence

By Al Pribula

Reprinted from the Conglomerate, Baltimore Mineral Society

Part 1: What's the Difference?

Probably all of us have heard the term fluorescence at one time or another, and it's very likely that all of us have fluorescent minerals in our collections (though you may not know it if you haven't tested for this property). And we have probably all seen a display of fluorescent minerals at a mineral show or in a museum, with the amazing "before and after" difference in color caused by shining an ultraviolet light on the samples. Phosphorescence is a less-commonly-heard term, because the phenomenon is much less common as well. To complicate things even further, minerals can also show tenebrescence (changing color when exposed to sunlight), triboluminescence (emitting light when scratched or crushed), cathodoluminescence (emitting light when bombarded with cathode rays (aka electrons)), and thermoluminescence (giving off light when gently heated). (See the references given below for more on those.) So—what's the difference between fluorescence and phosphorescence?

That's a question that can be answered in at least two different ways. Fluorescence was first observed in 1560 in the infusion of a particular type of wood. In about 1820, it was observed for the first time in a mineral specimen (fluorite, probably a sample from an English locality), and it was named after fluorite in 1852. It occurs when a material emits light of a different color (energy) than the light which is incident on it. This emission of light stops when the incident light is removed. Phosphorescence is similar, except that the emission of light continues for at least a short time after the incident light is removed. A phosphorescent material is colloquially said to "glow in the dark." So, it's very possible that you've observed this phenomenon even if you didn't know it by its fancy name.

So, that's the "operational" difference between them. But a deeper answer involves the physical cause of the two phenomena, and the cause of the difference between them. When light hits a sample of matter, a lot of things can occur. The light can simply bounce off and be reflected, and the sample will appear white or colorless. (That's assuming that the incident light is "white;" that is, a mixture of all the "colors of the rainbow," and usually higher and lower wavelengths as well. See the Appendix below for more on light waves.) It can be transmitted through the sample unchanged in energy (but perhaps changing its direction as it enters and exits the sample). It can be absorbed by the sample, causing a chemical change (a so-called "photochemical reaction" such as occurs in the development of traditional camera film or when your skin tans in the sun). If only certain energies in the incident light are absorbed, the sample will often show a color (that of the non-absorbed light, either transmitted or reflected). The light can also be absorbed and then re-emitted. It's this last possibility that's involved in fluorescence and phosphorescence.

The atoms which make up all materials are built up from three major types of smaller particles: protons, neutrons, and electrons. The energies which a sample can absorb or emit are primarily determined by the electrons in the atoms. Atoms join together to form molecules; in atoms and molecules, the energies that the electrons can have are restricted to only certain values. (Fancy term: anything which is restricted to having only certain values is said to be quantized.) An electron in one energy level can absorb energy and jump to another (higher) energy level, absorbing a very specific amount of energy in the process—sort of like walking up a set of steps, as opposed to a sloping ramp. Once an electron is in this higher-energy state (called an excited state), it wants to go back to the lowest-energy state that it can get to. (The lowest-energy state for any system is called its ground state.)

If the electron simply re-emits the same amount of energy it absorbed, that is equivalent to saying that the light was reflected. Sometimes the energy is absorbed and then re-emitted as heat, as when you leave an object out in the sun for a while. If only some of the wavelengths of the light are absorbed, all the others will be transmitted or reflected. Assuming that the sample absorbs only some of the wavelengths in the visible region of the spectrum, the sample will exhibit a color which is the complement of the absorbed light. For example, if a sample absorbs light in the blue-to-violet range, the remaining colors (red, orange, yellow, green) would be transmitted or reflected. If all visible wavelengths are absorbed, the sample will appear black.

But there's another possibility as well. The electrons in the sample can absorb energy, release part of it as heat (although the amount of heat is usually so small that you can't even detect it), then re-emit light of a lower energy (longer wavelength) than the incident light which was absorbed. This is the case for a material which is fluorescent or phosphorescent. In this case, the electron has absorbed enough energy to "jump over" a number of possible intermediate energy levels—kind of like climbing up a flight of steps two or three at a time. When returning to its ground state, the electron can drop to intermediate energy levels (giving off heat as it does so), rather than returning directly to the ground state in one "jump." In order for fluorescence to occur, there must be an appropriate set of energy levels for the electron to occupy so that it can absorb the incident energy. This is determined by what atoms are present, how they are arranged and bonded, etc.

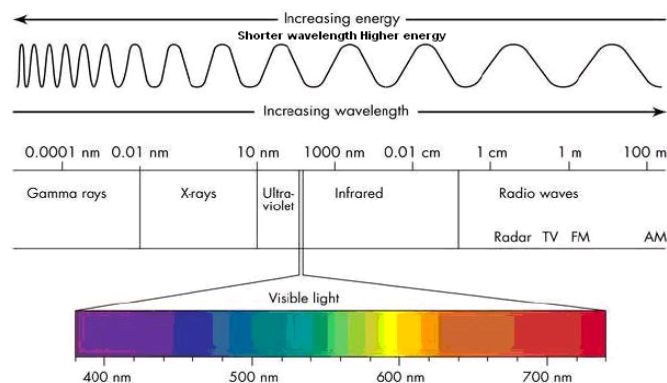
Because some of the energy initially absorbed is emitted as heat, it also means that the light emitted will be of a lower energy (corresponding to a longer wavelength) than the incident light. In the most familiar case, exposing a sample to ultraviolet (UV) light (sometimes referred to as "black light"), which has higher energy (shorter wavelength) than visible light, results in the emission of the lower-energy visible light. (Cases are also known where the absorption of UV light results in emission in the infrared region, lower in energy than visible light.) This means that a sample which may have little or no color in "white" light will suddenly exhibit one or more colors when exposed to UV light. Many samples which do not fluoresce, or fluoresce only weakly when exposed to "long-wave" (i.e., lower-energy) UV light (typically 350-400 nm), will fluoresce (or fluoresce more intensely or even in a different color) when struck by "short-wave" (i.e., higher-energy) UV light (typically 250-350 nm). Fluorescence can also be activated by EM radiation of higher energy than UV light, such as X-rays (this property is used for chemical analysis by X-ray fluorescence (XRF) spectroscopy) or gamma rays.

The mechanism behind phosphorescence is basically the same as for fluorescence, but with an important difference. In this case, the electron gets temporarily "stuck" either at the energy level to which it was initially excited (it is then said to be in a metastable state) or at an intermediate energy level before it returns to the ground state. For fluorescence, the re-emission of the light is essentially instantaneous. That means that the fluorescence will stop when the incident light source is removed. However, for phosphorescence, the emission is delayed by some amount of time while the electron is "stuck," and the sample will continue to "glow" for some time after the incident light source is removed. The lifetime of the phosphorescence is usually fairly short (a couple of seconds), but can be as long as hours or even days.

Most minerals are neither fluorescent nor phosphorescent. A few (such as scheelite, benitoite, and many uranium-containing minerals) are always fluorescent (indeed, this property is sometimes used to locate deposits of these minerals). However, most minerals only exhibit this property when an impurity (an "activator") is present at the proper concentration level, or some structural defect exists which changes the normal electron energies. There are also chemical species (which might be an essential component of the mineral or an impurity) which can hinder or eliminate fluorescence. These are referred to as fluorescence "quenchers." Fluorescence activators and quenchers will be further discussed in the next section.

Appendix: Energy, Frequency, and Wavelength of Light

Light is a form of electromagnetic (EM) radiation; that is, it is energy traveling through space in the form of coupled electric and magnetic fields in the form of waves. This means that the amplitude (height; intensity; brightness) of the field varies in a predictable and regular fashion. Stated differently, there is a series of alternating peaks (high points; maxima) and troughs (low points, minima) in the amplitude of the wave, as shown at the top of the diagram below (*found at image.slidesharecdn.com*).



Any wave can be characterized in a number of ways. The distance between peaks or between troughs is called the wavelength, usually symbolized by the lower-case Greek letter lambda (λ). The diagram above shows the wavelength increasing as you move from left to right. The number of waves (that is, the number of peaks or troughs) passing by a given point in space in a unit of time is called the frequency of the wave, usually symbolized by the lower-case Greek letter nu (ν). (Yeah, I know that it looks like a “v,” but it actually corresponds to the letter “n” in the Latin alphabet.) The distance that the wave travels in a unit of time is the speed of the wave. Mathematically, the product of the wavelength and the frequency of the wave gives its speed:

$$\lambda \cdot \nu = \text{speed}$$

For EM radiation, the speed is a constant (the “speed of light,” symbolized by c), so, for a light wave,

$$\lambda \cdot \nu = c$$

The speed of light is 300,000,000 meters per second, or 186,000 miles per hour. The amount of energy carried by a light wave (symbolized E) is given by product of its frequency and a constant (called Planck’s constant, symbolized by “ h ,” its mathematical value isn’t important here).

Mathematically,

$$E = h \cdot \nu$$

Since frequency and wavelength are related, we can also write

$$E = h \cdot (c/\lambda)$$

Thus it is true that as the wavelength of a light wave goes up, its energy goes down, and *vice versa*. (To be fancy, we say that the energy of a light wave is inversely proportional to its wavelength.)

Human eyes are sensitive to only a very short range of wavelengths of EM radiation, from about .0000004 - .0000007 meters (or 400-700 nanometers (nm), or 4000-7000 Angstrom units (\AA)). Within that range, red light has the longest wavelength, thus the lowest energy. As you progress through the visible spectrum (in the order red, orange, yellow, green, blue, violet), the wavelengths get progressively shorter (as shown above), and the energies correspondingly higher. EM radiation of shorter wavelengths (that is, higher energies) than violet visible light is referred to as ultraviolet (UV) radiation. This is the component of sunlight which causes your skin to darken and burn when exposed for too long a time. EM radiation of longer wavelengths (that is, lower energy) than red visible light is referred to as infrared (IR) radiation. This is not visible with our eyes, but can be sensed as heat. In addition to these, EM radiation of other wavelengths/energies is referred to as gamma rays, X-rays, microwaves (not shown on the above diagram, but with wavelengths between 0.1 and 10 cm, between infrared and radio waves), or radio waves, depending on their wavelength.

A good reference book on fluorescent minerals is Ultraviolet Light and Fluorescent Minerals by Warren, Gleason, Bostwick, and Verbeek. It mostly focuses on which minerals are known to fluoresce and localities where they are found, but also has nice sections on the science behind fluorescence and phosphorescence, and a long discussion of fluorescence activators and quenchers. (Since the book was published in 1995, it's probably somewhat outdated, but it's useful just the same.) Collecting Fluorescent Minerals, by Stuart Schneider, is a bit more recent (2004), but is somewhat light on technical details. It focuses much more on collecting these minerals and on some of the locations where they are found. It's a great source of pictures showing fluorescent specimens—almost 85% of its pages show color photos of actual specimens. The Ultraviolet Guide to Minerals by Gleason has an extensive listing of fluorescent minerals, plus information on identifying the minerals present, but I'm sure that its listing (probably fairly close to complete when published in 1960) is seriously out of date. A general article by Bob Jones on fluorescent minerals was published in the May, 2018 issue of *Rock and Gem* magazine. Mindat lists the fluorescent properties of many minerals, but does not discuss specific localities at which they are found (and, as far as I can tell, you can't use fluorescence as a search category).

Part 2: Fluorescence Activators and Quenchers

In Part 1 above, the differences between fluorescence and phosphorescence were discussed along with a few examples from the mineral kingdom. In that article, mention was made of activators and quenchers. These are chemical components (which might be an essential part of the chemical make-up of the mineral, but which more commonly are present as impurities) which can favor (in the case of activators) or suppress (in the case of quenchers) the fluorescence and/or phosphorescence of a mineral sample. But: A little chemistry interlude first.

Remember that most minerals are made up of ions—that is, particles with a positive or negative electrical charge. These might be just a single atomic nucleus (monatomic ions such as Na^+ , Mg^{2+} , Cl^- , or S^{2-}), or might consist of a group of atomic nuclei bonded together (polyatomic ions such as CO_3^{2-} , PO_4^{3-} , or NH_4^+). Ions with a positive electrical charge are called cations (“cat-eye-ons”), and ions with a negative charge are called anions (“an-eye-ons”). Because of sort-of-but-not-quite-correct use of chemical terminology, there is sometimes confusion as to what exactly a mineral contains. For example, if someone says “siderite and hematite both contain iron,” it does not mean that there are particles or atoms of the element iron present, but rather that they contain iron cations, combined with sufficient anions (CO_3^{2-} and O^{2-} , respectively) to balance the charges out to zero. (That is, to make the material electrically neutral.) Even further confusion can arise if an element (usually, but not always, a metal) can form two or more ions of different charge, as in the case of Fe^{2+} in siderite and Fe^{3+} in hematite. These two ions are referred to as iron(II) and iron(III) (pronounced “iron-two” and “iron-three,” respectively). (Before I, as a chemist, realized that chemical terms were sometimes used in a loosey-goosey way by mineral folks, I was told that an amethyst specimen contained red spots of “iron” and black spots of “manganese,” and I was pretty sure that what I was being told wasn't correct. Had they said “hematite” (an iron-containing mineral) and “pyrolusite” (a manganese-containing mineral), they would have been more chemically correct, and I would have been less confused and better informed.)

So: Why is this chemistry stuff important here? It's because the studies trying to figure out the cause of fluorescence activation and quenching can get pretty complicated. Studies on both natural and synthetic materials have shown that the specific chemical form of the impurity can have a crucial effect on the behavior of the material as a fluorescence activator or quencher. For example, Fe^{2+} ions have been shown to be a very common cause of fluorescence quenching, but Fe^{3+} ions can sometimes act as an activator and sometimes as a quencher. Europium(II) ions (“europium-two”; Eu^{2+}) typically causes a blue-violet fluorescence, but Eu^{3+} causes a red-to-orange fluorescence. Manganese(II) (Mn^{2+}) ions seem to be very good fluorescence activators (for example, the pink-red fluorescence of calcite from Franklin, NJ and from the Medford quarry here in MD is due to Mn^{2+}), but Mn^{3+} ions do not have a predictable effect. The concentration level of the impurity activator also is important. For example, the Mn^{2+} -

induced fluorescence of calcite from Franklin is only seen when the manganese level is between 1 and 5%, and about 3% seems to be optimal. The chemical environment of the ion can also have an effect on the fluorescence. For example, in calcite, the Mn^{2+} ions which substitute for the Ca^{2+} ions are surrounded by six oxygens from CO_3^{2-} ions and cause a strong red-pink fluorescence. A similar color is produced when the Mn^{2+} is surrounded by six chloride ions when present as an impurity in halite. However, in willemite, the Mn^{2+} substituting for the Zn^{2+} ions are surrounded by four oxygens from silicate (SiO_4^{4-}) ions and cause a strong yellow-green fluorescence.

Uranium presents an interesting case. Some minerals contain the simple U^{4+} ion, while many others contain the uranyl ion (UO_2^{2+}). Those containing U^{4+} show essentially no fluorescent characteristics, while UO_2^{2+} is very effective at producing fluorescence. Many minerals containing UO_2^{2+} as an essential component (e.g., andersonite, autunite, boltwoodite, liebigite, schoepite, sklodowskite, uranophane, zippeite) show a bright yellow-green fluorescence. (But see below for why some do not.) Even as an impurity, UO_2^{2+} can be the cause of this same fluorescent color, as when it is found in adamite, apatite, hyalite opal, or chalcedony/agate. The green fluorescence of so-called “Vaseline” glass is due to uranium, probably in the form of UO_2^{2+} ions. (And, yes, that type of glass is also radioactive from the presence of uranium.)

Other ions which often produce fluorescence include lead (Pb^{2+} , as in anglesite, cerussite, and pyromorphite, as well as an impurity in the halides from the Salton Sea in California), chromium (Cr^{3+} , as in uvarovite, spinel, corundum, and kyanite), mercury (Hg^{2+} or Hg_2^{2+} , or some combination, in the calcite and calomel from Terlingua, Texas), molybdate (MoO_4^{2-}), tungstate (WO_4^{2-}), borate (BO_3^{3-} and others), and ions of the rare-earth elements (such as Eu^{2+} , Eu^{3+} , Dy^{3+} , and Yb^{2+}). Samples containing the rare-earth ions show an especially wide variety of fluorescent colors because they almost always contain more than one of these ions (they are chemically very similar to one another, so usually occur together in nature), and the effects of the ions add to (and sometimes clash with) one another. The unusual S_2^{2-} ion¹ is the cause of a yellow-orange fluorescence in minerals in the sodalite and scapolite groups. And, to complicate things even further, sometimes an impurity by itself will yield only weak fluorescence, but its fluorescence is magnified by a second impurity which acts as a co-activator or sensitizer. For example, the red fluorescence of calcite from Franklin is activated by Mn^{2+} with Pb^{2+} as a co-activator.

And it isn't just ionic species which can cause fluorescence. Amber is frequently fluorescent, but it's due to various organic (carbon-containing) molecules present in some samples. Some samples of so-called “blue amber” from the Dominican Republic are so strongly fluorescent that the UV light from the sun produces such a strong blue fluorescence visible in daylight that the surface seems to be a hazy blue. Other examples of non-ionic fluorescent materials will be given in Part 3. It is also possible for defects in the crystal lattice to be the cause of fluorescence in a sample, as in the case of sphalerite which fluoresces blue due to zinc-ion vacancies.

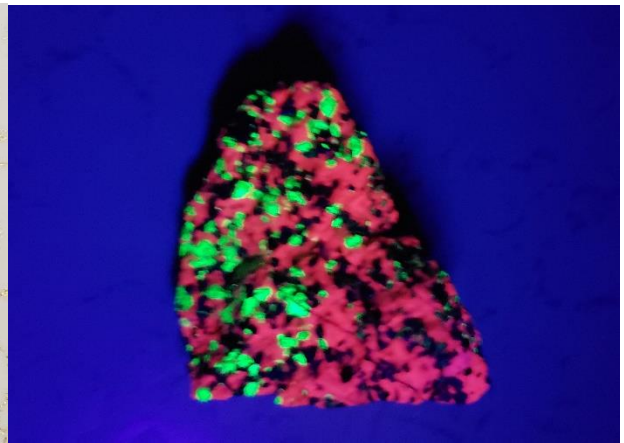
The variety of chemical species which can act as a fluorescence quencher is correspondingly large. Elemental oxygen (O_2) is a very efficient fluorescence quencher, but its effect is only strongly noted when the material being observed is dissolved in water. Since most observations of fluorescence in minerals are made on solid materials and not aqueous solutions, the oxygen in the air has essentially no effect. Among metal ions, iron, copper, nickel, and cobalt (Fe^{2+} , Cu^{2+} , Ni^{2+} , and Co^{2+} , respectively) all seem to be very efficient fluorescence quenchers. Very few (if any) minerals containing any of these show a noticeable fluorescence, whether as an essential part of their makeup (as in siderite (FeCO_3) and malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$)), or as an impurity substituting for some other cation. And, even though Fe^{2+} ions strongly quench fluorescence, Fe^{3+} ions (note the different charge) can act either as an activator or quencher, depending on the specific case being examined.

¹ Note that this is not the same as the much more common S^{2-} ion found in metal sulfides like galena. Whether it's the monatomic S^{2-} ion or the diatomic S_2^{2-} ion makes a big difference in the chemical behavior!

MINERALS RESPONDING TO SHORT WAVE ULTRAVIOLET

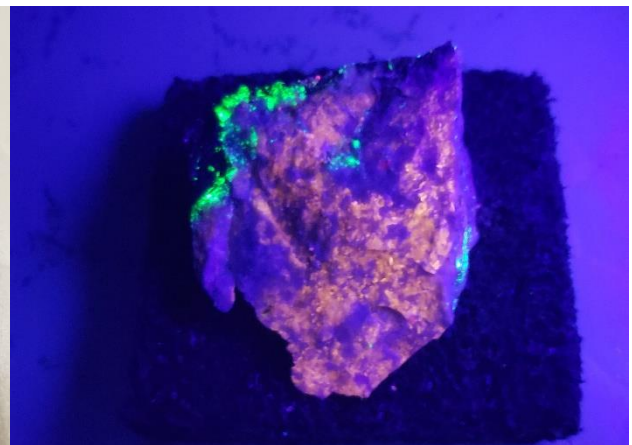
Visible light

Ultraviolet



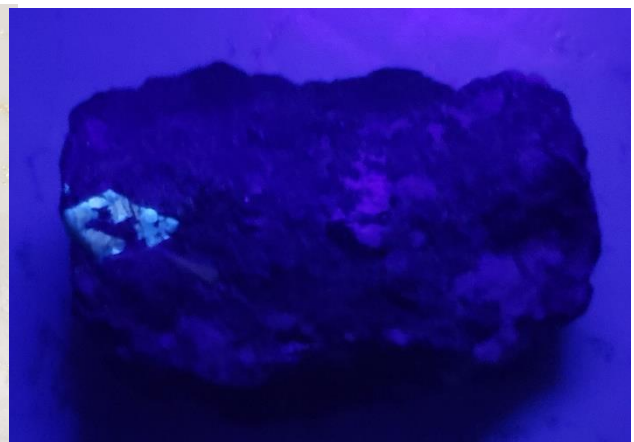
Willemite (*green*) and Franklinite (*black, non-fluorescent*) in Calcite (*red*)

Franklin, Sussex Co., New Jersey



Clinohedrite (*orange*), Hardystonite (*purple*) and Willemite (*green*)

Franklin, Sussex Co., New Jersey



Scheelite (*blue*) in Zinnwaldite

Zinnwald, Saxony, Germany

There are some interesting examples where an ion which normally acts as an activator and an ion which normally acts as a quencher “fight it out” in a single mineral—with the quencher usually the winner. Autunite is calcium uranyl phosphate, saléeite is magnesium uranyl phosphate, and both show the yellow-green fluorescence typical of the uranyl ion. But replace the calcium or magnesium with copper, to produce torbernite, and the copper ions completely quench the fluorescence. Similarly, heinrichite is barium uranyl arsenate, nováčekite is magnesium uranyl arsenate, and both show the typical fluorescence from the uranyl ion. But zeunerite, the corresponding copper uranyl arsenate, is nonfluorescent because of the quenching effect of the copper ions.

Part 3: What Fluoresces?

Fluorescence and phosphorescence aren't properties limited only to minerals. Some living organisms are fluorescent (not to be confused with bioluminescence, in which a chemical reaction inside an organism produces light, such as in fireflies and some deep-sea marine organisms), and a few exhibit phosphorescence as well. For example, most scorpions fluoresce a blue-green color, and puffins have a series of fluorescent stripes on their beaks during mating season. Chlorophyll, the green pigment in plants, fluoresces red. Tonic water fluoresces blue because it contains quinine. Crude petroleum often fluoresces, and this is used in oil exploration. (The hydrocarbon inclusions in “petro quartz” crystals frequently fluoresce blue.) In fluorescent lights, the electrical current passes into the gas in the tube, which contains mercury. This causes the mercury to emit ultraviolet light. When this strikes the fluorescent coating on the inside surface of the tube, visible light is emitted. Materials such as white paper and clothing (and probably “Day-Glo”™ paints) are treated with so-called “optical brighteners.” These are materials which absorb UV light and re-emit it as broad-spectrum visible light (essentially “white”), so more visible light is emitted by the sample than originally struck it, producing a “whiter than white” effect.

Fluorescence can also be used to detect a number of materials, and this has applications in forensic chemistry to detect blood, fingerprints, and other materials of interest. Fluorescent materials are used as security features for banknotes, postage stamps, and credit cards. Ringworm can be detected by medical personnel because the fungus which causes it is fluorescent. Fluorescent dyes are used as “tracers” to follow the flow of some material in medical and environmental applications. Fluorescent dyes are included in sea-survival kits to make it easier to spot those who need rescuing. Phosphorescence is a much less common phenomenon in natural samples, but many artificially-produced materials have been made for use in watch dials, “Day-Glo”™ paints, Halloween decorations, etc.

But back to minerals. Other than the examples cited previously, what minerals can show fluorescence, and what colors have been observed? I'd try to give a complete answer, but how many pages do you want me to take up? How many hours do you have to read the lists? The first systematic study of fluorescence in minerals was done by Kunz and Baskerville in the early 1900's, in which they walked through the mineral displays of the American Museum of Natural History in New York City at night with a huge, cumbersome UV light (the only type available at the time). They were surprised by the number of specimens on display which showed this property. Since then, studies have shown that of the 5000 or so known mineral species, about 600 of them are known to exhibit fluorescence and/or phosphorescence in samples from at least one locality, and more are being discovered all the time. And many of these can fluoresce in a variety of colors, depending on the activator(s) present. In rare cases, the initial fluorescence is one color, but it changes with longer exposure. Many of them are known from multiple localities. Some samples show fluorescence only in restricted portions of the crystals. (Is there such a term as “fluorescence-zoned,” analogous to “color-zoned?” If not, there should be.) At some localities, some samples fluoresce strongly, while other samples of the same mineral don't fluoresce at all. And it has also been found that the fluorescence of some samples is temperature dependent. Add to this the thousands of samples which have been synthesized and tested in laboratories for applications

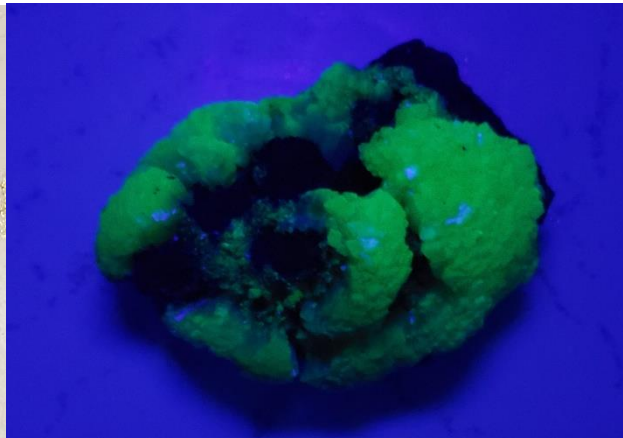
MINERALS RESPONDING TO SHORT WAVE ULTRAVIOLET

Visible light



Adamite (*green*)

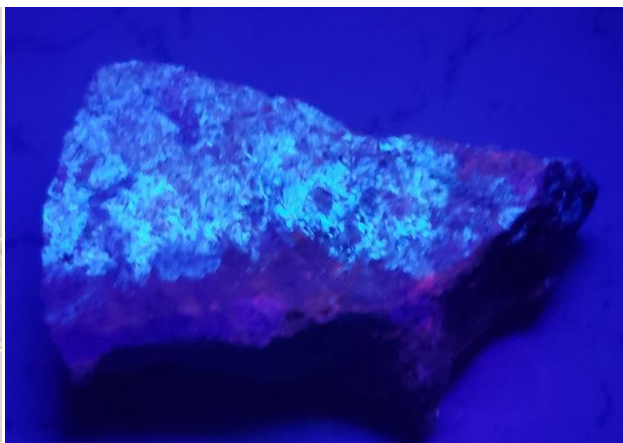
Ultraviolet



Ojuela Mine, Mapimi, Durango, Mexico



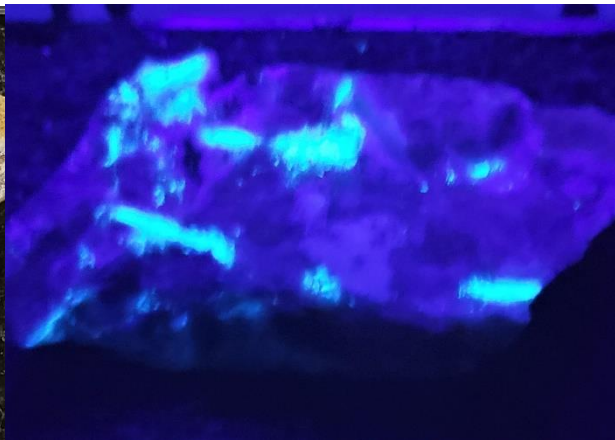
Hydrozincite (*blue*) on Calcite (*red*)



Hurricane, Utah



Carpathite (*blue-green*) with Cinnabar in Quartz



Picacho Mine, San Benito Co., California

such as fluorescent lighting, security features, TV and computer screens, signage, and dozens of other applications, and you've got quite the long list of materials to choose from. Here's a selection of some of the minerals which frequently occur in fluorescent samples.

- Fluorite is the mineral for which fluorescence was named, so it shouldn't be surprising that there are hundreds of localities where fluorescent varieties of this mineral can be found. Many different fluorescent colors have been observed, depending on the activator(s) or structural defect(s) present. Some of the best-known localities are the counties of Cumberland and Durham (particularly Weardale), England (blue fluorescence, some with noticeable daylight fluorescence, with the purple-colored samples generally giving the best fluorescence); Clay Center, Woodville, and other localities in northwest Ohio (white, cream); Hardin County, Illinois (white); Bingham, New Mexico (blue or purple), Madoc, Ontario; Yaogangxian, China; as well as localities in Arizona, New Hampshire (Westmoreland), China, Mexico, and South Africa.

- Since calcite is found at so many localities, there are a correspondingly high number of localities (numbering in the hundreds) for fluorescent calcite specimens. Almost any color can be observed, depending on the activator(s) or structural defect(s) present. Blue-fluorescing calcites typically also phosphoresce, as do some calcites of other colors. Some of the best-known localities are Franklin-Sterling Hill (F-SH), New Jersey (red, with a very brief phosphorescence); Terlingua, Texas (blue SW, pink LW, with strong phosphorescence); Joplin, Missouri (blue); Elk Creek, South Dakota (tan, with blue-fluorescing barite); Southern Utah (septarian nodules, blue-white); Broken Hill, New South Wales (red); Rio Grande Do Sul, Brazil (pink-red); and localities in Arizona, Colorado, New Mexico, South Dakota, Mexico, Peru, and Scotland. Other minerals in the calcite group such as magnesite and smithsonite often fluoresce, but not siderite or gaspeite, which contain the fluorescence-quenching ions Fe^{2+} and Ni^{2+} , respectively.

- Minerals in the dolomite group (such as dolomite and kutnahorite, but not ankerite, which contains Fe^{2+}) and aragonite group (aragonite, cerussite, strontianite, and witherite) are often fluorescent. Aragonite from Sicily and from Broken Hill, New South Wales often shows a bright pink fluorescence, and that from Friedensville, PA exhibits a golden-yellow fluorescence in LW UV and a white fluorescence in SW UV, as well as pale blue phosphorescence from either lamp. Aragonite from Santa Eulalia, Chihuahua, Mexico both fluoresces and phosphoresces a blue-white color. The aragonite "petals" in the "chrysanthemum stones" from China show a blue-white fluorescence. Other notable localities for fluorescent aragonite are in Arizona, California, and New Mexico.

- Sphalerite is non-fluorescent when pure (which it rarely is in natural samples), but can fluoresce blue, yellow, orange, red, or green, depending on the impurity activator(s) present. At Mont Saint-Hilaire (MSH), Quebec, it shows orange fluorescence; at F-SH, the fluorescence is usually blue. Fluorescent samples have also been found at Tsumeb, Namibia; Bisbee, Arizona; Broken Hill, New South Wales, at various localities in Colorado and Utah, among many others. The fluorescence behavior of synthetic sphalerite has been studied extensively; depending on the activator ion doped in, it can fluoresce almost any color. Synthetic sphalerite was used as a phosphor in early television tubes. Many samples of sphalerite also exhibit triboluminescence and thermoluminescence.

- Uranium minerals often fluoresce a bright yellow-green due to the presence of the uranyl ion (UO_2^{2+}). Over 80 different uranium mineral species have been shown to fluoresce. However, as mentioned in Part 2, exceptions are found, such as when quenchers like Cu^{2+} ions are also present. Uranium-containing fluorescent minerals are found in Washington and other states in the western US, Zaire, and in many other worldwide localities.

MINERALS RESPONDING TO LONG WAVE ULTRAVIOLET

Visible light



Scapolite variety Wernerite (yellow)

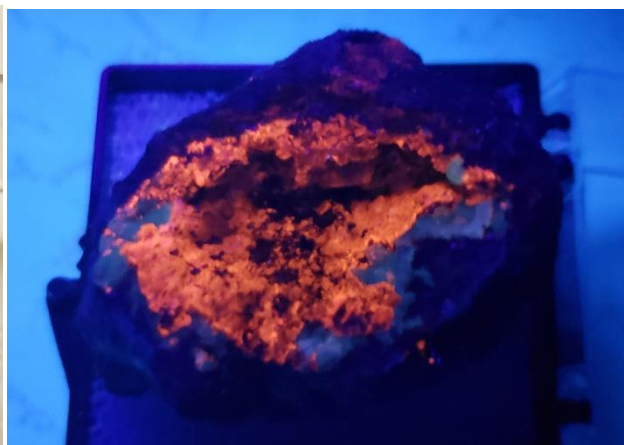
Ultraviolet



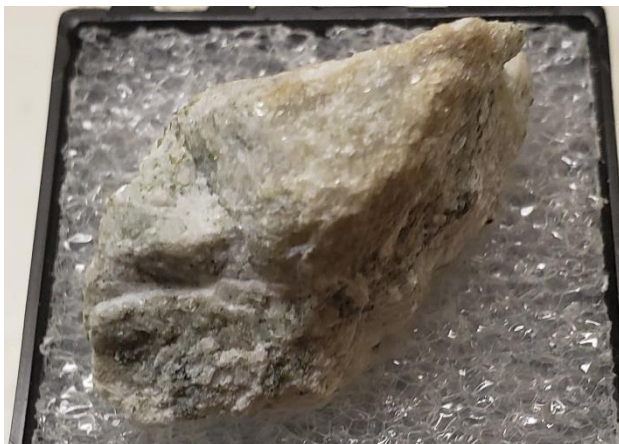
Grenville, Quebec, Canada



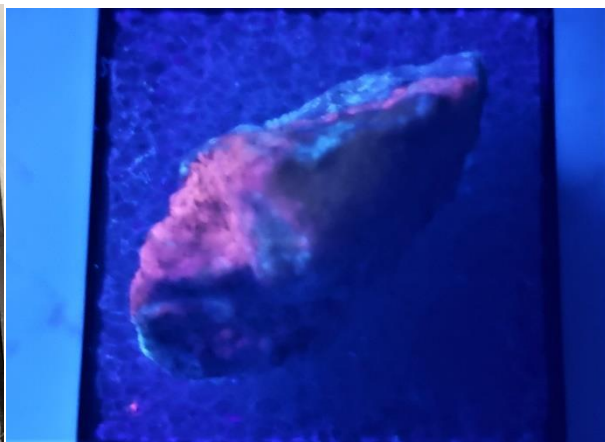
Calomel (red), Cinnabar and native Mercury



Red Bird Mine, Dixie Valley, Churchill Co., Nevada



Walstromite (pinkish red) with Cinnabar in Quartz



Esquire #8 claim, Big Creek, Fresno Co., California

- The activating effect of Pb^{2+} is shown in various lead minerals such as anglesite, cerussite, hydrocerussite, phosgenite, and pyromorphite. The fluorescence is normally white or yellow but can be other colors if co-activators are present along with the Pb^{2+} . Stolzite fluoresces a greenish-white color due to the presence of tungstate ion in addition to Pb^{2+} . Pb^{2+} ions are the cause of the orange fluorescence in halite samples from the Salton Sea in California.
- Samples in the scheelite/powellite series always fluoresce. The tungstate ion in scheelite fluoresces blue, while the molybdate ion in powellite fluoresces yellow; materials of intermediate composition fluoresce a mixture of these two colors. Use of a fluorescent light is one way in which prospectors detect the presence of scheelite, the most important ore of tungsten. The synthetic equivalent of scheelite is used as the basis for the phosphor in fluorescent lights. Good scheelite specimens have been found in the Southwest US, Canada, China (Mt. Xuebaoding), Korea, Sweden, and many other localities.
- Benitoite isn't a very common mineral (for practical purposes, it's only found at one locality), but it's included here because it's a popular collector species, and because all benitoite samples show an intense blue fluorescence.
- There are a number of minerals in the apatite group which show fluorescence in many samples. These include apatite itself (particularly from Panasqueira, Portugal; F-SH; New Mexico; and Pakistan), manganapatite (CT, ME), mimetite, pyromorphite, and vanadinite. Synthetic materials with the apatite structure are used as the phosphors in fluorescent lights.
- A particularly notable and unusual example is hackmanite. This is a variety of sodalite which contains some sulfur (probably in the form of the S_2^- ion). It was first found in Greenland in 1806, and later in India. A freshly broken surface has a pink color, but this changes to pale green on exposure to light. Much later, specimens were discovered at Bancroft, Ontario and their behavior in response to UV light was studied. (It has also been found in Afghanistan, the Kola Peninsula in Russia, and at MSH.) Specimens from Bancroft and from MSH show an orange fluorescent response to LW UV. However, the response to SW UV is even more unusual. After a minute or two of exposure to SW UV, the color of the specimen itself turns to purple-pink, much darker than the pink color of a fresh surface. This color will remain if the specimen is stored in the dark, but upon exposure to daylight, the color fades back to its original. This color-change sequence can be repeated multiple times. This phenomenon is referred to as *reversible photosensitivity* or *tenebrescence*. Some samples change to a blue color upon long exposure to SW UV which fades very slowly. Recently, sodalite (not the hackmanite variety) which fluoresces yellow-orange has been found in great abundance in pebbles on beaches around the Great Lakes and was named "yooperlite" by its discoverer.
- A number of materials cut as gemstones frequently show fluorescence. Many (but not all) diamonds fluoresce; most commonly they fluoresce blue, but are also known to fluoresce green, yellow, and red, and often phosphoresce as well, due mostly to structural defects. The "blue-white" color of fine diamonds is often enhanced by blue daylight fluorescence. The "ruby" varieties of corundum and spinel both show a red fluorescence caused by the Cr^{3+} ions substituting for Al^{3+} (which also cause the red daylight color). Various types of beryl are known to fluoresce, particularly emerald (and particularly those from Columbia), in which Cr^{3+} causes the green daylight color, but also the same red fluorescence seen in ruby corundum and spinel. Some samples of zircon (yellow-brown) and topaz (various colors) are also known to fluoresce, as well as many rarer gem materials.

In addition to the ones mentioned above, some common minerals which sometimes show fluorescence are adamite, barite, celestite, chalcedony (including agate), coemanite, crocoite, glauberite, gypsum, halite, hemimorphite, hydrozincite, microcline, opal, orthoclase, scapolite (var. wernerite), spodumene, talc, tremolite, trona, and wollastonite. Many more examples can be found in the references given at the end of Part 1.

Part 4: Where can Fluorescent Minerals be Found?

As with the mineral species themselves, there are thousands of localities at which fluorescent samples have been found, so a complete listing of these would go on for many pages. A few of them have been mentioned in passing above, but here I'll discuss a few more of the more prolific localities for producing fluorescent minerals.

The most famous and prolific locality for fluorescent minerals is Franklin-Sterling Hill (F-SH), New Jersey, which is self-proclaimed (but rightly so) "The Fluorescent Mineral Capital of the World." The primary ores at the zinc mines in this mining district were franklinite and zincite, neither of which fluoresce. But another important ore of zinc at those mines was willemite. The ore was sorted from the gangue minerals at the "picking table" using the green fluorescence of the willemite. (Not coincidentally, "The Picking Table" is the name of the newsletter of the Franklin-Ogdensburg Mineralogical Society.) Specimens from F-SH showing combinations of red fluorescent calcite and green fluorescent willemite are fairly common, but many specimens found there fluoresce in a veritable rainbow of colors due to the fluorescence of over 100 different minerals, including barite (fluoresces cream or yellow), esperite (yellow), fluorapatite (orange), hemimorphite (yellow), hydrozincite (sky blue), sphalerite (orange or blue), tremolite (blue), wollastonite (orange or yellow), and a host of rare species, some found only at F-SH. (Almost 400 mineral species have been identified from the Franklin mining district, and it is the type (and often only) locality for over 70 of them.) The book Rainbow Minerals by Bob Jones has a brief introduction to the minerals of F-SH, but is mostly a series of photos showing the daylight and fluorescent colors of specimens from that location. An extensive table of fluorescent minerals from F-SH can be found in Schneider's book mentioned at the end of Part 1.

Many Canadian localities have produced good fluorescent specimens. A large number of fluorescent species have been found at the quarries at Mont Saint-Hilaire (MSH), Montreal, Quebec. The material quarried there is primarily used as crushed stone for road-building. Schneider's book lists about 50 mineral species which can be found in fluorescent samples at MSH, including albite (fluoresces red or green), analcime (green), elpidite (yellow-green), fluorapatite (violet blue), genthelvite (green), hackmanite (orange), natrolite (green), pectolite (pink), polyolithionite (yellow), willemite (green), and zircon (yellow-orange), along with many less-common species. Similar to F-SH, the activators are Mn^{2+} and Pb^{2+} . The lists of fluorescent minerals from F-SH and MSH have only very few minerals in common. The Long Lake Zinc Mine in Parker, Ontario has produced fluorescent specimens of aragonite (blue-white), calcite (red), diopside (blue-green), humite (yellow), and hydrozincite (blue-white). At Oka, Quebec, fluorescent calcite, natrolite, and sodalite are found. And, even though the locality only produces one mineral, the beautiful selenite "roses" found at the Red River Floodway in Winnipeg, Manitoba fluoresce a strong green color.

Another well-known locality is the Terlingua, Texas mining district and nearby Mexico (especially Músqiz, Coahuila). A limited number of fluorescent species are known from there—calcite, calomel, periclase, terlinguaite, and a couple of even rarer species. However, a large quantity of "Terlingua calcite" (in quotes because not all of it literally comes from the Terlingua district) has been found and is fairly readily available. Some of this material fluoresces lemon-yellow, but the most well-known and popular specimens fluoresce a strong sky-blue or violet-blue in SW UV (and sometimes phosphoresce the same color) and fluoresce pink in LW UV.

The area around Balmat, New York is home to a number of mines. The zinc and manganese mines (what is it about zinc mines that causes them to be such good sources of fluorescents?) have closed, but there is still a working talc mine. At these mines, a number of different fluorescent species have been found. These include calcite (fluoresces sky blue), diopside (sky blue or blue-white), phlogopite (yellow), scapolite (var. wernerite; orange), sphalerite (green, pink, gold, blue, orange), talc (yellow), tirodite (red/pink), tremolite (orange or red), willemite (green), and a host of other species.

In Arizona, there are many localities which yield good fluorescent specimens. The Purple Passion Mine in Wickenburg, Yavapai County, produces good specimens of wulfenite (mostly non-fluorescent but which occasionally fluoresce orange or tan) on fluorite, calcite, or galena, as well as a number of other species. In addition, fluorescent specimens of aragonite (fluoresces blue-white), calcite (pink or orange, sometimes with a coating of caliche which fluoresces peach), fluorite (blue), and willemite (yellow fl and phos) have been found there. Occasionally, specimens showing four different colors of fluorescence on a single specimen are found. The Pure Potential Mine (North Geronimo Mine) in LaPaz County has red-fluorescing calcite and purple-fluorescing fluorite. Localities in Yavapai and Yuma counties produce a variety of fluorescent specimens of andersonite, barite, calcite, cerussite, fluorite, mimetite, pyromorphite, scheelite, and many other species.

There are a number of localities in California which have produced fluorescent specimens, the most prolific of which is the Crestmore Quarry. Specimens of aragonite (phosphoresces green-white in SW UV), calcite (fluoresces orange, red, or blue), jurupaite (magnesian xonotlite, fluoresces blue-gray), okenite (pale blue), and serpentine (green) have been found at that locality. At Searles Lake, many fluorescents are found, including aphthitalite, borax, dawsonite, glauberite, halite, pirssonite, sulphohalite, and trona. Localities in Inyo County have produced fluorescent hyalite (green), trona (blue-green), and scheelite (blue). Many localities in Mexico have produced fluorescent specimens. Two of the best-known are Mapimi, Durango, where excellent green-fluorescing specimens of adamite have been found, as well as calcite (red), fluorite (red), and hydrozincite (blue-white SW, peach LW), and Santa Eulalia, Chihuahua, which has produced fluorescent specimens of aragonite (fluoresces green or white, with white phosphorescence) and calcite (fluoresce red, blue-gray, or white).

In Greenland, fluorescent specimens have been found at a number of locations. The hackmanite variety of sodalite, discussed in Part 3, was first found here, and other localities have produced other fluorescents as well. A number of these are found in the Ilimaussaq Complex in the Southwestern part of the island. The geology of this formation is broadly similar to that of MSH, so it should be no surprise that it would be the source of fluorescent specimens. These include Kvanefjeld, where red-fluorescent tugtupite which is also tenebrescent is found. Other localities in this complex include Kangerluarsuk and Tunulliarfik Fjords, and the Tasaq Slopes. The fluorescent minerals found there are, for the most part, not exactly household names (chkalovite, polyolithionite, sorensite, ussingite, and many others), but do include more familiar species such as albite, analcime, calcite, fluorite, natrolite, and sodalite. A first-person account of collecting trips to Greenland is found in Schneider's book, along with a list of almost 50 different mineral species found as fluorescent specimens on the island.

A number of localities in Europe produce fluorescent specimens. The fluorites from various localities in England were mentioned in Part 3. In addition to world-class (non-fluorescent) specimens of sulfur, mines in Sicily have produced specimens of aragonite (pink fluorescence), calcite (orange, cream, or pink), and celestite (pale blue or blue-white). Specimens showing celestite on calcite, with their contrasting fluorescence colors, are especially striking. And, down under in Australia, the mines at Broken Hill, New South Wales have been the source of red-fluorescent aragonite and calcite.

In our local area, there are a number of localities which have produced fluorescent specimens. The hot-pink fluorescence of many of the calcite specimens from the Medford Quarry in Carroll County is well-known to local collectors. This fluorescence is probably activated by manganese, although I have seen it reported that it is due to ions of the element niobium. In Baltimore County, magnesite which fluoresces white or pale green has been found in the Delight area, and the Bare Hills area has produced deweylite specimens which fluoresce white. White-fluorescing laumontite was found at the Harris Quarry along the Jones Falls in Baltimore, and green-fluorescing amber has been found in the Severn River in Anne Arundel County.

Going north into Pennsylvania, the mines in the State Line area along the border between Lancaster County, PA and Cecil County, MD have produced specimens of white-fluorescing serpentine, brucite which fluoresces blue-white (Woods Chrome Mine), deweylite which fluoresces white (Cedar Hill Quarry and other localities, and in Chester County and in Newcastle County, Delaware), and magnesite (Cedar Hill). Some of the calcites and strontianites from the Faylor-Middlecreek Quarry in Winfield fluoresce white, as do some of the strontianites from the Meckley Quarry in Mandata, the Valley Quarry in Shippensburg, and the National Limestone Quarry in Mount Pleasant Mills. At the Wheatley Mines in Phoenixville, white-fluorescing stolzite and green-fluorescing cerussite have been found. And, going south into Virginia, white-fluorescing albite has been reported from Amelia Court House. (Rhetorical question: Why is it that almost all the fluorescents from the MD/PA/VA region fluoresce only a boring white? Why aren't there any prettier or more exciting colors? I guess we don't have enough manganese, uranium, or lead in our rocks to act as activators.)

In addition to these localities, there are hundreds (thousands?) of worldwide localities which have produced at least a few fluorescent samples, and there are probably many more which haven't been investigated fully enough to know the extent to which they might produce fluorescent minerals.

To learn more about fluorescence, the references given earlier are good places to start. The Franklin Mineral Museum and the Sterling Hill Mining Museum and Museum of Fluorescence have outstanding displays and information about the subject. There are numerous websites (including one by Stuart Schneider) with information about fluorescence, and videos about fluorescence and fluorescent minerals are available on-line. And, if you're really serious, you'll join the Fluorescent Mineral Society (website: uvminerals.org), which has a newsletter and lots of connections with other folks interested in this fascinating aspect of mineral collecting.

So, if you collect (or want to collect) fluorescent mineral samples, you have plenty of specimens and lots of information sources to choose from. If you don't already have one, get yourself a fluorescent light source (pocket-sized, battery-operated long-wave units can be had for under \$10, but you can pay hundreds for larger, more powerful, multi-wavelength units) and start shining it on the specimens you already own to check for fluorescence. Then bring it with you (assuming it's portable) to the next mineral show you attend (whenever that will be; the COVID virus will determine when shows will begin to be held again) and enjoy searching for new specimens. Some very rare examples can be pretty pricey, but a colorful representative collection of good fluorescent specimens can be assembled without too large a monetary investment.

Rare Fluorescent Minerals

Donald G. Howard
Portland, Oregon

The recent article by Al Pribula on “Where can Fluorescent Minerals be Found?” got me to thinking about some of the rarer minerals that are fluorescent and how that often helps in identifying them.

One of the special California minerals that always fluoresces is Benitoite, $\text{BaTiSi}_3\text{O}_9$. It was named for San Benito Co., where it was first found in a massive natrolite vein as large, blue trigonal bipyramids with neptunite and joaquinite. I peeled the specimen shown in Fig. 1 off the face of a piano-sized boulder, brought it home, and carefully etched away the natrolite as a teen-ager over sixty five years ago. Clearly these crystals do not require fluorescence to identify them.

But a closely related species, Bazirite, $\text{BaZrSi}_3\text{O}_9$, is not so easy to spot. It occurs in the sanbornite area along Rush and Big Creeks in Fresno Co., California as tiny clear grains in a matrix of granular material composed of other colorless barium silicates. Fortunately, the replacement of titanium by zirconium does not affect its ability to fluoresce, and the tiny grains stand out blue-white under the short-wave UV light. That at least tells me where to look under the microscope. For obvious reasons, I do not include a picture.



Fig. 1 *Benitoite, Neptunite & Joaquinite
Dallas Gem Mine, San Benito Co., Calif.
This piece is about 5" in diameter.*



The same area proves to be the type locality of another rare barium silicate, Walstromite, $\text{BaCa}_2\text{Si}_3\text{O}_9$. The substitution of two calcium ions in place of titanium or zirconium causes a major reshaping of the structure, so this mineral is triclinic and fluoresces red. In fact, Bob Walstrom has told me that the red fluorescence is the only sure way to identify walstromite.

Fig. 2 *Walstromite
Esq. #8 claim, Big Creek,
Fresno Co., Calif.*

Another fluorescent rare mineral is Zektzerite, $\text{NaLiZrSi}_6\text{O}_{15}$, which is reasonably abundant in the granites of Washington Pass in the northern Cascade Mountains of the state of Washington. When forming freely in a vug, zektzerite is easily distinguishable from the microcline that forms the bulk of the granite, since its crystals are pseudo-hexagonal. However, the two minerals are very similar in color and texture, making them difficult to tell apart when the zektzerite is embedded, as almost all of it is. Fortunately, zektzerite has a blue-white fluorescence. I can attest that, collecting by day at the Silverstar



Fig. 3 *Zektzerite crystals*
Washington Pass, Okanogan Co., Wash.

Slide along the state highway, you would be hard pressed to identify any zektzerite. However, after dark (and it gets *very* dark) with a fluorescent light in hand, the hillside sparkles with an amazing number of little spots of light. So collecting there works best in the dark!

One final example of how useful fluorescence can be in studying minerals. Several years ago, Bumpy Barwood brought material from Arkansas to the give-away tables at the annual meeting of the Northern California Mineral Association. It contained several unusual minerals, among them some lovely sprays of Lorenzenite, $\text{Na}_2\text{Ti}_2\text{O}_3\text{Si}_2\text{O}_6$, that proved very photogenic, though not fluorescent (Fig.4). However, ultraviolet light revealed the presence of nearly invisible Burbankite, $(\text{Na,Ca})_3(\text{Sr,Ba,Ca,REE})_3(\text{CO}_3)_5$, by its bright orange emission. This was best done using the 405nm laser, which Bumpy was promoting as a cheap, rather intense source of light in the near ultraviolet. The intense, concentrated light was ideal for use under the microscope for locating and photographing some fluorescent minerals, requiring only

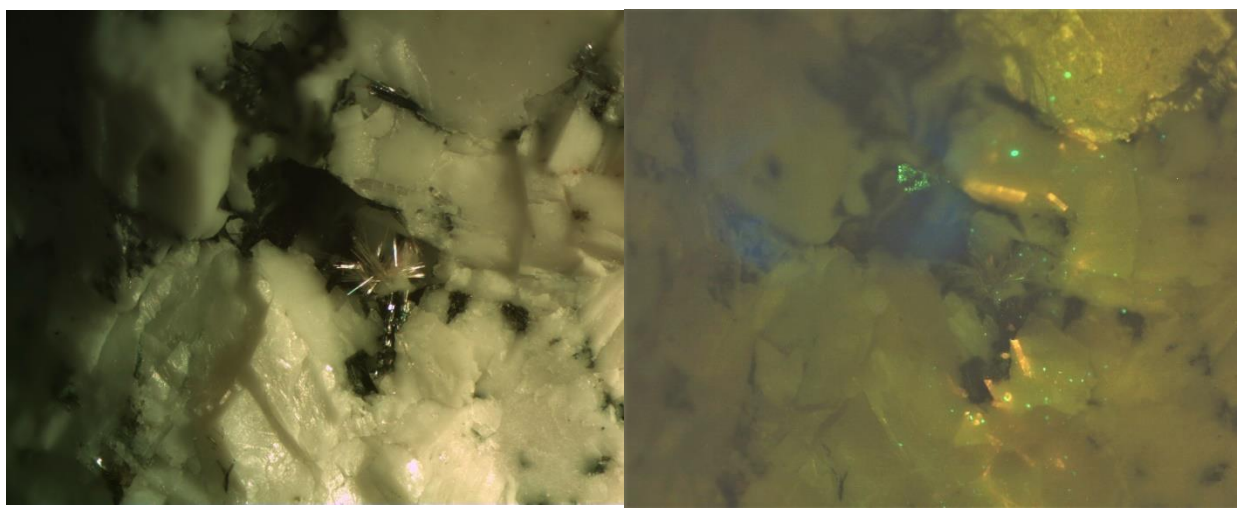


Fig. 4 *Lorenzenite and burbankite*
Jones Mill Quarry, Magnet Cove, Hot Springs Co., Arkansas
At left in regular light, at right in 405nm illumination to reveal the burbankite.

a usual yellow photo filter to be installed on the microscope.. The second frame of fig. 4 is the same place on the specimen taken instead in 405nm radiation. Looking back to the left, you can barely make out the colorless burbankite crystals. These lasers are excellent for exciting fluorescence in the reds, oranges, yellows and greens. They are particularly effective in exciting the uranyl ion, and make photographing the uranium minerals rather easy, as shown in fig. 5. I find this easy, bright fluorescence most useful in sorting out the uranyl sulfates from southeastern Utah.

The 405nm laser does not have sufficiently energetic photons to excite minerals in the blues and whites, like benitoite, zektzerite, or scheelite. I have had to resort to the old reliable mercury source to pick out the scheelite and powellite in samples from ore bodies containing molybdenum or tungsten.

I hope that gives you some new perspectives on the use of fluorescence.

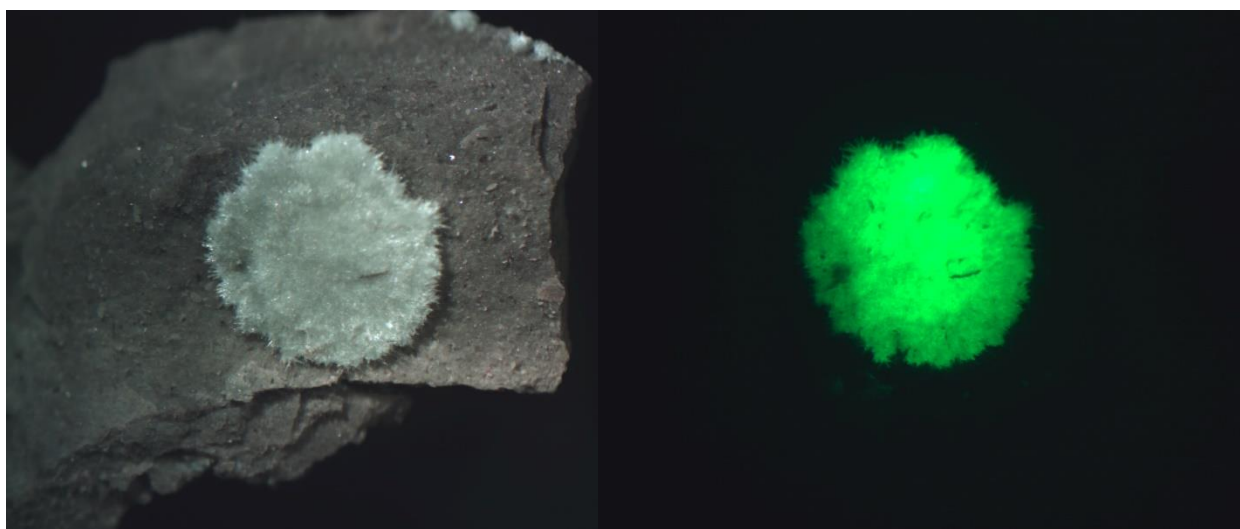


Fig. 5 *Plasilite* $\text{Na}(\text{UO}_2)(\text{SO}_4)(\text{OH}) \cdot 2\text{H}_2\text{O}$
 Area 8, Blue Lizard Mine, Red Canyon, San Juan Co., Utah
 At left in regular light, at right in 405nm illumination.

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