FLUORESCENT MINERALS

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These activities, demonstrations and content address these content expectations in the Michigan Merit Curriculum for high school science: E1.1A, C, D, E; E3.p2A; P2.p1A; C2.1; C2.2A, B; C2.4b, c, d; P4.2A; P4.3A; P4.9B.

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The Chemistry of Fluorescence

Fluorescence is the property of a mineral to emit visible light when it is stimulated by ultraviolet (UV) radiation. Ultraviolet light is electromagnetic radiation with a wavelength between 10 and 400 nanometers. It is sometimes called “black light”. Long wave ultraviolet is not dangerous- it is used for special effects, checking for invisible stamps and markings, pet urine and plant “grow lights”. Mid range and short wave UV can cause sunburns, eye injury or even blindness, so care should be taken to never shine it in the eyes or to view an intense reflection of it. Many science catalogs sell special UV safety goggles that block >99% of short-wave light. Simple latex gloves provide hand protection.

Many minerals fluoresce when viewed with ultraviolet light due to the presence of trace minerals called <u>activators</u>. The unique ability of activators is due to their electrons being spaced at just the right distance from the nucleus to absorb UV light and emit it in visible wavelengths.

There is an optimum concentration for activators within a mineral. A general rule of thumb is that an activator level of >2% causes an effect called concentration quenching. As some atoms emit light, it is reabsorbed by other nearby activator atoms. The net result is no fluorescence.

Sometimes activators require the presence of a second trace mineral in order to be effective. <u>Co-activators</u> or <u>sensitizers</u> fill this role. An example is Pb^{+2} and Mn^{+2}. Manganese produces a red fluorescence, but can only be effective in the presence of lead- the lead electrons absorb the UV light, then transfer their energy to manganese electrons which emit visible light.

Fluorescence can be <u>quenched</u>, or <u>deactivated</u>, by a number of factors. Some trace minerals, when present in large amounts, quench fluorescence. An example may be seen in rubies. Chromium+2 is the activator in ruby crystals. However as iron+2 concentrations increase, fluorescence is quenched. The iron ions compete to absorb UV energy, then release it as heat and vibrational energy instead of light.

High temperatures quench fluorescence for two reasons. First, some activators or sensitizers cease functioning as they absorb energy. Second, the vibrational energy releases some electrons prematurely from "traps". When this happens, the electrons do not emit light.

Electron traps are zones within a mineral that are concentrations of negative charges. They are created by improper ionic substitutions within a growing crystal. For instance, Aluminum+3 may replace iron+2 in a structure. This creates an excess of positive charge and acts as a temporary electron magnet. This model explains a few other effects described elsewhere in this document: why chilling minerals may induce better fluorescence (opposite of quenching), and why heating some minerals may cause a temporary increase in their fluorescence as electrons exit from their traps.

Fluorescence is not limited to the classical example of electrons absorbing UV and emitting visible light. Electrons may absorb at visible and infrared wavelengths as well, and many emit energy in the infrared. Just as visible light fluorescence is a characteristic identifier of minerals, their infrared signatures can also be used. This technique, called thermal emission spectroscopy, or TES, is employed by planetary geologists to remotely identify surface minerals.

Regardless of the wavelengths involved, all fluorescent materials follow Stoke's Law. This law states that the wavelength absorbed is always shorter (higher frequency and energy) than the wavelength emitted. This is due to conservation of energy effects: Some of the absorbed energy is always transformed into kinetic energy in the crystal structure.

Special Types of Fluorescence

Phosphorescence is a delayed release of electrons from higher energy levels. This release may occur over a few seconds or a number of years. The result is the mineral glows even after the UV light source is turned off.

Polarized fluorescence This effect is often seen in calcites. Illuminate the mineral with UV light and view it through a plane polarizing filter. Rotating through 90° will show zones in the crystal that alternately brighten and darken. When specimens emit polarized light, they do so because the electric fields of their activator atoms are aligning to each other and to the axis of the host crystal.

Thermoluminescence Often if a specimen is held under hot water or heated in an oven, it will glow much more strongly for a period of time.

Triboluminescence describes minerals that glow when they are crushed, scratched or even rubbed. These minerals contain elements or other agents that emit light when even mechanical energy is imparted to them. Minerals that have been known to show this unusual property are: calcite, fluorite, lepidolite, sphalerite and some feldspars. You can demonstrate this effect by biting or crushing Wintergreen Lifesavers in a dark room. Wintergreen Altoids are even better!

Photochromicity The variety of sodalite called hackmanite exhibits an unusual property. When irradiated by short wave UV, it becomes pink-purple. Subsequent exposure to visible (white) light causes a bleaching of this color. This effect can be cycled back and forth at will. Alternatively, leaving the hackmanite in darkness for a few hours or days will also restore the raspberry blush. See the "Chemistry of Fluorescence" page for a full explanation.

Cold Temperature Fluorescence Minerals such as scapolite and some feldspars may fluoresce more strongly when chilled. Observe their fluorescence at room temperature, then chill them in a freezer for a minimum of two hours. An even better idea is to pack them in dry ice. See the "Chemistry of Fluorescence" page for a full explanation.

Fluorescent Demonstrations and Common Examples of Fluorescence

Stokes Law and "Preferred Wavelengths"

Stokes Law states that the wavelength of emitted light in a fluorescent material must be longer than the wavelength of the light absorbed. This is the typical observed behavior of fluorescent minerals: they absorb in UV and emit in visible light. This activity illustrates Stokes law well, and also demonstrates the concept the fluorescent chemicals, like minerals, require a specific wavelength of energy to become excited.

You will need to buy some special materials, but they are well worth it! First, get a 1 foot square of phosphorescent vinyl sheet and attach it to a sturdy board like foam core or tag board. Then acquire 2 Photon Microlights, one red and one violet. (Sources for these materials are listed in the back of this guide)

In a dark room, shine the red LED light on the plastic. Not much happens. Then try violet- it glows bright green. This is yet another example of how, then reemit that energy at a lower wavelength (absorbs violet-UV and emits green).

__The Design of a Fluorescent Light Bulb__

A fluorescent light bulb reduced to simple terms is a gas discharge tube filled with mercury vapor and coated on the inside with a mixture of fluorescent compounds. When an electrical current is applied, electricity passes from one end of the tube to the other with an assist from the mercury vapor. Electrons in the mercury atoms get "knocked into higher orbits." When they drop back they give off electromagnetic radiation (wavelengths of visible light and both long and short wave ultraviolet (UV)). If it weren't for the coating on the inside of the light tube they would look just like the bluish mercury vapor street lights. The phosphorescent coatings on the inside react to the short wave UV generated by the mercury giving off the nearly continuous spectrum seen. Different blends of the fluorescent compounds sift the emissions to accentuate red or blue and are called warm or cool fluorescence respectively.

It should be pointed out that short wave UV is capable of causing damage to eyes and should never be looked at directly. Fortunately the glass in the fluorescent lights absorbs the short wave UV so there is no danger to our eyesight. The long wave UV does pass though the glass of the fluorescent tube however.

__Gems__

Synthetic gems often fluoresce much more strongly than the natural gems they imitate. Fraud is not uncommon when gems have great value. One method of deception involves cementing a natural gem on top of a far cheaper synthetic base. Under visual inspection it is nearly impossible to detect. A black light has a much better chance of illuminating the differences between the parts. Some clear diamonds (mostly from Russia) glow blue in visible light, because of UV in sunlight.

Urine for a Surprise!

Pet owners with unruly pets take notice. Many pet supply stores actually rent black lights. It seems pet urine fluoresces. The black lights are used to locate the accidents on your carpet so enzyme based deodorizers can be applied only to the necessary spots. Perhaps a more disturbing realization is found in the knowledge that restaurant inspectors for the health department employ black lights in the course of their jobs: Rodent urine is also strongly fluorescent.

Disinfectants

The purplish blue glow that bathes those electric razors that are sometimes found in airport rest rooms comes from a short wave UV source put there to disinfect the razors in between uses. (This might help to explain/illustrate why life didn't emerge from the oceans before the UV filtering ozone layer had become established. The short wave UV rays are very harmful to life!) The same lights are used at barbershops and hair salons to disinfect their scissors and combs.

The goggles cabinets that are used to store and disinfect the safety goggles that many school science labs use employ a strong short wave UV light source. Hint: want to turn the hackmanite in your kit a vivid magenta/ raspberry color??? The goggles case will do an excellent job. The hackmanite will revert back to its white color as it is exposed to white light. You can easily recycle it back and forth in a class period. (two minutes in a bright light beam and the hackmanite is white again)

Going Postal

The post office uses black light as well. On the back of many envelopes are short letter and number codes that are used to identify the places where the letter was handled or processed. The metered stamps are often applied with fluorescent ink. The latest addition from the postal service are fluorescent bar codes printed on the backs of envelopes. Black lights can also be used to detect fraud. Stamps that have been soaked off and reused can be detected by the contrasting effect the black light has on the glue vs. the stamps.

Fluorescence on the Beach

Suntan lotion blocks a certain amount of UV light. Try painting a sign with it on white photocopier paper or any other fluorescent paper. When viewed in UV light, the letters will appear dark against the light background. How dark? It depends on the rating of your suntan lotion! Experiment with different SPF ratings.

Dab the lotion on a fluorescent mineral and observe what happens. A total UV block will result in a loss of fluorescence. A partial UV block brings about a color change in the affected area.

The opposite effect can be demonstrated by smearing petroleum jelly on a non-fluorescent piece of paper such as black construction paper, then viewing under UV light. Petroleum jelly as well as many oils and greases also fluoresce.

Glowing Money

The security strips in paper money fluoresce. Fives glow blue, tens glow orange, twenties glow green, fifties glow yellow and hundreds glow pink. Michigan driver's licenses now fluoresce, too.

Glowing Veggies

Slice open a green pepper and check it out under long wave UV. The inside glows magenta while the outside glows a different color. Does temperature make a difference? What about different varieties of peppers? Is it due to chlorophyll? If so, why do onions glow with their crazy colors (Check them out!)? Rotting bananas glow blue – why? What other vegetables look different under UV light?

Scorpions

Scorpions blend in well with the desert sand, but a night they are easy to spot because of their bright green fluorescence. Southwest locales sell a mini UV flashlight billed as a "scorpion light" in stores, but it is not exactly the same wavelengths as a standard long wave mineral lamp.

Fluorescence in the Laundry Aisle

A trip down the grocery store aisle provides the consumer with a multitude of product choices. Manufacturers are interested in you buying their brand. In an effort to attract the consumer's attention, boxes are often printed with fluorescent inks that respond to the long wave UV given off by the fluorescent lights in the store. This is especially true in the detergent section where. according to **Consumer's Reports,** few differences actually exist between the national brand name products, so it seems to be left to a matter of which box catches your eye in the crowded detergent aisle. (Turn off the lights and test a variety of boxes with your black light and see.) The single use detergent boxes sold at your local laundry make great space saving examples of their larger counterparts used at home.

The detergents themselves also contain small amounts of fluorescent dyes so that when you wash your clothes and then go out in the sunlight, they will appear to be "whiter than white", almost glowing. Try mixing a small amount of detergent in water, then view it with a black light for a glowing good time.

<u>Fluorescence and Detergents: An experiment</u>

Materials Needed:

An assortment of detergent boxes	rubbing alcohol
A long/short wave ultraviolet light	beakers & jars with lids
funnel & filter paper	scissors

Instructions:

Turn out the lights and observe the effects of short wave UV light on the detergent boxes. Repeat the observations for long wave UV light. Have the students record in a data chart which colors fluoresce under each condition.

Next cut out the fluorescent designs from the detergent boxes. Sort the cuttings by color. Peel as much of the cardboard away as possible. Soak each separate color in a capped jar of rubbing alcohol. After several days, the dye should have leached from the paper. Filter the solution into a capped glass container. Test each color dye with both the long and short wave UV lights.

<u>Discussion Questions:</u>

Are most papers reactive in mostly the short wave UV, or are most papers most fluorescent under long wave? (As a third choice: are they about the same?)

Do the same colors when extracted as dyes fluoresce under the same conditions as on paper? (Note any differences, and state the pattern.)

How do you account for any differences in fluorescence between the paper and liquid dyes?

Why do you suppose that the soap companies use the sorts of dyes that they do?

Explaining Fluorescence by Spectroscopy

Materials: Overhead projector, fluorescent liquid in a clear beaker, some cardboard for masks and a piece of diffraction grating (5 x 5 cm).

Prepare these materials for your overhead projector: First, cut a piece of opaque cardboard large enough to cover the entire stage surface. Cut a hole in the center of it slightly smaller than the size of the clear beaker you will use. Next cut a smaller piece of cardboard, large enough to completely cover the hole in the first piece. Cut a clean slit, about 1 cm wide by 5 cm long, in its center.

Next, cut another square of opaque cardboard, big enough to completely block the exit of light from the projector's top prism or mirror. In the center of the square, cut out a 5 x 5 cm opening and cover it with a piece of diffraction grating. Tape this so it hangs down over the exit of light from the prism or mirror.

Cover the stage of the overhead projector with the mask and slit. Darken the room. Turn on the projector and adjust it so the slit is in focus. This will project two large continuous spectra onto a screen or white wall, one on either side of the slit. (You may have to adjust its orientation by rotating it 90° so that the spectrum is to the right and left of the slit instead of above and below it.

The best solution to use for this activity is made with Biodegradable Tracer Dye tablets or Rhodamine B. You can also soak fluorescent markers in water to remove their dye, or mix up a solution of fluorescein. Another alternative is to prepare an extract of any green leaf by mixing a small amount of crushed leaves with an ethanol-water solution.

Activity 1
Place a beaker containing fluorescent solution over the slit. The solution will selectively absorb some part of the continuous spectrum, leaving a black absorption area. If you cover only half of the slit with the beaker, you may compare the spectrum with and without the solution.

Activity 2
Cover the stage of the overhead projector with the mask and hole. Remove the slit from the stage mask and the diffraction grating over the prism exit that was used for Activity 1. Place the beaker containing the solution over the hole, and turn on the projector.

Note the light of the transmitted solution on the screen. Many solutions will appear one color in visible light (due to scattering), another color when fluorescent, and a third color when light is transmitted through them. Note that the fluorescent liquid will absorb a wavelength of color that is shorter (higher in frequency) than the color it emits as it fluoresces. This is known as *Stokes Law*.

As an example, a Rhodamine B solution appears pink in visible light, orange when fluorescent, and magenta in transmitted light. Now, if you flip the diffraction grating back over the light, you can see that its absorption spectrum shows that it absorbs the green-yellow portion. The remaining colors (the blues and the reds) combine upon transmission to produce magenta.

FLUORESCENT RESOURCES

Fluorescein ($C_{2}0H_{12}O_{5}Na_{2}$) is one of the most fluorescent substances known. In addition to its widespread use as a water dye and current indicator, it is also used to reveal small cracks in engine blocks, aircraft bodies and the corneas of eyes. A fluorescein solution is painted over the suspect area. Inspection under long wave UV will reveal concentrations in leaking or torn areas.

Most antifreeze has fluorescein in it. It can substitute for demonstrations in a pinch, but a lifetime supply of fluorescein can be purchased inexpensively from most school chemical suppliers.

A dramatic demonstration of fluorescence: In a darkened room, sprinkle a small amount of fluorescein crystals on the top of a large cylinder of water. Illuminate it with long wave UV. As the crystals work their way down and into solution, they will leave glowing trails. Fluorescein is also excellent for explaining the color changes observed in transmitted and absorbed wavelengths. (Refer to the handout on Spectroscopy and Fluorescence).

A variation known as "red fluorescein" is sold as red water dye tablets or solutions. The active ingredient is Rhodamine B, a biological stain.

Where to order & prices (2012)

Flinn Scientific offers the dyes mentioned above plus kits and even how to make "fluorescent gummy worms": www.flinnsci.com/media/450771/ff2012-3.pdf

Fluorescein, 25 g for about $ 11 from various suppliers, such as Flinn Scientific, Sargent-Welch, Carolina, Lab Safety Supply, etc. Fluoresces yellow-green.

Red Fluorescein or Rhodamine B : Available as biodegradable dye tracer tablets or 1% solutions from various suppliers (see above) Fluoresces orange-pink. www.LabSafety.com

Educational Innovations has lots of UV and fluorescent demos, from glowing sand to UV beads to the diffraction grating needed to view spectra: http://www.teachersource.com/category/light-ultraviolet
Two additional products from Ed Innovations are helpful:
Phosphorescent vinyl sheet, 1 for $11.95
Photon Microlights, in all colors from for $16.95 each.

Arbor Scientific is another source for UV beads ($21 for 1000): http://www.arborsci.com

Mineral UV lamps and materials
Fluorescent minerals often change color or intensity when viewed in different wavelengths, and some minerals fluoresce only in one band of UV.

It is best to have a UV lamp with both short and long wavelength bands in order to collect minerals or to demonstrate their fluorescence. Small, hand-held models start around $15 for the mini LW only "flashlights". More powerful multiband lamps will run about $250- $400 or higher.

The following companies produce UV lamps and viewing boxes specifically designed for observing fluorescent minerals:

Way Too Cool Lamps* www.fluorescents.com/html/lamps.html
*these lamps offer a mid-range setting in some models and have excellent power

UV SYSTEMS	www.uvsystems.com
RAYTECH	www.raytechultraviolet.com
Ward's	www.wardsci.com

Mineralman also carries Way Too Cool lamps and UV safety glasses ($9.95/ pair): http://www.mineralman.net/id26.html

UV safety glasses ($5/ pair) and inexpensive black lights may also be purchased on Amazon.

We do not recommend using a plant grow-light, a poster black light, a small UV LED flashlight or a scorpion light to view minerals. They are not very powerful and may not show their fluorescent effects.

The Fluorescent Mineral Society is a helpful group to join. They have extensive web pages, an active listserv, and annual meetings. This would be a good resource group for advice, or to consult if you are considering places to collect fluorescent minerals. Their web page is: www.uvminerals.org

Books on Fluorescent Minerals

The Story of Fluorescence by Harry C. Wain is available from Raytech for $2.95 or FREE as a downloadable pdf. Well worth it! http://www.raytechultraviolet.com/product-story.php

Fluorescence: Gems and Minerals Under Ultraviolet Light, by Manuel Robbins. Published by Geoscience Press, Inc., 1994. ISBN 0-945005-13-X. List price $120. Outstanding book that offers numerous research projects for fluorescent minerals and also provides a thorough treatment of the basic chemistry of fluorescence.

Ultraviolet Light and Fluorescent Minerals, by Thomas S. Warren, Sterling Gleason, Richard C. Bostwick, and Earl R. Verbeek. Published by Thomas S. Warren and distributed by Williams Minerals, Rio, WV, 1995. ISBN 0-9635098-0-2. List price $20.

Collecting Fluorescent Minerals, by Stuart Schneider, 2011. Schiffer Publishing, Ltd., Algen PA. $25.44. Covers the U.S., Mexico and Canada. Includes what may become an international standard for rating fluorescent colors.

The Henkel Glossary of Fluorescent Minerals by Dr. Gerhard Henkel. Journal of the Fluorescent Mineral Society, volume 15 (1988-9). This is the most exhaustive listing of fluorescent minerals known: 566 mineral species and 59 related substances are listed. The glossary is printed in small-book format and is available from the FMS. $18.50

Fluorescence and Luminescence in Minerals, edited by Wendell Wilson. This issue of the "Mineralogical Record" magazine features a 15 page article dealing with luminescence in minerals. The second feature in this magazine is a 10 page summary of a symposium covering fluorescence and luminescence in minerals. This magazine was published by the Mineralogical Record, Inc., Tucson, AZ, as Volume 27, No. 1. Price: $30.00