[Version of 2016-03-09, with minor updates on 2025-05-31]

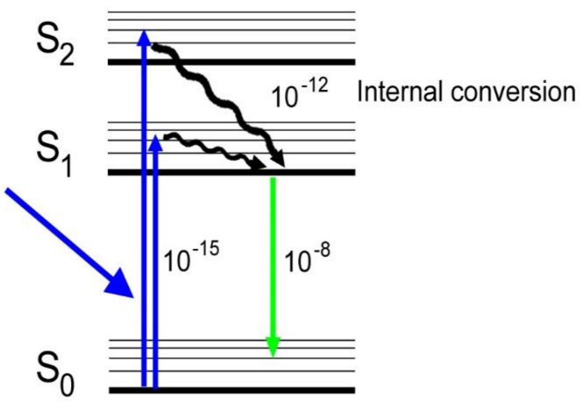
Why Minerals Fluoresce

Nearly everyone who has first experienced the vivid, beautiful colors displayed by fluorescent minerals wonders what can produce this glow and how does this process work?

It is important to realize that minerals generally don't glow on their own, but in response to some external energy source. Usually that energy source is ultraviolet light, which is much like visible light, but more energetic and lies beyond the range of light detectable by the human eye. About 15% of the 6,000 or so known mineral species are known to fluoresce under ultraviolet light. Others fluoresce under the influence of X-rays, an electron or proton beam, or even mechanical stress (e.g., when scratching, striking, or breaking a mineral). The key point to consider is that fluorescence arises as the *electrons in a mineral undergo energy transitions*, absorbing energy from some source and re-emitting part of it as visible light.

It is also important to realize that fluorescence arises from "emission centers" within a mineral. There are various kinds of emission centers – a few will be mentioned later – but commonly they are specific ions (electrically charged atoms) in the mineral, such as divalent manganese (Mn^{2+}) substituting for zinc in the mineral willemite (Zn_2SiO_4). Here the superscript 2+ after the Mn symbol indicates that the manganese ions have each lost two electrons and are no longer electrically neutral. Such ions within the willemite structure are highly susceptible to having some of their electrons boosted to higher energy states by ultraviolet light, and then having those same electrons emit green light as they fall back to the ground ("resting") state. This is what we call fluorescence.

The standard model for visualizing this process likens the nucleus of an ion to the Sun and the electrons orbiting around it to planets: a miniature Solar System. In this view, an electron that absorbs sufficient energy jumps to an orbit farther from the nucleus; it is then said to be in an *excited state*. When, later, the electron falls back to its *ground state*, where it began, light is emitted and fluorescence occurs. This model is useful as a readily grasped mental construct, but it departs from reality in several important respects, notably as regards orbital shapes of individual electrons (not to mention the physics involved!).



A much more useful model is an energy-level diagram, a simple version of which is shown at left. In this diagram, the possible energy states of electrons within an ion are depicted by the bold horizontal lines. The lowest of these is the ground state, S_0, the energy of an electron under "normal" conditions. The thin horizontal lines above each of these energy states are vibrational/rotational sublevels. If, for example, a mineral at room temperature is mildly heated, electrons in the S_0 state will jump to higher sublevels within that state (the vibration of electrons is, in fact, what we sense as heat). Other, more energetic sources of energy, such as ultraviolet light (indicated by the blue line entering from left), may propel electrons to levels above the ground state (S_1 or S_2

in the diagram). This process, indicated by the blue, upward-pointing arrows, takes place quite quickly, on the order of about 10^{-15} seconds (one quadrillionth of a second), and leaves the electrons in an excited state.

Electrons do not stay long in an excited state and soon lose some of their energy to vibration (heat), a process called *internal conversion*. This is illustrated by the wavy lines in the diagram, which show the electrons falling to the lowest level of the first (S_1) excited state. This process takes place in about one trillionth of a second – still fast, but 1000 times slower than the excitation process before. From the S_1 state the electrons then fall back to one of the sublevels in the ground state, each emitting a photon (light) in the process. The wavelength of this emitted light, as depicted by the green arrow in the diagram, is equivalent to the energy difference between the two states. The light emitted by billions of such electrons in a mineral is what we see as fluorescence.

Note that the green arrow, showing the amount of energy emitted as the electrons fall back to the ground state, is shorter than the blue arrows of the excitation phase. This means that the wavelengths of the light emitted as fluorescence are longer (that is, less energetic) than the ultraviolet light that was used to excite the electrons originally. This longer-wavelength emitted light often falls within the visible range and enables us to enjoy, in the form of glowing minerals, an electronic process that is taking place before our eyes.

Minerals can be placed in several groups, depending on the general cause of their fluorescence:

1. Intrinsic activators. The activator of fluorescence in these minerals, as the term implies, is a component intrinsic to the mineral. Scheelite is a mineral with the chemical formula $CaWO_4$. Its blue fluorescence is due to electron transitions within the tungstate ion, WO_4^{2-}. Many uranium minerals are another example; in these the characteristic yellowish-green fluorescence is due to the uranyl ion, UO_2^{2+}.
2. Impurity activators. Hundreds of different mineral species will fluoresce when some chemical impurity is present, often in only minor or trace amounts. Calcite ($CaCO_3$), willemite (Zn_2SiO_4) and wollastonite ($CaSiO_3$) are examples of minerals that in their pure state do not fluoresce, but add a little divalent manganese (Mn^{2+}) and they will fluoresce red, green, and yellow, respectively. Impurity activators in minerals can be single ions, as in the example just mentioned, or polyatomic ions such as disulfide ion (S_2^-) and the uranyl and tungstate ions mentioned above.
3. Defect activators. The way a mineral's ions are arranged in three-dimensional space is called its *crystal structure*, but it is important to realize that the perfect, idealized structures we see in textbooks do not exist in nature. Real minerals contain a host of defects (missing ions, extra ions, misplaced ions, partial rows of ions, etc.), all of which distort the electron cloud in the vicinity of the defect and thereby alter the way the ions in that part of the mineral absorb light energy and dissipate it. In some instances the defects result in the fluorescence of a mineral that would not otherwise exhibit that property. In diamond, for example, a nitrogen atom substituting for carbon, coupled with a vacancy (missing carbon atom), is responsible for yellow fluorescence.
4. Inclusions: The fluorescence of some minerals is due not to the mineral itself, but to inclusions of some other substance within it. When these inclusions are of microscopic dimension it appears that the mineral host is glowing, when in fact it is not. Molecular inclusions of organic compounds are a common cause of white or near-white fluorescence in calcite from many caves worldwide. Tiny droplets of oil included in fluorite cause some specimens to fluoresce yellow to pale blue; the same is true of quartz. The pale yellow fluorescence of some quartz is due to microscopic grains of powellite, $CaMoO_4$, disseminated within it.

5. Coatings and intergrowths: Here too the apparent fluorescence of some minerals is due not to the mineral itself, but to a second mineral coating or intergrown with it. Two of our local minerals, clinohedrite from Franklin and willemite from Franklin and Ogdensburg, often form coatings so thin they are difficult to detect except under magnification, but they cause a spurious orange (clinohedrite) or green (willemite) fluorescence in many specimens of other mineral species. Coatings of calcite on some of the local minerals likewise fluoresce green, but in some cases the fluorescence is due not to the calcite, but to microscopic intergrowths of opal.

It should also be mentioned that some minerals thought to fluoresce may not be fluorescing at all. Coatings of quartz on zinc ore from Franklin fluoresce bright green in some specimens, but here one is observing not fluorescence within the quartz, but fluorescence *through* the quartz. Quartz is transparent to shortwave ultraviolet light, allowing that light to penetrate to the willemite in the zinc ore beneath and produce a green response. And finally, the early hobbyist literature is replete with mention of minerals that fluoresce weak red to violet, but in many cases this is simply light emitted by the ultraviolet lamp and reflected from the specimen. Care must be taken to ensure that one is observing actual fluorescence.

In addition to activators – those ions, polyatomic ions, or defect centers in a mineral that actually emit the light that we see as fluorescence – the role of *coactivators* should be mentioned. Coactivators serve to transfer energy to an activator ion so the latter can fluoresce. Calcite, for example, is a poor absorber of ultraviolet light, so even if it contains a potent activator of fluorescence such as divalent manganese (Mn^{2+}), the resultant fluorescence will be feeble at best. If, however, ions of lead are present in addition to those of manganese, the lead will strongly absorb ultraviolet light and transfer part of that absorbed energy to the manganese ions, thus causing them to fluoresce much more strongly than before. As with activators, a host of different elements can serve as coactivators in minerals.

Finally, a few words about *quenchers* of fluorescence. These act to prevent rather than cause fluorescence and thus are unwelcome among those who enjoy the hobby of collecting and observing fluorescent minerals. Quenchers act by providing nonradiative transitions of electrons from excited states to the ground state, which means that the return of the electrons to the ground state does not result in the emission of photons (light), but only in the production of a little heat. Common quenchers of fluorescence, often present as impurity ions in a mineral, include nickel, iron, and cobalt.

Author: Dr. Earl R. Verbeek, Curator, Franklin Mineral Museum, in collaboration with Professor Lincoln Hollister, Professor Thomas S. Duffy, Laurel Goodell (all of Princeton University), and Haig Kasabach (retired Director, New Jersey Geological Survey). Author contact: earlrverbeek@gmail.com.