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ABSTRACT

The causes for many of the colors exhibited by minerals are presented to students. Several theories of modern physics are introduced. The nature of light, the manner in which light interacts with matter, atomic theory, and crystal structure are all discussed in relation to the origin of color in minerals. Included are color pictures of many minerals. (Author/RE)

ESCP Pamphlet Series PS.

COLOR of MINERALS

George Rapp, Jr.

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An understanding of the causes for the many colors exhibited by minerals involves an introduction to several of the theories of modern physics. The nature of light, the manner in which light interacts with matter, atomic theory, and crystal structure are all discussed in this pamphlet in relation to the origin of color in minerals. Included are many pictures of especially interesting minerals in full color.

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Color of Minerals

George Rapp, Jr.

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All color photos are from the collection of the author. Cover photo courtesy of Dr. Cornelius S. Hurlbut, Jr., Harvard University.

Color of Minerals

INTRODUCTION

For thousands of years man has marveled at the variety of colors found in "stones" and has attributed magical, curative, and protective powers to certain minerals, especially the many-colored gems. The beauty of amethyst was secondary to its value as a safeguard against intoxication; hematite, from the Greek word for blood, was believed to cure all manner of blood diseases, and beryl to promote conjugal love. Perhaps when properly mounted in a ring, green beryl (emerald) may still have these magical powers.

Even today certain colors are considered appropriate on some occasions and inappropriate on others. Colors as symbols, magic or otherwise, have retained their authority: Brides wear white, priests black; red signals stop (or else!), green approves go; and so on.

Alchemists, in many ways forerunners of modern experimental scientists, equated color with the essence or true nature of a substance. They tried to find a way to dye, tinge, alloy, or otherwise color metal, believing that such an alteration would indeed transform one substance into another. If their "synthetic gold" tarnished, they knew they had failed.

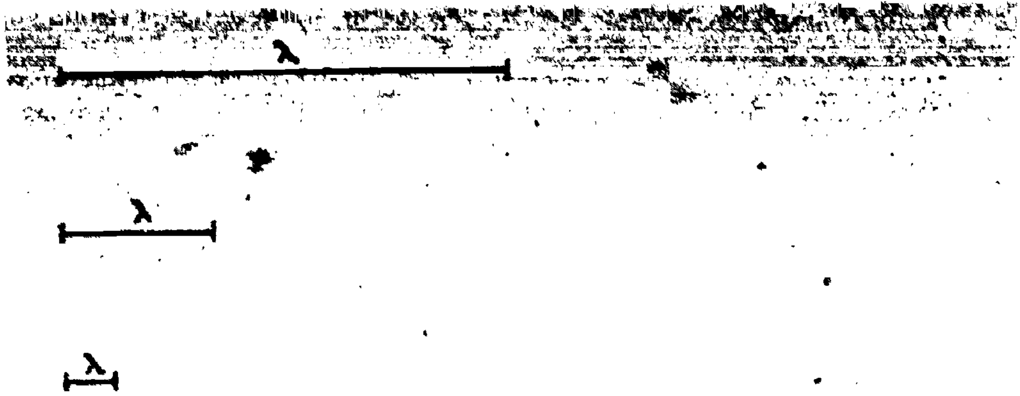


Figure 3. The wave nature of light. Waves with different wavelengths. The Greek letter [illegible] used to denote the wavelength. The [illegible] light [illegible] approximately [illegible] 7500 Angstrom units. (One Angstrom equals 10^{-8} centimeter.)

The alchemists' lack of understanding of the structure of matter was matched, and in some measure governed, by their ignorance of the nature of color and light. If there is no light, there is no color: thus it is with light that we must begin.

THE NATURE OF LIGHT AND COLOR

Information gathered by the human eye as it perceives light governs the way men think about the material world. As our knowledge of the nature of light has increased, so, correspondingly, has our knowledge of the materials and forces that make up the universe.

Beginning in the 17th century, when scientists first devised experiments to check their ideas on the nature of the physical world, a running controversy developed on the nature of light. Experiments like those showing that light could be made to go around corners, that it could interact to produce "beats" similar to those produced by sound waves, and that sunlight could be separated into colors and then recombined seemed to indicate that light traveled in "waves." However, Sir Isaac Newton proposed that light consisted of a series of particles, which, because they traveled in straight lines, could be considered "rays."

Experiments conducted from Newton's time until the beginning of the 20th century gave ever-increasing support to the wave theory as opposed to the particle theory. In fact, it became the custom in science to designate a particular color in terms of its "wavelength." We still use this system.

In the latter part of the 19th century, James Clerk-Maxwell showed that visible light as well as infrared and ultraviolet radiation (both invisible to the eye but able to be sensed by special equipment) are all forms of *electromagnetic radiation* (Figure 1). All forms of electromagnetic radiation travel at a constant speed in empty space, approximately 3×10^{10} centimeters per second. Types of radiation differ only in their wavelengths (λ in Figure 1).

Shortly after Clerk-Maxwell's work, radio waves (with wavelengths longer than infrared radiation) and X rays (with wavelengths much shorter than ultraviolet) were discovered. Thus the "electromagnetic spectrum" was greatly extended at both ends of the range of visible light, and today it is known that visible light occupies only a very narrow portion of that spectrum (Figure 2). The only other portion of the electromagnetic spectrum which man can sense himself is the infrared, the region of heat radiation. We feel the warmth of infrared radiation generated by particles colliding in the hot gases of the sun, as well as the infrared radiation from a hot stove, electric iron, and similar heat-producing implements of man.

At about the time radio waves and X rays were discovered, a young scientist, Albert Einstein, created a "new physics" by relating electromagnetic energy to the mass concept of matter and the velocity of light. "Particles!" said Einstein, as

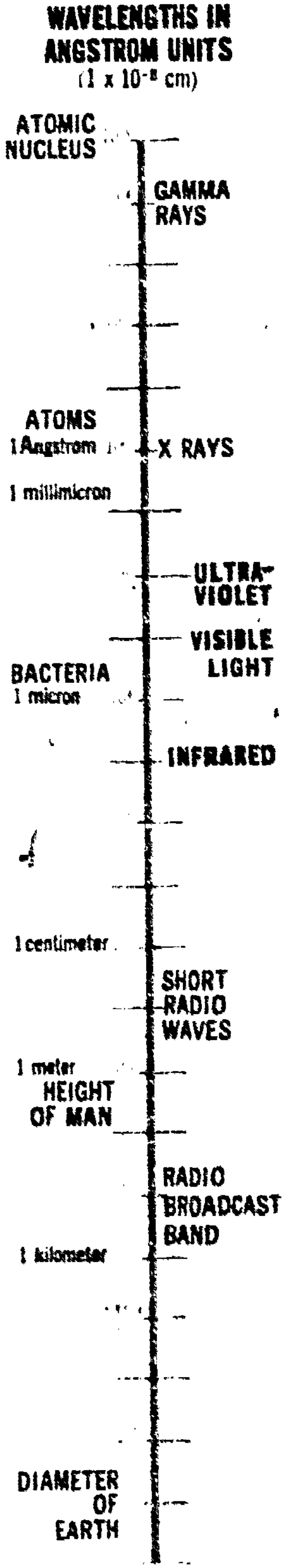


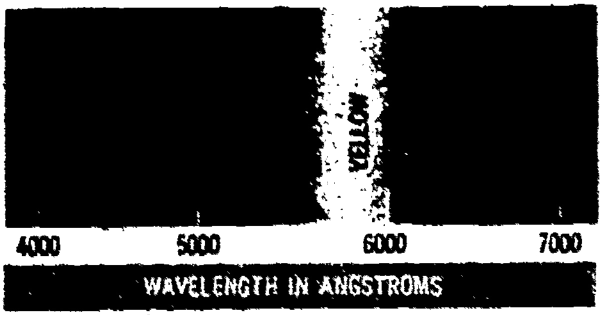
Figure 2 Types of electromagnetic radiation The scale is in powers of 10 Visible light covers only a small band

he revived the controversy. "Light consists of particles." According to this concept, radiation comes in discrete packets, later called *photons*. The more energetic photons correspond to radiation with short wavelengths; the less energetic, to radiation with long wavelengths.

Light, then, can be considered either an electromagnetic wave with a specific wavelength or a stream of light particles called photons, each possessing a specific amount, or *quantum*, of energy. Scientists today use either the wave model or the particle model of light, depending on the problem at hand.

The narrow band of the electromagnetic spectrum occupied by visible light, or light that registers on the average human eye, can be further broken down by wavelength into colors (Figure 3). The longest waves in the visible spectrum form the color we call red; the shortest waves produce blue or violet; and the remainder of the rainbow hues fall in between. Wavelengths of light recognized by the human eye range from about 4000 to 7500 Angstrom units. *One Angstrom equals one hundred-millionth of a centimeter* (10^{-8} centimeter), about the diameter of an atom.

The possibility of separating sunlight into its different wavelengths, or colors, was first recognized by Sir Isaac Newton, who allowed a narrow circular beam of light to pass through a glass prism and fall on a white surface (Figure 4). The individual colors contained in sunlight were spread out in a rainbow-like display, recorded by Newton as red, orange, yellow, green, blue, indigo, and violet.



COLOR	RANGE	AVERAGE
VIOLET	3900—4300	4100
INDIGO	4300—4600	4450
BLUE	4600—5000	4800
GREEN	5000—5700	5350
YELLOW	5700—5900	5800
ORANGE	5900—6100	6000
RED	6100—7500	6800

Figure 3. Wavelengths of light in the visible spectrum.

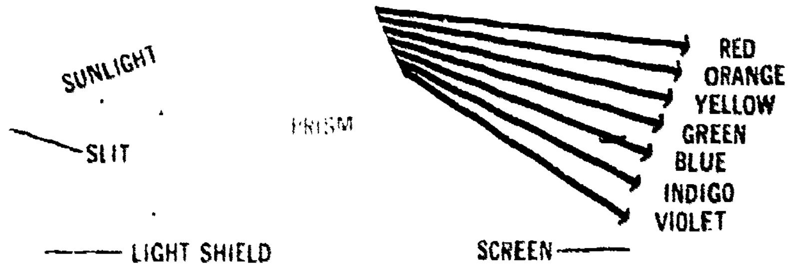


Figure 4. Formation of a spectrum from sunlight by a glass prism. In a continuous spectrum such as that produced by sunlight different colors blend into one another smoothly.

Thus sunlight, or *white light*, which appears to have no color, is really a mixture of all colors. Droplets of water in the atmosphere act like Newton's prism and produce a rainbow.

Interaction of Light with Crystals

For color to be perceived, however, light waves must interact with the object. Light striking the surface of a crystal undergoes reflection, refraction, scattering, and absorption.

Reflection is the return to the original medium, normally air, of a portion of the light striking a surface. The amount of light reflected depends on the composition and structure of the solid object. Metals reflect a high percentage of the incident light. If the metal is colored, the reflection will also be colored. Light reflected from the surface of a transparent substance, on the other hand, is generally not colored even if the substance is colored.

Refraction is the change in direction of a light ray when it enters a material of a different optical density at an angle (Figure 5). Differential refraction causes the color spectrum seen by Newton in his experiment with a prism. Each wavelength (color) of light has a different angle of refraction, so the colors separate as they emerge from the prism. Blue light is bent the most; red, the least.

Scattering arises from imperfections or flaws in the regular arrangement of atoms in a crystal. In this process, light energy is taken from the light

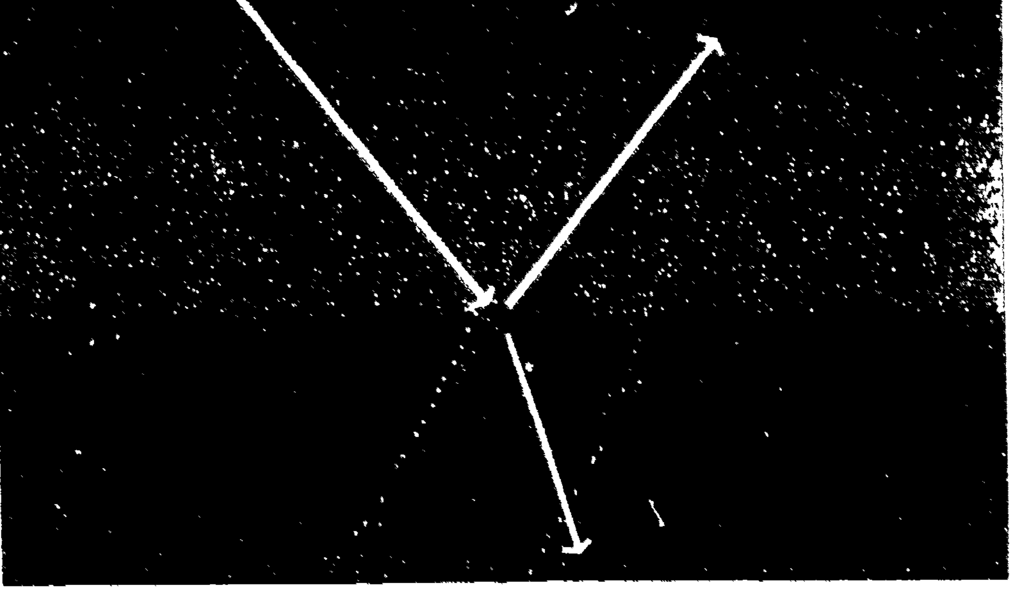
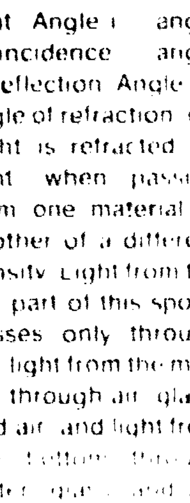


Figure 5 (A) Reflection and refraction of light Angle i angle of incidence angle of reflection Angle r angle of refraction (B) Light is refracted or bent when passing from one material to another of a different density Light from the top part of this spoon passes only through air light from the middle through air glass and air and light from the bottom through water glass and air



beam and reradiated as spherical light waves from each "scattering center." Thus some energy is lost by the beam as it travels in an altered direction. Solids that transmit light scatter and reduce it to such an extent that transmitted patterns cannot be clearly seen are *translucent*; solids that transmit light with no appreciable loss in clarity are *transparent*; and solids that transmit no light are *opaque*.

Absorption in crystalline substances is the process by which certain wavelengths in the visible spectrum are neither transmitted nor reflected. If some portions of the spectrum are absorbed and others transmitted or reflected, the wavelengths that are reflected combine to make the apparent color of the substance. For some substances the absorption is general, or approximately the same for all wavelengths. If the absorption is general and complete, or nearly so, we see the object as black, a complete lack of color. The object is seen as white if there is little or no absorption and all wavelengths are reflected or scattered, so the whole visible spectrum is contained in the reflected light. The difference between a white material and one that is clear or colorless is that the white material reflects or scatters all wavelengths without selective absorption, while a colorless substance transmits the light without appreciably altering anything but the path of the light as it enters and leaves the substance.

When a board that has been painted red is viewed in sunlight, it appears red because pigment in the paint selectively absorbs all the wavelengths shorter than red. However, if this same "red" board is viewed in light from a light source containing only the shorter (bluer) wavelengths, the board appears black because all the blue light is absorbed and there is no incident red light to be reflected. An otherwise "white" board appears red if illuminated by exclusively red light.

Color Development in Crystals

To understand how electrons can absorb electromagnetic energy in the visible light region, one must understand the electronic structure of atoms. The element iron contributes heavily to the color of many minerals. Figure 6 shows a simplified diagram of its electron shells. These shells are more or less spherical and concentric with the nucleus. Within the shell each electron is restricted to a

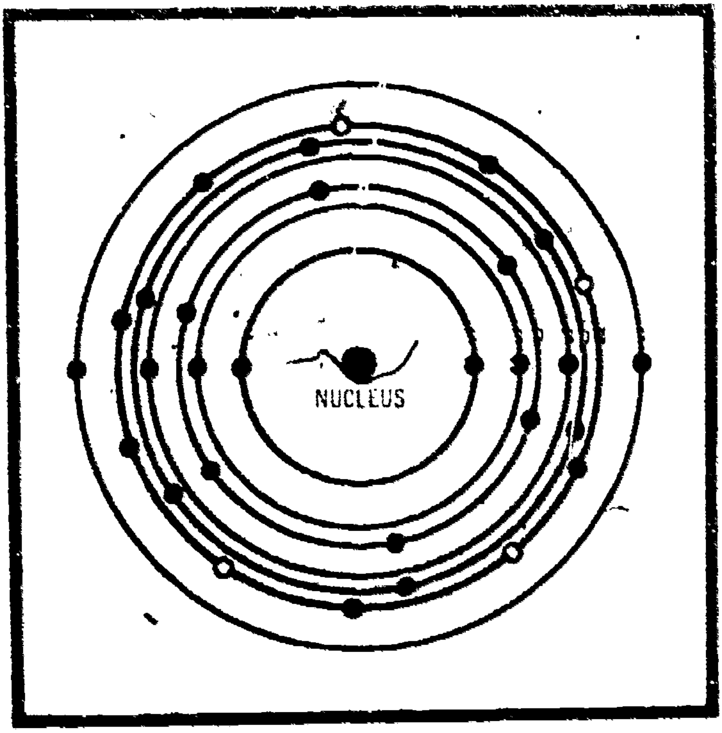


Figure 6 Atomic structure of iron. Each shaded ring represents a shell of electrons. Within each shell, each circle represents an orbital (*s*, *p*, *d*). Closed dots represent filled electron positions, open dots represent unfilled electron positions. Unfilled *d* orbital electron positions contribute to the absorption of light.

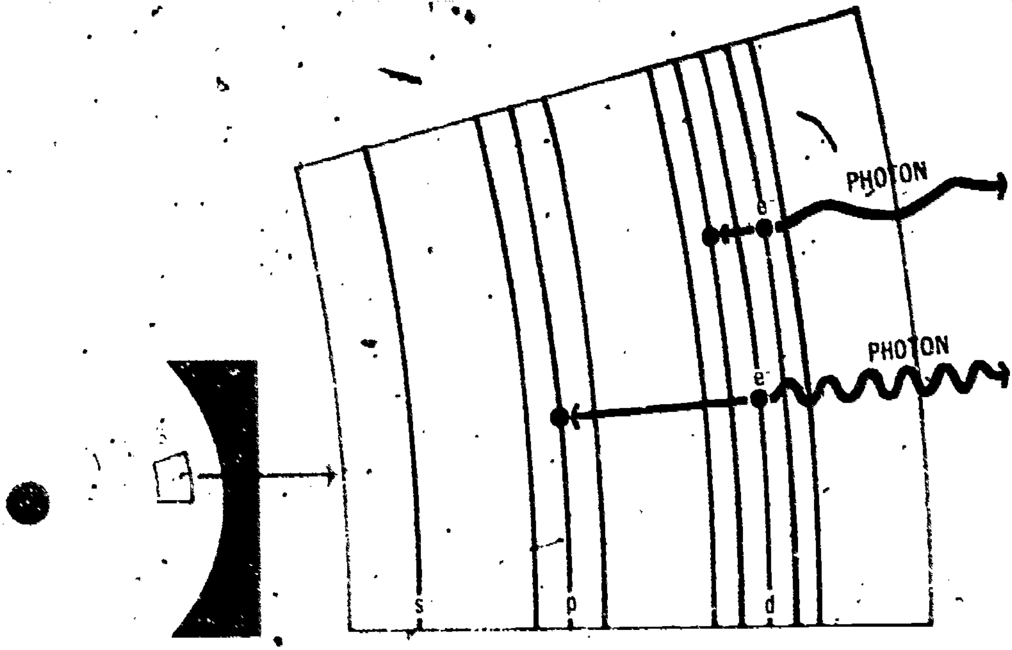


Figure 7. Electron jumps producing light rays (photons) Each electron jumps to an unfilled electron position of lower energy and emits a photon whose energy is equivalent to the energy difference between the two orbitals The larger the energy, the shorter the wavelength of the photon

certain energy level called an *orbital.* The orbitals, designated *s, p, d,* and *f,* each have a certain number of "positions" for electrons. The *s* orbital electrons have the lowest energy, and the energy increases through the *p, d,* and *f* orbitals. Not all shells have all types of orbitals. In some atoms the electron positions in the orbitals are not all filled. It is in these atoms with partially-filled orbitals that mechanisms exist to develop many of the colors observed in minerals.

For every distinct quantity of energy contained by Einstein's photons or light packets, there is one and only one associated wavelength. When light of a specific wavelength enters a crystal and encounters an electron that can accept the amount of energy associated with that particular wavelength, the light is absorbed. A given electron is able to accept and absorb the amount of energy stored in the light photon if the energy corresponds exactly to the amount necessary for the electron to "jump" from its normal position to a position of higher energy.

Conversely, when an electron drops to a lower energy level, a photon is emitted containing energy equivalent to the energy difference between the new and old positions of the electron (Figure 7). The whole field of spectroscopic analysis is based on this principle. Each chemical element has a unique set of energies associated with its particular set of electron orbitals and therefore has its own distinguishing emission wavelengths. For example, common table salt (sodium chloride) placed in a nonluminous flame will emit a strong yellow color. This color is due to the photons of light emitted when electrons in sodium, having been "excited" by the heat, return from a higher to a lower energy level.

At ordinary temperatures electrons lack the energy to jump from one type of orbital to another. However, electron jumps from one orbital to another orbital of the same type within the same shell require only a small amount of energy, and the associated wavelength often lies in the visible region.

SOURCES OF COLOR IN MINERALS

Transition Elements

It takes two electrons to fill the *s* orbital of a shell in an atom, six to fill the three *p* orbitals, ten to fill the five *d* orbitals, and fourteen to fill the seven *f* orbitals. Whenever an atom with a partially-filled *d* or *f* orbital is present in a mineral, there is a good chance that the electrons will jump between the various *d* or *f* orbitals, absorbing energy in the visible region. Because the energy differences between electron positions in these orbitals correspond to the wavelengths of visible light, the mineral will be colored.

The *transition elements* (Figure 8) have such partially-filled orbitals and play the major role in mineral color. Elements like iron, manganese, chromium, and vanadium have partially-filled *d* orbitals. Elements in the so-called lanthanide and actinide series have partially-filled *f* orbitals.

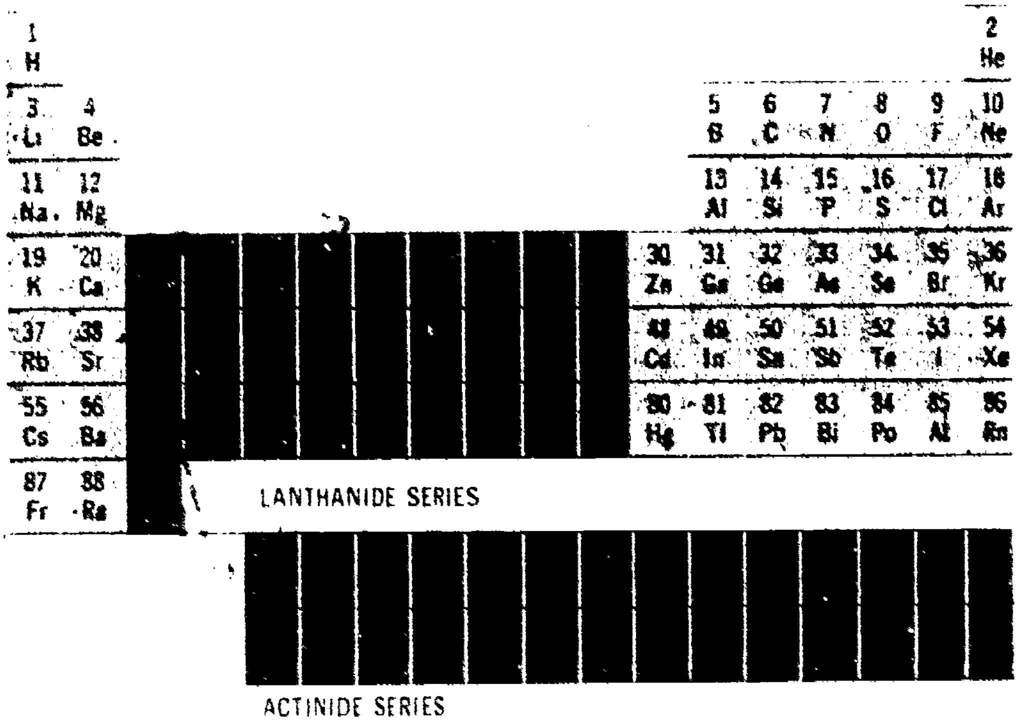


Figure 8 The periodic table of the elements. The transition elements are shaded in color

A given element does not always cause the same color, however. This is because the energy required for an electron jump from one position to another is influenced by the environment of the atom—the types and number of nearby atoms—and also by its *oxidation state*—the number of electrons it has in excess or in deficit of its atomic number Z (the number of protons). Some elements, notably the transition metals, can assume more than one oxidation state. For example, manganese can assume oxidation states +2, +3, +4, and +7, corresponding to a deficit of 2, 3, 4, or 7 electrons.

When an atom has more or fewer electrons than it has in its neutral or uncharged state, it is called an *ion*. An ion with a shortage of electrons has a positive charge. An ion with an excess of electrons has a negative charge. Elements such as sodium that give up an electron in chemical bonding become positive ions (Na^+); those like chlorine that receive electrons become negative ions (Cl^-).

TABLE 1. ELECTRONIC CONFIGURATION OF THE FIRST THIRTY-SIX ELEMENTS

TRANSITION ELEMENTS are in capital letters
s, p, d, f are orbital designations

Atomic Number	Name of Element	Symbol	Number of Electrons in									
			1st shell	2nd shell		3rd shell			4th shell			
			s	s	p	s	p	d	s	p	d	f
1	Hydrogen	H	1									
2	Helium	He	2	INERT GAS								
3	Lithium	Li	2	1								
4	Beryllium	Be	2	2								
5	Boron	B	2	2	1							
6	Carbon	C	2	2	2							
7	Nitrogen	N	2	2	3							
8	Oxygen	O	2	2	4							
9	Fluorine	F	2	2	5							
10	Neon	Ne	2	2	6	INERT GAS						
11	Sodium	Na	2	2	6	1						
12	Magnesium	Mg	2	2	6	2						
13	Aluminum	Al	2	2	6	2	1					
14	Silicon	Si	2	2	6	2	2					
15	Phosphorus	P	2	2	6	2	3					
16	Sulfur	S	2	2	6	2	4					
17	Chlorine	Cl	2	2	6	2	5					
18	Argon	Ar	2	2	6	2	6	INERT GAS				
19	Potassium	K	2	2	6	2	6		1			
20	Calcium	Ca	2	2	6	2	6		2			
21	SCANDIUM	Sc	2	2	6	2	6	1	2			
22	TITANIUM	Ti	2	2	6	2	6	2	2			
23	VANADIUM	V	2	2	6	2	6	3	2			
24	CHROMIUM	Cr	2	2	6	2	6	5	1			
25	MANGANESE	Mn	2	2	6	2	6	5	2			
26	IRON	Fe	2	2	6	2	6	6	2			
27	COBALT	Co	2	2	6	2	6	7	2			
28	NICKEL	Ni	2	2	6	2	6	8	2			
29	COPPER	Cu	2	2	6	2	6	10	1			
30	Zinc	Zn	2	2	6	2	6	10	2			
31	Gallium	Ga	2	2	6	2	6	10	2	1		
32	Germanium	Ge	2	2	6	2	6	10	2	2		
33	Arsenic	As	2	2	6	2	6	10	2	3		
34	Selenium	Se	2	2	6	2	6	10	2	4		
35	Bromine	Br	2	2	6	2	6	10	2	5		
36	Krypton	Kr	2	2	6	2	6	10	2	6	INERT GAS	

You can see from Table 1 that an inert gas is formed when each successive electron shell is completed. A filled shell (as opposed to a filled orbital, or subdivision of a shell) gives a stable arrangement. Certain atoms may achieve a stable arrangement of filled shells by giving or receiving electrons. The resulting ions are said to have an inert gas configuration (Figure 9). Elements with filled shells rarely contribute to absorption in the visible range by the electron-jump mechanism. The electrons do not have any place to jump to. All electron positions are filled.

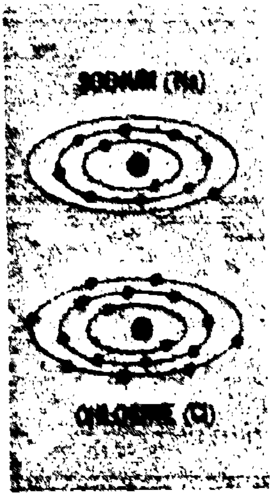


Figure 9. In sodium chloride (halite), sodium becomes Na^+ by giving one of its eleven electrons to chlorine, making it Cl^-. Then each has eight electrons in its outer shell, an inert-gas configuration.

The great majority of highly-colored minerals contain transition metals. Iron, the most abundant transition metal, is the coloring agent in a great variety of minerals. In addition to having unfilled *d* orbital positions, iron can exist in two oxidation states (+2 and +3); this leads to further complexities that result in the absorption of light. A given iron ion, say ferric iron (Fe^{+3}), does not have a characteristic color since the specific absorption will be modified by the environment of the ion. The colors of compounds where the same ion is surrounded by a nearly identical arrangement of other ions are quite similar. For instance, the two iron silicates, olivine, $(Fe,Mg)_2SiO_4$ (Figure 14), and tremolite-actinolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$ (Figures 13A and 13B), are both green since the ferrous ion (Fe^{+2}) has a similar environment.

Consider also the coloring effect caused by varying amounts of the transition metal iron in these two minerals. Both olivine and tremolite-actinolite are magnesium-iron silicates, which means that magnesium and iron may substitute for one another at the same site in the crystal structure. The magnesium ion (+2) has all orbitals and shells filled (an inert gas configuration), and does not contribute to absorption in the visible region. Therefore as the transition metal iron replaces magnesium in the structure of these minerals, the minerals range from white into dark greens.

The intensity of the color seems to increase when the transition element in the mineral is present in more than one oxidation state, a situation made possible by a process called charge transfer. Many minerals containing only the ferrous ion (Fe^{+2}) or only the ferric ion (Fe^{+3}) are relatively pale in color, whereas iron-containing silicates like pyroxenes (Figure 16C) and amphiboles (Figure 13C) that contain both ions are dark green to black. This feature is shown dramatically by the mineral vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$. The fresh mineral is usually colorless, but exposure to air, with the accompanying partial oxidation of ferrous to ferric iron as the ferrous ion gives up an electron to an oxygen atom, causes vivianite to turn bluish black.

Charge transfer among atoms, a mechanism related to light absorption, may also take place when an element capable of more than one oxidation state is present. Since an electron is a charged particle, a transfer of an electron from one ion to another is a charge transfer. This transfer is possible when the energy difference between the different oxidation states of the same element is small. Under these circumstances, an electron may transfer or jump from one ion to another, thus changing the oxidation state of both. The small energy difference between Fe^{+2} and Fe^{+3} causes the deep color of magnetite, Fe_3O_4, and is a contributing factor in the color of biotite, $K(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2$ (Figure 16B), and tourmaline, $(Na,Ca)(Al,Fe,Li,Mg)_3B_3Al_3(AlSi_2O_9)_3(O,OH,F)_4$.

When a small amount of chromium, another transition element, is present in corundum, Al_2O_3, a red color develops and the corundum is called ruby. Both natural and synthetic rubies are colored in this manner. However, if a large amount of chromium is forced into the corundum structure, the resulting color is green. The same phenomenon occurs in chrome spinel, $Mg(Al,Cr)_2O_4$. Minor amounts of chromium produce a red color; larger amounts, green. This may be interpreted as follows: Placing the chromium ion, which is larger than the aluminum ion, in the aluminum position results in a squeezing of the chromium. The strain energy from the squeezing causes the red color by absorption of the blue-green portions of the spectrum. When sufficient chromium replaces aluminum to expand and distort the structure, the strain energy changes and the absorption shifts, producing the green. Chromium is also the green coloring agent in uvarovite garnet, $Ca_3Cr_2(SiO_4)_3$, chromium muscovite, $K(Al,Cr)_2AlSi_3O_{10}(OH)_2$, and emerald, $Be_3Al_2Si_6O_{18}$.

Manganese usually lends a pink, lavender, or violet color to silicates and carbonates such as lepidolite, $K(Li,Al)_3(Si,Al)_4O_{10}(OH,F)_2$; rhodonite, $MnSiO_3$; rhodochrosite, $MnCO_3$ (Figure 17A); and thulite (zoisite), $Ca_2Al_3Si_3O_{12}(OH)$. The prefix "rhodo-" is used to indicate a rose color. Manganese oxides such as manganite, $MnO(OH)$, and pyrolusite, MnO_2, however, develop a deep black color as a result of charge transfer in the manganese.

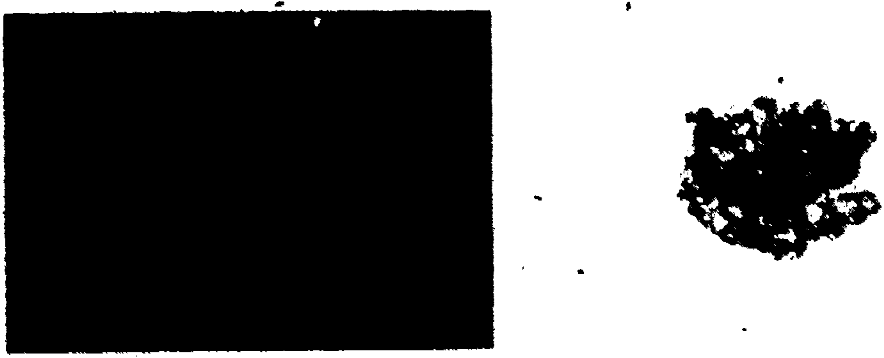
Copper minerals occur in a variety of colors. When copper is bonded to oxygen in minerals such as malachite, $Cu_2CO_3(OH)_2$ (Figure 18B), and azurite, $Cu_3(CO_3)_2(OH)_2$, the resulting colors are green and blue, respectively. The copper sulfides, however, display a variety of colors due to the interaction of the copper ion with loosely held electrons of the sulfur atoms. Different structures and different copper-sulfur ratios produce absorption in different portions of the visible spectrum. Exposure to a moist atmosphere causes oxidation and tarnishes the metallic gray of chalcocite, Cu_2S, and the metallic pink of bornite, Cu_5FeS_4, to an iridescent purple. These color changes are in response to the chemical change on the surface of the mineral. The material beneath the surface does not change color.

Some transition metal ions whose *d* orbitals are either empty or completely filled do not cause coloring. An example is Ti^{+4}. Note in Table I that titanium when neutral has two *d* electrons in the third shell. However, in becoming a +4 ion, ti-

Figure 12. Quartz, SiO_2.

(A) Impurity-free quartz crystal.

(B) Smoky quartz.



(C) Citrine quartz.

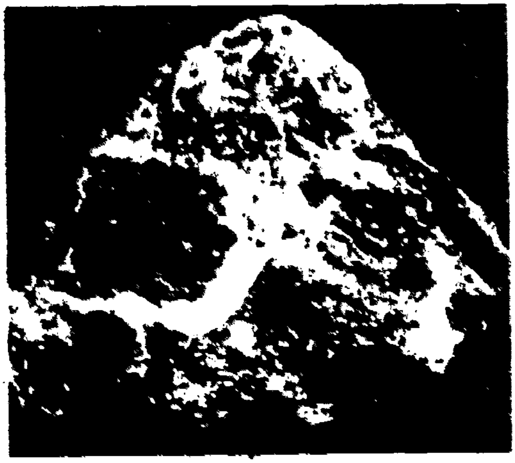
(D) Amethystine quartz.

Figure 13. Tremolite-Actinolite.

(A) Low-iron tremolite-actinolite. $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$.

(B) High-iron tremolite-actinolite. $Ca_2(Fe,Mg)_5Si_8O_{22}(OH)_2$.

Figure 13 (C) Amphibole containing large amounts of the transition elements (mostly iron, but also manganese, chromium and titanium)



(B) High-iron olivine, $(Fe,Mg)_2SiO_4$

(B) High-iron sphalerite

Figure 14 Olivine

(A) Low-iron olivine, $(Mg,Fe)_2SiO_4$

Figure 15 Sphalerite, ZnS

(A) Typical honey-colored sphalerite with minerals.

Figure 16

(A) Microcline feldspar $KAlSi_3O_8$, containing no transition elements

Figure 16. (B) Biotite mica. $K(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2$.

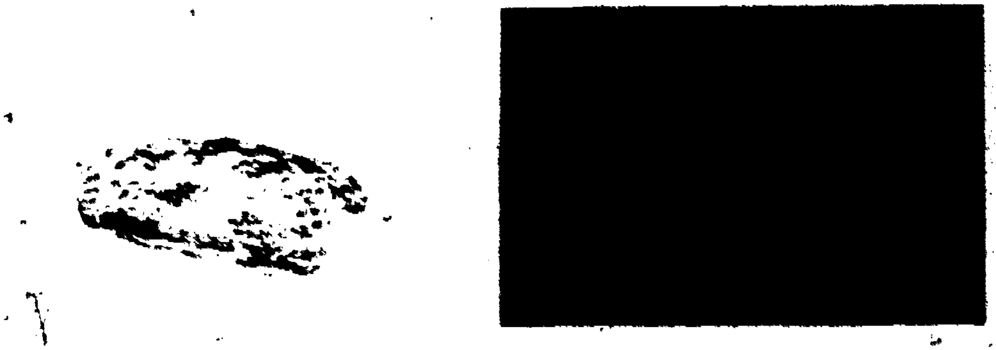
(C) High-iron pyroxene on rhyolite

Figure 17. Carbonates.

(A) Rhodochrosite, $MnCO_3$, on quartz.

(B) Siderite, $FeCO_3$

Figure 18.



(A) Graphite, C, native carbon

(B) Malachite, $Cu_2CO_3(OH)_2$.

Figure 18. (C) Gold, Au, on quartz.

(D) Pyrite, FeS_2, on quartz.

Figure 19. Halite, NaCl.

(A) Halite cleavage fragments.

(B) Blue halite.

(C) Normal halite with blue halite.

Figure 20. Fluorite, CaF_2, with purple color centers

tanium loses these two *d* electrons, along with the two *s* electrons in its fourth shell. Therefore no electrons are present in the *d* orbitals to jump around from one *d* orbital to another. The intense absorption observed in rutile, TiO_2, is due to an excess of titanium over the Ti:O ratio of 1:2. The excess titanium results in the development of Ti^{+3} with one electron in a *d* orbital. There may also be charge transfer between Ti^{+3} and Ti^{+4}.

Zinc minerals display a variety of colors, depending on their impurities, because zinc is not a transition element and does not contribute to color in minerals. Sphalerite, ZnS, is colorless when pure and assumes its typical honey-brown color (Figure 15A) when iron substitutes for zinc in the structure. Willemite, Zn_2SiO_4, is also colorless when pure but develops a variety of colors through chemical substitution of other elements in the structure. The following transition elements produce the color indicated in parentheses when introduced into willemite: copper (light green), iron (gray), manganese (yellow), chromium (gray), and cobalt (intense blue).

It is often difficult to determine completely the cause of color when transition metals are present, because effects arising from partially filled *d* orbitals may be masked by the strong absorbing power of charge transfer phenomena also common in minerals containing transition metals.

Chemical Bonding

The manner in which elements are bonded to one another in crystals provides additional mechanisms for the absorption of light. In *ionic bonding*, positive and negative ions are held together by the attraction of opposite electrical charges. Each electron is restricted to a particular atom, as in sodium chloride. In *covalent bonding*, atoms share certain orbital electrons by means of overlapping orbitals. Each electron remains restricted to a molecular orbital, as in diamond. *Metallic bonding* consists of a loose overlapping of orbitals in metal atoms; the result is that a number of the electrons remain "free"—not tightly bound to one or two atoms—as in copper. The high thermal and electrical conductivity of a metal is due to the large number of electrons not strongly bound to any particular atom. Materials formed by ionic or covalent bonding, on the other hand, are poor conductors of heat and electricity because electrons are not free to move and the energy must move slowly by vibration of the whole atom.

"Free" electrons also give metals their characteristic opacity to light (by absorption), their high reflecting power ("metallic" luster), and in many cases their color. Two distinct mechanisms, both dependent on the different manner in which the electrons in metals respond to different parts of the visible spectrum, are important in defining the optical properties of metals. One is *selective reflection*, and the other is *selective absorption*. Selective reflection may be the dominant mechanism in highly reflecting minerals such as metals. Gold exhibits a yellow color due to selective reflection of yellow light, not selective absorption. Light transmitted through thin gold foil is bluish green; the yellow has been reflected and the red absorbed.

Finely powdered metals show a strong general absorption and appear black due to the large number of small light traps between the particles. Light is continually reflected back and forth among the small metal grains. On each contact with a metal surface a little more light is absorbed, ultimately resulting in total absorption and extinction of the light.

The color absorption characteristics of covalently-bonded minerals depend on how tightly the bonding electrons are held by the elements. In diamond these electrons are held securely, resulting in electromagnetic wave absorption only in the ultraviolet region; therefore, a diamond crystal appears colorless and transparent. In silicon the electrons are not as tightly held, so absorption occurs in the visible spectrum, and the material is colored or opaque. Tin has the same crystal structure as diamond and silicon, but the electrons are so loosely held that pure tin is opaque and has properties we normally associate with metals, although it is not a true metal.

The element carbon illustrates well the color variations due to different bond strengths in the same element. In diamond the strong bonding results in a dense, very hard mineral that is transparent and colorless. The mineral graphite, however, is also composed solely of carbon. Here a different type of bonding produces a large number of loose electrons that absorb almost the entire visible spectrum, resulting in a deep black opaque mineral.

Pure quartz, SiO_2, is transparent and colorless (Figure 12A). Crystals of quartz are transparent to wavelengths of electromagnetic radiation ranging all the way from 1,800 to 300,000 Angstrom units. However, since impurities are often included in the crystal, colored varieties of quartz are common. Some amethystine quartz (Figure 12D) owes its color to thin films of iron oxide incorporated on faces of the growing crystal. It has been suggested that the lemon color of citrine quartz (Figure 12C) is produced either by colloidally dispersed particles of hydrous iron oxide too small to be seen with a microscope or by the presence of Fe^{+3} in noncrystalline surroundings. Amethyst may be decolored or changed to the citrine color by heating. Some blue quartz is found in igneous and metamorphic rocks. The blue color of light reflected from this quartz is due to selective scattering of the blue wavelengths by the oriented patterns of needlelike inclusions of rutile within its structure. Milky quartz owes its color to the light scattered by the large number of tiny cavities or flaws in the crystals.

Small flakes or bands of mixed material often impart a distinct color to otherwise colorless or pale-colored minerals. For example, the red color of some feldspar, $KAlSi_3O_8$ (Figure 16A), is produced by the distribution of small flakes of hematite, Fe_2O_3, within the crystal.

Reflection and refraction of light from layers of dissimilar optical properties near the surface of a mineral produce the play of colors observed in some varieties of opal, $SiO_2 \cdot nH_2O$, and labradorite, $(Ca, Na)(Al, Si)AlSi_2O_8$.

Color Centers

Another mechanism that produces color in crystals is the selective absorption of light by certain imperfections in the crystal structure called *color centers*. An imperfection may be a foreign atom or ion, or it may be a "vacancy" in the structure as, for example, an excess of positive ions accompanied by "negative" vacancies. A negative vacancy would be a site where a negative ion belonged but was missing. Such a negative vacancy may be filled by an electron that has become trapped there through displacement from its normal position by bombardment with X rays or other high-energy particles (Figure 10).

The energy of an electron trapped in a negative vacancy may be the proper magnitude to absorb light; this energy will depend on the environment of the site in which the electron is located. When a crystal is irradiated with white light, any photon in this light with the appropriate amount of energy will be absorbed by the electron and excite it to jump to a higher energy state. An induced color center like that in Figure 10 is usually easily bleached by exposure to strong light or by heating.

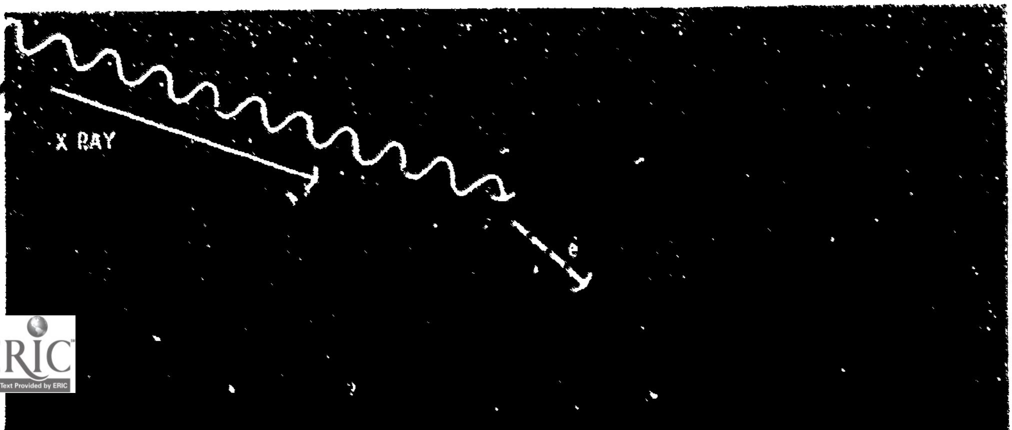


Figure 10 X ray producing a color center by knocking an electron from a negative ion into a negative vacancy. Light impinging on this crystal will be subject to selective absorption by this electron.

since supplying enough energy will release the electron from the color center.

Impurities in a crystal may cause color by

1) acting as direct absorbers of a portion of the visible spectrum,
2) straining the structure sufficiently to produce imperfections if the impurity is a larger ion than the normal ion, or
3) promoting positive or negative vacancies allowing for color centers, if the impurity is an ion of different charge.

The so-called "colloidal colors" result from the inclusion of colloid-sized impurities in solid material. Glass manufacturers have long added colloidal gold, copper, cadmium, and selenium to glass for color effects. These colloidal particles promote color by direct absorption, *selective scattering* (removing part of the optical spectrum by scattering and thus destroying some colors), and the development of *strain imperfections* (irregularities in the crystal structure similar to impurity or vacancy imperfections).

Crystals of the mineral fluorite, CaF_2, commonly exhibit a variety of colors; many, if not most, of these are caused by color centers. Transparent and clear fluorite specimens can be colored blue by radium irradiation. Undoubtedly the development of imperfections and electron traps by the bombarding radiation imparts new light-absorbing properties to this mineral.

Some fluorite colors have been correlated with the size of the color centers. Small centers develop green, medium-sized centers develop blue, and larger centers produce a violet color (Figure 20). Why? The size of the electron trap or color center is related to the amount of energy holding the electron in the trap. Therefore, since each wavelength of light is associated with a different energy, the size of the color center will control the wavelength absorbed. One portion of the spectrum will have energy just equal to the amount required to cause an electron jump from the color center.

In some crystals color centers seem to be stable indefinitely; in others the centers are unstable. Apparently impurities help stabilize color centers. Color induced by the formation of color centers may change with time as the electronic environment of the color center is altered. The violet color of some natural fluorites may be a result of radioactive bombardment of blue fluorite.

Not all the colors observed in fluorite crystals are due to the development of color centers. Incorporation of transition metals or rare earths into a fluorite structure in place of some of the calcium will impart a color to the specimen. Lanthanides in fluorite usually give rise to a yellow color. Small amounts of Mn^{+4} will produce a violet, and Mn^{+3}, a pink fluorite. Most green fluorite contains ferrous iron, Fe^{+2}.

Many blue fluorites contain a small quantity of Fe^{+2} plus Fe^{+3}. Is the blue color due to these impurities, or has an earlier irradiation produced blue color centers? Probably the best test is to see if strong light or heat will bleach out the color by releasing electrons from traps. If so, the specimen probably contains color centers.

Halite, common table salt (sodium chloride), is normally colorless and transparent to light over a wide range of wavelengths. This transparency ends, however, in the ultraviolet at about 2,000 Angstrom units. Radiation with wavelengths shorter than this has sufficient energy to excite electrons in the crystal to higher energy states. A strongly irradiated halite crystal turns yellow, but exposure to the radiation of sunlight turns it blue. This blue is not easily bleached out but can be removed by heating. Many natural halite crystals that have been subjected to heavy X-ray bombardment by nearness to radioactive minerals exhibit a semipermanent blue to purplish black color (Figure 19).

What is taking place in a halite crystal on an atomic scale? In a perfect sodium chloride crystal each Na^+ ion is surrounded by six Cl^- ions, and each Cl^- ion has six Na^+ ions as its nearest neighbors (Figure 11A). However, this picture of a crystal is idealized. In nature, crystals have defects: Every so often in a crystal an ion is missing. Half the missing ions will be positive ions, the other half negative, because the overall charge balance must be maintained. The type of defect that contributes to color centers is shown in Figure 11B.

Some of the negative vacancies in the halite crystal that indicate a missing chloride ion may trap an electron that has been agitated by strong X rays from outside the crystal. Such trapped electrons form color centers. When a halite crystal containing these trapped electron color centers is exposed to visible light the electron is excited and jumps from the vacancy in which it was trapped, thus destroying the color.

Celestite, $SrSO_4$, is commonly blue, a color resulting from natural radioactive bombardment. Pure celestite, however, resists artificial coloring by irradiation. Impure celestite with some sodium ions (Na^+) substituting for strontium ions (Sr^{+2}) will develop radiation-induced colors. Every two

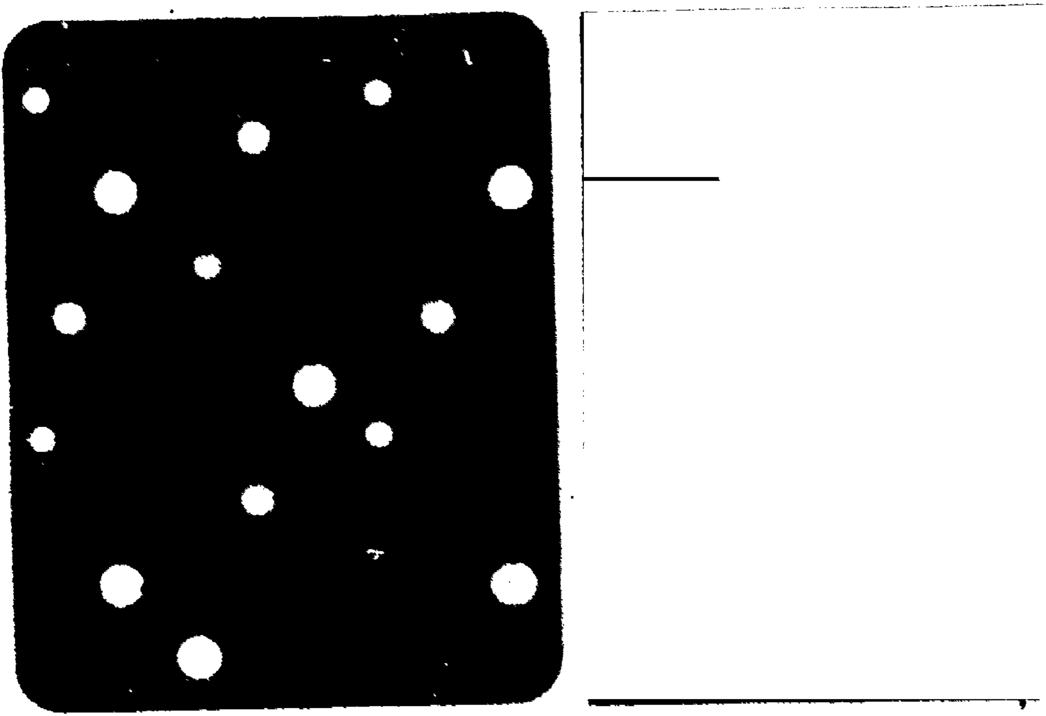


Figure 11. (A) Structure of halite, NaCl. (B) Vacancies in halite crystal giving defective structure.

sodium ions substituted in the structure may lead to one SO_4^{-2} vacancy that could become a color center electron trap.

Other materials develop colors in response to different types of radiation. Colorless glass bottles usually become pink or violet from long exposure to the sun's radiation. In other materials, including halite, the sun's rays may have a bleaching effect. In each case, electrons are excited to jump to a different position by the energy contained in a given wavelength of electromagnetic radiation.

REFLECTIVITY, LUSTER, AND LUMINESCENCE

Reflectivity is a precise measure of the quantity of light reflected from a surface, usually recorded as a percentage of the incident light of a given wavelength that is reflected. Reflectivity varies with (1) the angle of refraction of the light as it enters the mineral and (2) the absorption. The governing factor is absorption, since any light absorbed cannot be reflected. Reflectivity of minerals ranges from less than 5 percent (ice) to approximately 95 percent (native silver). Most common minerals have a reflectivity of less than 25 percent.

Some light that we think of as purely reflected may be made up of rays that have traveled extensively in a mineral before returning to the air. A good example is snow. The small six-sided snow or ice crystals are minerals with a definite crystal structure. When light falls on a layer of snow, only three or four percent is reflected directly, but the random arrangement of billions of tiny crystal faces causes the reflections to be returned in a great variety of directions. Most of the light is refracted into the crystals and travels through them until it strikes their lower faces. The greater part will then be refracted deeper into the snow, but the angle made by the light with the lower faces of many snow crystals will cause reflection back into the mineral and upward toward the air. Light striking the billions of tiny, randomly arranged snow crystals bounces back and forth and in and out of the individual crystals, with most of it finally returning to the air. This gives the snow an appearance of high reflectivity. A thin layer of snow will not appear as white as a thicker layer because in the thin layer more of the light will escape into the ground rather than return and contribute to the twinkling effect.

Luster has been described historically in terms indicating the similarity of mineral luster to the luster of other common objects. A "pearly" luster simulates mother-of-pearl. The luster of glass is described as "vitreous"; "adamantine" luster comes from the Greek word for diamond. Most metals have the typical "metallic" luster.

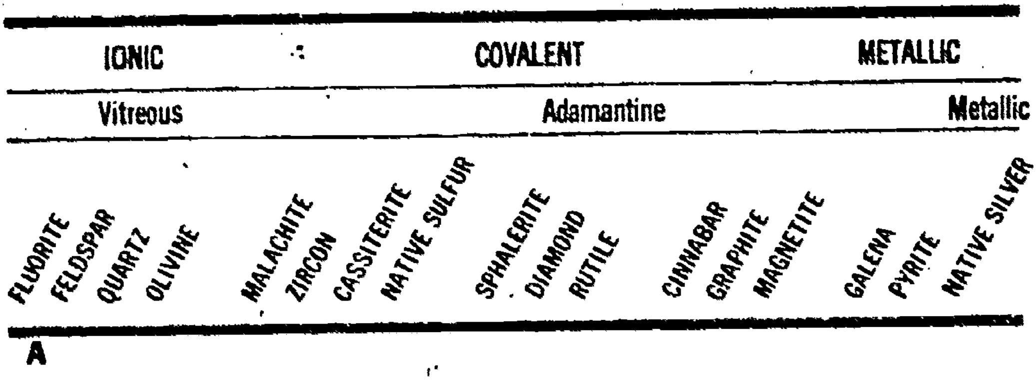
The property we call luster is related to the manner and intensity of reflection of light from surface and near-surface atomic layers in a mineral. Some minerals have been named on the basis of luster. Galena (PbS) means "lead glance."

The nature of this optical property is determined by four factors:

1) chemical composition,
2) type of chemical bond (ionic, covalent, metallic),
3) smoothness of surface, and
4) size of the reflecting grains.

A reduction in the smoothness of the surface and a reduction in grain size are really the same, since both give smaller plane reflecting surfaces.

Considering the luster of minerals having reasonably smooth surfaces allows luster to be correlated with chemical composition and type of bonding (Figure 21A). Ionic, covalent, and metallic bonds each provide a distinctly different type of electronic interaction with light waves. Most minerals, however, appear to have a combination of ionic and covalent, or of covalent and metallic bonds (Figure 21B).



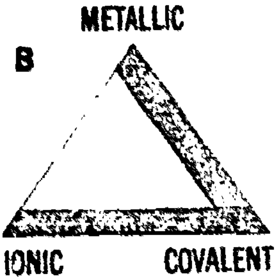


Figure 21. (A) Variation of luster with bond type in minerals. (B) Typical crystal bonds lie in the shaded area. Bonds that could be considered a mixture of ionic and metallic are not known.

Minerals falling in the ionic-covalent group usually have a luster that is vitreous (at the ionic end) to adamantine (at the covalent end), and a comparatively low index of refraction (ratio of the sine of the angle of incidence to the sine of the angle of refraction) at the ionic end and a high index at the covalent end. In general the more covalent the bond, the greater the absorption and the greater the index of refraction.

Covalent, adamantine minerals are often compounds combining an element that is a certain number of places to the left of the Group IV elements (C, Si, Ge, Sn) in the periodic table (Figure 8) with an element an equal number of places to the right of Group IV. For example: sphalerite, ZnS, cinnabar, HgS, and greenockite, CdS.

Those minerals with covalent-metallic bonds contain transition elements with *d* orbital electrons or heavy metals with *s* orbital electrons not involved in bonding (for example, lead). The electronic field of such minerals strongly interferes with the passage of light, and absorption is correspondingly large. The opacity and refractive index in this group depend on the number of loosely bonded electrons or weakly overlapping orbitals. A greater number of loosely held electrons results in a more metallic luster and a greater opacity to light. Opaque minerals have a metallic, black, or at least strongly colored streak (powder of the mineral on a porcelain plate), whereas transparent minerals usually have a white or weakly colored streak.

Whether or not a mineral has a metallic luster depends on the amount of energy necessary to re-move an electron from the metal ion and allow it to become a "free" electron. If energy greater than that of visible light is required, the mineral has a luster that is not metallic; if smaller, it has a metallic luster.

Luminescence is a glow some minerals exhibit when they are heated or exposed to ultraviolet rays. A mineral is said to *fluoresce* if it is luminescent only during the period of thermal or ultraviolet excitation and to *phosphoresce* if the luminescence continues for some time after the excitation has ceased.

Luminescence is illustrated in Figure 22A by picturing the energy changes attending the absorption and emission of radiation. Each atom or molecule begins with its electrons in a stable or ground state, G Fluorescence may be considered as absorption of radiation moving the electron to energy level F, followed by a drop of the electron to lower energy state A by radiating a wavelength longer than the stimulating radiation. In practice fluorescence usually involves the absorption of radiation in the invisible ultraviolet portion of the electromagnetic spectrum, with the simultaneous emission of radiation of a longer wavelength in the region of visible light. The word "fluorescence" was first suggested to describe this mechanism in the brilliant blue luminescence of many specimens of fluorite found in England. Probably no other mineral shows so many different fluorescent hues as fluorite.

As with some other light absorption phenomena, fluorescence is due to the presence of foreign ions acting as absorbers. In some minerals the activator or foreign ion is known. Manganese (+2) is the cause of fluorescence in calcite, $CaCO_3$, and willemite, Zn_2SiO_4; lead and molybdenum generate fluorescence in scheelite, $CaWO_4$. In some instances a special combination of foreign ions is needed. The bright red fluorescence of halite from California dry lake deposits and from a salt spring in Idaho is due to cooperative activation by minute

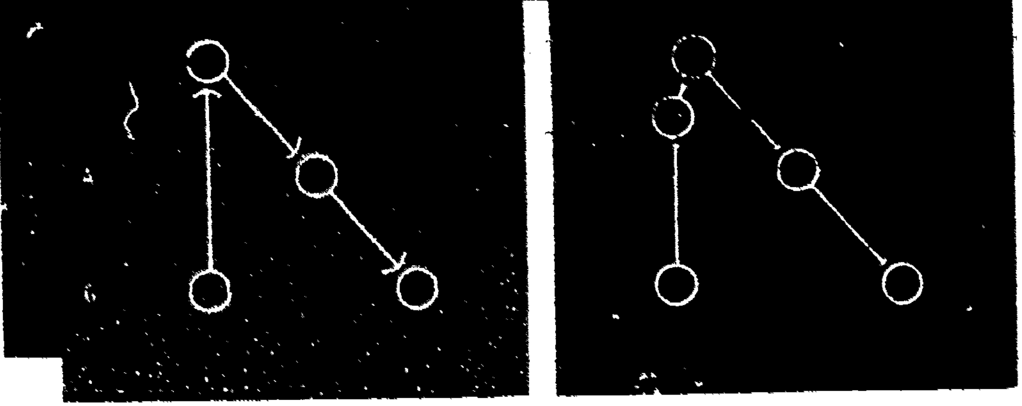


Figure 22. (A) Luminescence. Starting from the ground state, G, an electron absorbs energy from ultraviolet radiation and rises to a higher energy state. Then it falls back to G in two or more steps, emitting a photon at each step. (B) Thermoluminescence. An electron is driven into a trap by high-energy radiation. Heating gives it enough extra energy to escape from the trap and return to the ground state.

amounts of manganese and lead. Alone, neither element will generate fluorescence in halite. Apparently Pb^{+2} acts as an absorber, Mn^{+2} as an emitter.

The blue fluorescence in fluorites is caused by the lanthanide elements. They fluoresce by electron transitions involving unfilled *f* orbitals.

There are few minerals of which every specimen is fluorescent. Most minerals, however, have at least one occurence of fluorescence when activator ions are incorporated into the growing crystal during its formation, producing fluorescence when it is exposed to radiation at one or more wavelengths. Fluorescent specimens of halite; gypsum, $CaSO_4 \cdot 2H_2O$; barite, $BaSO_4$; apatite, $Ca_5(F,Cl)(PO_4)_3$; and leucite, $KAlSi_2O_6$, have been found. The most interesting fluorescent mineral is hackmanite, $Na_4(S,Cl)Si_3Al_3O_{12}$, which changes color under the influence of different wavelengths of light. A purplish-pink when freshly exposed, hackmanite bleaches rapidly in sunlight, but the color returns when the strong light is removed. With ultraviolet stimulation the mineral becomes an intense pink or purple. The source of these color changes in hackmanite is thought to be the chemical substitution of S^{-2} for Cl^{-}, resulting in the development of color centers.

The fluorescence characteristics of a mineral obtained in one locality will generally not be identical with those of the same mineral from other localities. Minor changes in the quantity or type of activator ion incorporated in the mineral structure will produce different fluorescent properties from locality to locality.

When heated many limestones, fluorites, and potassium feldspars exhibit *thermoluminescence* because electrons that have been driven into traps by earlier radiation from a nearby radioactive mineral are released. If these specimens are kept at a constant, high temperature, the thermoluminescence nearly vanishes in about one minute. After cooling, these specimens will not luminesce if reheated. Exposure to X rays or gamma rays is necessary to restore the thermoluminescent character of the mineral. Such radiation dislodges electrons; some of them become trapped in imperfections in the crystal and are later released through heating with the accompanying emission of light (Figure 22B).

Feldspar crystals that contain tiny particles of radioactive material will have thermoluminescent haloes around the radioactive element. Gamma radiation will induce thermoluminescence in calcite, dolomite, corundum, gypsum, quartz, the feldspars, and certain clays. You will find that most limestones, when crushed to a powder and dropped into a red-hot frying pan in a dark room, will luminesce a bright white or orange for several seconds. Under the same circumstances dolomite, $CaMg(CO_3)_2$, will emit a pale yellow to orange glow; feldspar will be white to bluish-violet. Fluorite containing uranium gives a particularly brilliant thermoluminescence.

Phosphorescence is due to the formation of electron traps during the period of irradiation and occurs as excited electrons return to their normal state after the excitation radiation has been removed, emitting the energy difference as light photons. Impurities play an important role in phosphorescence. They may be present as ions substituting directly in the crystal structure, extra atoms deforming the structure and causing imperfections, or atoms located at a defect. An increase in the concentration of the foreign activator atom will increase the intensity of the phosphorescence to a point that varies from mineral to mineral. The best concentration of silver or copper in zinc sulfide for phosphorescence is one part per million.

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Glossary

absorption—the phenomenon of taking in and neither returning nor transmitting electromagnetic radiation.

charge transfer—in the context of this book, the transfer of an electron from one atom to another atom of the same element; for example, an electron may transfer from an Fe^{+2} ion to an Fe^{+3} ion, thereby making the first ion Fe^{+3} and the second Fe^{+2}.

colloid—very small particles that tend to remain suspended indefinitely in a liquid.

electromagnetic radiation—waves of electric and magnetic fields at right angles to each other and to the direction of travel. Visible light, ultraviolet light, radio waves, and X rays are examples of electromagnetic radiation.

fluorescence—light emitted from a substance undergoing stimulation by electromagnetic radiation; the light emission ceases when the stimulation ceases.

gamma rays—very short-wavelength electromagnetic radiation; for example, radiation emitted from an atomic nucleus during some nuclear energy transitions.

heat rays—electromagnetic radiation in the infrared wavelengths.

incident radiation—radiation which strikes a material surface.

luminescence—light emitted from a substance following the absorption of electromagnetic energy.

orbital—the path of the electron around the atomic nucleus; each electron within an orbital has a discrete amount of energy.

oxidation state—the number of electrons in excess or deficit of the number of protons associated with a given atom in a compound. An excess of electrons produces a negative oxidation state; a deficit, a positive oxidation state.

phosphorescence—luminescence similar to fluorescence, except that light continues to be emitted after the stimulation ceases.

photon—quantum (discrete amount) of energy transmitted by light waves.

quantum—small discrete amount or bundle of energy; quantum theory holds that emission or absorption of electromagnetic energy is not continuous but takes place in quanta.

selective absorption—unequal absorption of the parts of an electromagnetic beam; thus some parts of a spectrum are relatively enhanced, some reduced, and some may even be completely removed by selective absorption.

selective reflection—the phenomenon of returning only some of the incident radiation from the surface; other wavelengths are transmitted, or weakened or destroyed by absorption.

shell—surrounds the atomic nucleus and contains the orbitals of electrons revolving around the nucleus.

spectroscopic analysis—analysis of the light absorbed or emitted by a substance. Each chemical element has a unique spectrum—the distribution of the intensity of emitted or absorbed radiation as a function of wavelength.

spectrum—radiant energy series arranged according to wavelength, frequency, or similar property common to the series.

thermoluminescence—luminescence in response to heat rays.

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