PRELIMINARY OBSERVATIONS ON THE LUMINESCENCE ACTIVATION OF ZEOLITE MINERALS BY BASE EXCHANGE*

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Abstract

Luminescence may be artificially induced in natural zeolite minerals by introducing activator elements (Mn, Pb, Ag, Cu) through base exchange. Base-exchanged Cu-zeolites and Ag-zeolites show green and blue cathodoluminescence, respectively. After dehydration, some Cu- and Ag-zeolites also develop photoluminescence, under ultraviolet excitation. Mn-, Pb-, and (Mn+Pb)-zeolites, which in their normal hydrated state are unresponsive to any excitation source, also develop cathodoluminescence and/or photoluminescence after being dehydrated.

Development of luminescence in base-exchanged zeolites is a reversible process dependent on the state of hydration or dehydration. The open-ness of the zeolites' crystal framework and its structural water are significant.

Introduction

It seems somewhat surprising, in view of their remarkable base exchange properties, that natural zeolite minerals do not luminesce; the literature records only one instance (Engelhardt, 1912), a specimen of natrolite from Oberscheffhauser, Germany, which fluoresces yellowish white under 3650Å excitation. The authors have found that luminescence may be artificially induced in natural zeolite minerals by the introduction of activator elements through base exchange.

The zeolites form an unusual group of hydrous aluminum silicates ($Al:Ca+Na=1:1$, $Al+Si:O=1:2$), which according to Dana (1932) are closely related in composition and occurrence. When heated, water is readily and continuously given off. This is in marked contrast to the normal release of water from minerals in discontinuous steps of definite amounts of water at definite temperature levels. The partially dehydrated zeolite can take up again its lost share of water, or even replace it by other substances such as air, ammonia, alcohol, hydrogen sulfide, iodine or mercury vapor. Moreover, the alkali or alkaline earth metal (usually Na and/or Ca) present may be replaced artificially by other metals, such as Ag, K, etc., by soaking in aqueous solution.

The atomic structure of the zeolite crystals (Wells 1945, Barrer 1949) consists of a more or less open framework of SiO_4 tetrahedra (with Al

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substituting for as much as half of the Si atoms), and linked together by shared oxygen atoms. The excess negative charge resulting from substitution of Al^{+3} for Si^{+4} allows for the introduction of positive ions (Ca^{++} or Na^{+}) into the cavities. Due to lattice defects in real crystals, these cations may move throughout the whole volume of the crystal rather than remain in a fixed position. In analcite (Taylor 1930), for example, 16 Na^{+} ions may occupy any of 24 vacancies. It is probable that the cations show six-fold coordination in all the zeolites.

The molecules of water (Taylor 1930, Wells 1945, Eitel 1941) are accommodated in the wide channels of the lattice, the number of molecules present being limited by the specific structure. Because of the electrostatic charge distribution in the water molecules they are found to require definite sets of nearest neighbors. In natrolite (Taylor, Meek, and Jackson 1932), the water molecules and oxygen atoms of the tetrahedron framework form double columns parallel to the *c* axis and passing through each channel; each of the 16 Na^{+} ions in the unit cell being surrounded by four oxygen atoms and two water molecules. Zeolitic water, then, is truly "structural" water.

Three types of zeolite structures can be distinguished: the analcite type, which contains a robust tri-dimensional lattice of tetrahedra cross-linked into 4- and 6-membered rings; the heulandite type, which is lamellar, consisting of close-knit sheets or layers of tetrahedra; and the natrolite type, which has chains of tetrahedra with only few cross-linkages, giving rise to the fibrous zeolites.

EXPERIMENTAL TECHNIQUE

Preliminary studies have been made with the following zeolites, which were kindly supplied us by Dr. William Foshag of the U. S. National Museum: chabazite (Pennsylvania), heulandite (Essex Co., N. J.), natrolite (Moore's Station, N. J.), and stilbite (Essex Co., N. J.). All three lattice structure-types of zeolites are represented, chabazite having the tri-dimensional network, heulandite and stilbite having the layer lattice, and natrolite, the fibrous structure. Most of our detailed work was based on stilbite since this was available in larger quantities.

Before treatment, all the mineral specimens were inspected under ultraviolet and cathode ray excitation[1] and found to be non-luminescent.

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[1] The "Mineralite," a low pressure mercury-vapor lamp of the cold cathode type, fitted with a Corning #9863 filter (to absorb visible blue light) emits primarily the mercury 2537Å resonance line. Sylvania's "Blacklite" bulb with a #9863 filter was used as a source of 3650Å radiation. Electron bombardment was supplied by a special demountable cathode ray tube or by spark coil discharge in partial vacuum.

A sample of each mineral was then examined spectrographically for conspicuous impurity elements. These are listed in the table following:

TABLE 1. MINOR AND TRACE IMPURITIES IN ZEOLITES

Chabazite:	Ti, V, Fe, Mn, Mg, Sr, Ba, Cu,[2] Ag,[2] (B)
Heulandite:	Ti, V, Fe, Mn, Mg, Sr, Ba, Cu, Ag, B
Natrolite:	Ti, V, (Fe), (Mn), Mg, Ca, (Cu), Ag, B
Stilbite:	Ti, V, (Fe), (Mn), Mg, (Sr), Cu, Ag, B

( ) indicates bare trace

The presence of trace impurities of Cu, Ag and Mn, so-called activator elements, does not invalidate the test results, since the zeolite minerals were completely unresponsive to all sources of excitation before treatment.

X-ray powder patterns were obtained for each zeolite mineral and compared with *d*-values (interplanar spacings) as listed in the American Society for Testing Materials' index of *X*-ray diffraction data. All gave reasonably good correlation.

Weighed samples of the powdered minerals (ground to pass 100 mesh sieve) were placed in glass-stoppered vials with a constant, measured volume of aqueous solution containing the desired concentration of activator. Unless otherwise specified, all preparations were made at room temperature. After treatment, the mineral powders were filtered off through sintered glass crucibles, washed with water and acetone, and air-dried.

LUMINESCENCE EFFECTS

In the earliest survey, samples of each of the zeolite minerals were treated for one week with 1×10^{-3} M aqueous solutions of the following metals (known to act as luminescence activators under suitable conditions): Cu, Ag, Mn, Pb, and Mn+Pb. None of the preparations luminesced under ultraviolet excitation, either 2537Å or 3650Å. Under electron bombardment from a spark coil discharge, however, the Cu-zeolites, with the exception of natrolite, luminesced a bright green. Later natrolite also was made luminescent after treatment with a more concentrated copper solution. The Ag-zeolites also responded to cathode ray excitation, with a blue-green luminescence (see Table 3).

Further studies were confined to Cu-activation. The effect of varied

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[2] Copper impurity may have been introduced with the graphite powder which was added as a spectrographic "flux," or from the solder in the stainless steel-meshed sieve. Silver also may possibly be a foreign contaminant, from previous materials passed through the sieve.

concentrations of copper and varied immersion periods were investigated first. Stilbite was treated with copper solutions ranging in concentration from 1×10^{-6} M to 1 M, at ten-fold intervals, and with a saturated solution. For a study of the time factor, stilbite preparations were taken after 15 and 30 minutes; 1, 2, 4, 8, and 16 hours; 2 days and 8 days.

It was found that after as little as 15 minutes' immersion in 1×10^{-3} M Cu^{++} solution (maximum Cu available by base exchange $=15\times10^{-4}$ g. per g. sample), stilbite developed its characteristic green luminescence under cathode ray excitation. On the basis of chemical evidence, Eichhorn (1859) likewise noted that considerable exchange with other ions took place within the first few minutes, although equilibrium was not established for some time. The lowest concentration to produce noticeable luminescence was 1×10^{-5} M Cu^{++} (maximum Cu available $=15\times10^{-6}$ g. per g. sample), after treatment for one week. There were no appreciable differences in the luminescence intensity of the other preparations.[3] A powdered sample of stilbite immersed in 1×10^{-3} M Cu^{++} solution in a sealed tube and heated at 100° C. for one hour did not develop noticeably brighter luminescence than the corresponding room temperature preparation.

In order to study more closely the nature of the luminescence emission of the Cu-zeolites, a bright-luminescing stilbite (treated with 1×10^{-3} M Cu^{++}, 1 week, room temperature) was selected for spectrophotometric measurement. Samples of the Cu-stilbite and the natural stilbite were set up within a special demountable cathode ray tube; the system was evacuated to a pressure of less than 2×10^{-5} mm. Hg and then subjected to electron bombardment. The luminescence emission spectrum was then determined photoelectrically using a motor-driven monochromator, a photomultiplier-tube, D. C. amplifier, and an Esterline-Angus Recorder. The emission spectrum is reproduced as Fig. 1.

DISCUSSION

Consideration of the available evidence leads us to believe that luminescence of the zeolites is connected with the entry of Cu^{++} ions into the crystal lattice structure and not with surface adsorption (as is the case with some organic phosphors in silica gel).

By spectrochemical analysis of a series of substituted stilbites, it was determined that approximately all of the Cu^{++} originally present in the less concentrated solutions was taken up by base exchange after one

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[3] Because of limitations inherent in the cathode ray equipment and the low luminescence intensity of the samples, it was not practicable to make exact measurements. Samples were inspected by eye, and only three or four at most could be compared simultaneously.

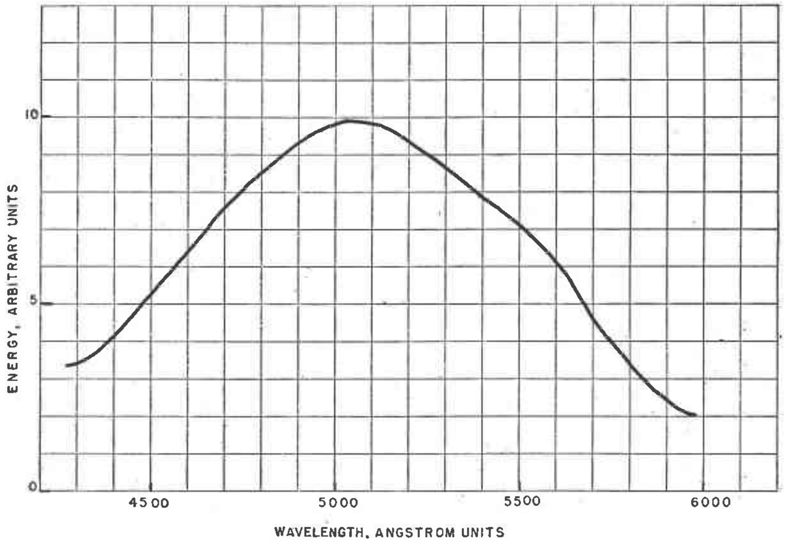

FIG. 1. Spectral emission of Cu-stilbite, under cathode ray excitation.

week at room temperature. Chemical analysis for residual Cu^{++} in the corresponding filtrates from these preparations confirmed the results.

TABLE 2. DETERMINATION OF CU IN SOME BASE EXCHANGED ZEOLITES

Sample Preparation	Cu added, as wt. % in zeol.	Cu found spectr., as wt. %	Cu found chem., as wt. %
Stilbite, nat'l.	None	$\leq$.0001 impurity	—
Stilbite in $10^{-4}M$ Cu^{++}	.002	.003	.002
Stilbite in $10^{-3}M$ Cu^{++}	.02	.05	.02
Stilbite in $10^{-2}M$ Cu^{++}	0.2	abt. 0.3	0.13
Stilbite in $10^{-1}M$ Cu^{++}	2.0	abt. 1.	1.

Zoch (1914) conducted base exchange studies with copper, but its valence state was not specifically indicated. Judging from the fact that her Cu-substituted zeolites were colored green, it is assumed to have been the cupric ion. Those of our zeolite samples which had been treated with the more concentrated Cu^{++} solutions, 1×10^{-2} M and higher, also became green in color. Zoch found, furthermore, that the green coloration could be discharged by soaking the specimen in ammonium chloride solution, the Cu^{++} ion being reexchanged for NH_4^+ as shown by chemical analysis. There was a definite quantitative relationship between the amounts of replaced Na^+, Cu^{++}, and NH_4^+.

Similarly, we were able to discharge the green color of a Cu-stilbite sample by digesting with hot sodium chloride solution. The colored Cu-stilbite luminesced bright green; the decolorized material (Na-stilbite) was dead. Chemical tests established that Cu^{++} had been removed from our green-colored zeolite and had been transferred to the leaching solution.

To eliminate the possibility that the observed luminescence phenomena were surface adsorption effects, experiments were carried out with silica gel, amorphous silica (H_2SiO_3), and finely powdered alumina. Treatment with Cu^{++} solutions produced completely negative results.

X-ray powder patterns showed no change in the lattice dimensions of the Cu-zeolites. That lattice distortion does occur in substituted zeolites has been demonstrated by the researches of Taylor, Meek and Jackson (1932) and Hey and Bannister (1932), among others. Their studies were made with *completely* base-exchanged zeolites. Since our prime interest was luminescence activation, no special effort was undertaken to attain complete base exchange. It is probable that immersion at room temperature in the very dilute solutions used effected only partial exchange. Where concentrated solutions were employed it is likely that partial decomposition of the zeolite (by the free acid resulting from unavoidable hydrolysis of the copper salt) deposited a protective coating of silica around the mineral grains, which then prevented extensive base exchange.

It may be of interest at this point to call attention to Hey and Bannister's (1932) statement that natrolite does not take up Cu^{++} by base exchange even after four months' immersion at room temperature. Their criteria were optical and *X*-ray behavior. That luminescence activation is a much more sensitive test for base exchange is apparent from the fact that natrolite (treated with 10^{-2} M Cu^{++}, 1 week, room temperature) shows distinct green cathodoluminescence.

Effect of Dehydration and Rehydration on Substituted Zeolites

The literature contains voluminous reports, some of it contradictory, on the peculiar dehydration properties of the zeolites, including some *x*-ray studies on the structural significance of water in the crystal lattice. Hey (1930), in reviewing the general properties of the zeolites states: "In some zeolites the water may probably be all removed without any discontinuity at all; as dehydration proceeds, there is a tendency for the whole structure to shrink somewhat, provided the temperature is maintained high enough for a long enough period, and after such shrinkage, the reabsorption of water is prevented, or at least slowed. If, however,

TABLE 3. LUMINESCENCE RESPONSE OF BASE-EXCHANGED ZEOLITES

Sample	Hydrous Preparations			Dehydrated (Heated) Preparations								
	3650Å	2537Å	Cathode Ray	3650Å				2537Å				Cathode Ray
				Fresh	Aged	Refired	Rehydr.	Fresh	Aged	Refired	Rehydr.	Fresh
Chabazite, nat'l	dead	dead	dead	gray	dead			gray	dead			dead
Heulandite, nat'l	dead	dead	dead	whitish	dead			whitish	dead			dead
Natrolite, nat'l	dead	dead	dead	whitish	dead			whitish	dead			dead
Stilbite, nat'l	dead	dead	dead	whitish	dead			whitish	dead			dead
Chabazite: Mn	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead	v. pale pink
Heulandite: Mn	dead	dead	dead	dead (?)	dead	dead	dead	dead (?)	dead	dead (?)	dead	pale pink
Natrolite: Mn	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead	white
Stilbite: Mn	dead	dead	dead	pink	dead	dead	dead	pink	dead	pale pink	dead	v. pale pink
Chabazite: Pb	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead	dead
Heulandite: Pb	dead	dead	v. pale pink	whitish	dead	dull white	dead	whitish	dead	whitish	gray	blue
Natrolite: Pb	dead	dead	dead	bluish-white	dead	dull white	dead	bluish-white	dead	whitish	gray	bluish-white
Stilbite: Pb	dead	dead	dead	bluish-white	dead	dead	dead	bluish-white	dead	whitish	dead	dead
Chabazite: Mn+Pb	dead	dead	dead	dead	dead	dead	dead	pink	dull pink	pink	dull pink	pink
Heulandite: Mn+Pb	dead	dead	dull pink?	dead	dead	dead	dead	dead	dead	pink	dull pink	pale pink
Natrolite: Mn+Pb	dead	dead	dead	bluish-white	dead	bluish-white	gray	pale blue	dead (?)	whitish	gray	bluish-white
Stilbite: Mn+Pb	dead	dead	dead	bluish-white	dead	bluish-white	gray	pink	pale pink	pink	dull pink	pink
Chabazite: Ag	dead	dead	green	dead	dead	blackened on standing		dead	dead	blackened on standing		green
Heulandite: Ag	dead	dead	dull green	white	dead			white	dead			dead (?)
Natrolite: Ag	dead	dead	blue	white	dead			white	dead			blue
Stilbite: Ag	dead	dead	v. dull green	dead	dead			dead	dead			dead
Chabazite: Cu	dead	dead	green	dead	dead	dead	dead	dead	dead	dead	dead	green
Heulandite: Cu	dead	dead	green	dead	dead	dead	dead	pale green	dead (?)	pale green	dull green	green
Natrolite: Cu	dead	dead	pale green	dead	dead	dead	dead	white	dull white	dead (?)	dead	green
Stilbite: Cu	dead	dead	green	dead	dead	dead	dead	white	dull white	white	bluish-white	green

the dehydration is carried out at low temperature in vacuo, the lattice-shrinkage ('Gitterreaktion') of Rinne and Scheumann is largely or entirely avoided, and the rehydration is rapid." The completely dehydrated zeolites, or "metazeolites" (high-temperature forms), still retain structural resemblance to the parent material, although *x*-ray patterns may indicate shrinkage or "collapse" of the unit cell.

It is impossible to effect extensive base exchange in a completely dehydrated zeolite. Beutell and Blaschke (1915) believe that removal of the water decreases the mobility of the cations. This loss of mobility may be due, they suggest, to the lattice shrinkage and/or increased electrical attraction between ions after the removal of the highly polar water molecules.

In an attempt to study the effect, if any, of the structural modifications produced by dehydration on the luminescent properties of base-exchanged zeolites, the cathodoluminescent Ag- and Cu-zeolites, as well as the non-luminescent Mn-, Pb-, and (Mn+Pb)-substituted zeolites, were subjected to thermal treatment. After heating for 30 minutes at 300° C. in a muffle-type furnace and cooling to room temperature, several of these base-exchanged zeolites, including some of the previously inert samples, luminesced under 2537Å and/or 3650Å excitation. Natural zeolite minerals which had not undergone base exchange but only thermal treatment were found to show indications of feeble photoluminescence.

Upon re-examination some eight months later, it was noted that the luminescence had weakened considerably and even disappeared completely from some of the heat-treated zeolites. After another heat treatment, however, luminescence was restored to these samples, although not all were returned to their original intensity. The entire suite of samples was subsequently stored over water in desiccators. After two weeks, the luminescence had again noticeably dimmed. This reversible development and loss of luminescence is obviously related to the hydrous condition of the zeolite mineral structure.

Table 3 lists the luminescence response of the various zeolite preparations studied.

Our most recent experiments indicate interesting possibilities in developing zeolites which will both fluoresce and phosphoresce under ultraviolet excitation with intensity comparable to efficient commercial phosphors. This has been accomplished by certain variations in thermal treatment and will be reported at a later date.

SUMMARY

The luminescence data can be correlated with the hydrous condition of the zeolites and summarized, as follows:

(1) Natural (normally hydrated) zeolite minerals do not luminesce under any excitation source but after heating at 300° C (dehydrated, to an undetermined extent), the zeolites develop indications of weak white luminescence under 2537Å and 3650Å excitation. (Some impurity in the mineral may be responsible for the weak activation.)

(2) Base-exchanged zeolites in their fully hydrated state (our room temperature preparations) do not exhibit photoluminescence, and only the Cu- and Ag-zeolites show cathodoluminescence.

(3) Some of the same base-exchanged zeolites dehydrated (to an undetermined degree) by heating at 300° C develop photoluminescence and/or cathodoluminescence. Specifically, the Mn-zeolites become responsive to cathode ray excitation; some of the Pb-zeolites respond to all excitation sources; of the (Mn+Pb)-zeolites, all respond to cathode ray and some to ultraviolet excitation as well; and some of the Cu- and Ag-zeolites become responsive to ultraviolet excitation.

(4) When these same heated, base-exchanged, luminescent zeolites are rehydrated (either by aging in the open or storing in an atmosphere of water vapor) they lose their luminescence activity, wholly or partially.

(5) The development of luminescence in base-exchanged zeolites is a reversible reaction and can be produced or suppressed directly by a comparable shift in the dehydration-rehydration process (within the limits noted in the literature).

(6) Since the zeolite minerals contain different amounts of structural water, show different dehydration rates and reach complete dehydration at different temperatures, it is to be expected that their correlated luminescence development should likewise differ in rate and extent.

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