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Candoluminescence of cave gypsum

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Abstract:

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A selection of gypsum specimens from a variety of caves as well as CaSO_4 synthesized in the laboratory emit both a green and yellow candoluminescence when excited by a hydrogen diffusion flame. The green emission is attributed to dehydration of gypsum to bassanite and the yellow emission appears upon further dehydration to anhydrite. The source of the luminescence is ascribed to minor concentrations of Mn^{2+} in the gypsum.

Keywords: *Gypsum, anhydrite, bassanite, candoluminescence, cave*

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INTRODUCTION

Candoluminescence is a form of luminescent emission excited by flames, usually diffusion (brush) flames of burning hydrogen. Interest in the subject has a long history going back to attempts to understand the light emitted from gas mantles in the late 19th Century. This early work essentially ended when a major review article was published (Nichols et al., 1928). Following a lengthy hiatus, there was renewed interest in the 1970's motivated by interest in producing a more efficient incandescent light source (Ivey, 1974). Following our own early work on candoluminescence (Sweet et al., 1970; Hess et al., 1974), it seemed of interest to investigate candoluminescence in the Earth sciences (White, 1990). The present report deals with the candoluminescence of cave minerals, specifically gypsum and anhydrite.

Calcite, the most common mineral in caves exhibits a range of photo- and cathodo-luminescence depending on incorporated impurity ions and organic molecules (Shopov, 2004) but it has not been found to be candoluminescent. In contrast, gypsum from several localities emitted both green and yellow luminescence in the hydrogen flame but was inactive under UV excitation. The luminescence of gypsum is

exceptional, first in that hydrated compounds are not usually luminescent and secondly in the low activator concentration required. The characterization of these phenomena is the subject of this paper.

EXPERIMENTAL METHODS

Table 1 lists the eleven cave gypsum samples examined and includes a laboratory gypsum used for comparison. As a reconnaissance, the minerals were tested by brushing them with a hydrogen flame and observing the luminescence visually. These minerals were also tested under UV excitation and under plasma excitation. Both long wave (365 nm) and short wave (254 nm) UV was tested. High energy (cathodo-) excitation was achieved by placing chips of the minerals in a test tube, pumping a weak vacuum, and exciting a gas plasma in the tube with a high frequency, high voltage vacuum leak detector. Table 1 summarizes the results.

Emission spectrographic analyses were obtained on three of the samples (Table 2). As expected, cave gypsum is quite pure except for silicon which may be present as traces of quartz. Manganese, the most likely candidate for a luminescence activator, is uniformly low, 10-25 mg/kg. No other elements that might act as activators were detected.

The basic experimental setup is shown in Figure 1. The mineral sample was ground to a fine powder, slurried with water, and painted onto a Kanthal heating rod with a cooling jacket so that the phosphor temperature could be controlled independently of the flame. Tank hydrogen was burned in air at a small silica-glass jet to form a diffusion flame. The flame

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Table 1. Observations of luminescence in gypsum.

Sample*	Description and Location	Candoluminescence	Cathodoluminescence	Photoluminescence
279	Crusts, Fitton Cave, Arkansas	Bright green	None	None
348	Crystals, Fitton Cave, Arkansas	Bright green	None	None
701	Needles, Cumberland Caverns, Tennessee	Green	None	None
115	Massive crystals, Cumberland Caverns, Tennessee	Faint green	Spots of green	None
229	Crusts, Wind Cave, South Dakota	Faint green	Faint green	None
254	Crusts, Wind Cave, South Dakota	Green	Faint pinkish	None
302	Crusts, Butler Cave, Virginia	Green	None	None
747	Dark crystals, Gypsum Cave, Texas	Green	None	None
747	White crystals, Gypsum Cave, Texas	Green	None	None
414	Crusts, Turner Ave., Mammoth Cave, Kentucky	Faint green	Faint pinkish	None
1425	Gypsum bedrock, Parks Ranch Cave, New Mexico	Bright green	Faint pinkish	None
	Laboratory gypsum	Bright green	None	None

*Sample numbers refer to a reference collection of cave material maintained by the corresponding author. Photoluminescence examined with both long and short wavelength ultraviolet excitation.

Table 2. Results of emission spectrographic analysis of gypsum samples

Sample	Description	Mg	Al	Si	Ti	Fe	Mn
115	Massive crystals	40-70	80-100	Minor	50-75	20-50	10-25
279	Gypsum crust	10-20	n.d.	Major	n.d.	5-10	10-25
1425	Gypsum bedrock	20-40	20-40	200-400	n.d.	5-10	10-25

n.d. = not detected. Detection limits vary but are less than 1 mg/kg. Elements sought but not detected: Cr, Ni, V, Cu, Zr, Be, Mo, Ag, Yb, Y, Ge, Sb, Ga, In, Bi, Sn, Gd, Zn

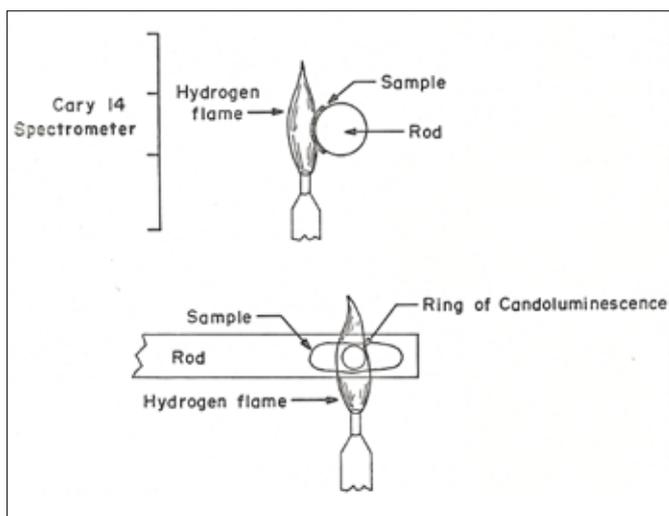


Fig. 1. Experimental set-up for measuring candoluminescence spectra.

was played over the sample and the emitted light focused onto the entrance slit of a Cary Model 14 spectrophotometer. Spectra were recorded directly by using the instrument in single beam mode.

The emission of the flame itself was measured by moving it slightly toward the spectrometer just barely out of contact with the sample. The flame spectrum consisted of a faint continuum and a cluster of strong lines near 580 nm arising primarily from Na and Ca in the flame. This background has been subtracted from the spectra shown in the figures and also a correction factor for photomultiplier response has been included.

The temperature dependence of the luminescence could be measured with the same setup by first setting the Cary monochromator to the wavelength

of the emission peak and recording intensity while cycling the temperature up and down. Temperatures were recorded directly using a chromel-alumel thermocouple.

Phase purities of the samples before and after exposure to the hydrogen flame were determined by X-ray diffraction. The powder samples were prepared for the diffractometer on a special silica glass slide and the X-ray patterns measured. Then the slide and sample were heated in the flame, immediately returned to the diffractometer, and re-measured.

RESULTS

Screening tests on the collection of cave gypsum samples from various locations (Table 1) showed that all produced at least a weak candoluminescent emission and no photoluminescence. All showed the same green candoluminescence upon brief exposure to the flame, although the intensity varies markedly among the samples. A few of the samples gave a faint pink cathodoluminescence and two showed very pale spots of green, much weaker than the green excited by the flame.

The spectrum of the green emission (Fig. 2) consists of a broad band peaking near 540 nm. The peak wavelength varies somewhat from sample to sample. The spectra in Figure 2 have been smoothed; the original spectrometer plots contain considerable noise due to flicker in the flame during the time required for the spectra to be scanned.

The green emission appears with only brief heating of the samples in the flame. Upon extended heating, the green luminescence gave way to a bright lemon yellow emission. The spectrum of the yellow emission (Fig. 3) is a smooth symmetrical band with a peak wavelength of 580 nm. When a gypsum sample was heated in the flame just sufficiently to develop a uniform green emission, its X-ray diffraction pattern indicated a mixture of bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and anhydrite (CaSO_4) with only traces of the original gypsum remaining. The green emission appeared quickly and persisted for some minutes under continuing excitation. When the same sample was further heated to achieve a uniform yellow emission, the resulting X-ray pattern indicated a pure anhydrite phase. After cooling, the green emission did not immediately recur, but did recur after the sample remained in the laboratory over night.

The cathodoluminescence of the bassanite phase was found to be green, very similar to the flame-excited emission. The anhydrite phase yielded a more orange emission under cathodo-excitation. Anhydrite that was allowed to absorb atmospheric moisture overnight luminesced green indicating that it had rehydrated only to the bassanite phase.

To pursue the hypothesis that the activator for the luminescence was Mn^{2+} , two synthetic samples were prepared. For sample A, 20 grams of gypsum were boiled for three one hour intervals in 250 mL of an aqueous solution containing first 1, then 2 and then 4 grams of MnSO_4 . The solutions were filtered between intervals to extract the solids before transferring the solids back into the next most-concentrated solution. Measurement of the samples at each interval gave the same intensity green candoluminescence. Sample B was prepared by a solid state reaction between gypsum and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. The components were ground together and fired at 780-810 °C for 13 hours, then reground, and fired again for 2.75 hours to produce a compound with the composition $\text{Ca}_{0.95}\text{Mn}_{0.05}\text{SO}_4$. Sample A produced first green, then with increased temperature a bright yellow candoluminescence. Sample B produced only the bright yellow candoluminescence. Neither sample was photoluminescent.

A characteristic of candoluminescence is that the brightness exhibits a pronounced maximum at some temperature in the range of a few hundred degrees centigrade. The temperature dependence of the intensity of the yellow luminescence was measured for samples A and B (Fig. 4). The spectra of these two samples are similar but the temperature dependences of the peak intensities are quite different. Sample A delivered peak brightness near 150 °C while peak brightness for sample B occurs near 375 °C. In addition, greater absolute intensities were achieved during the cooling cycle rather than during the heating cycle. All curves were reproducible to a fair degree, implying that the difference should be ascribed to the samples themselves and are not a measurement artifact.

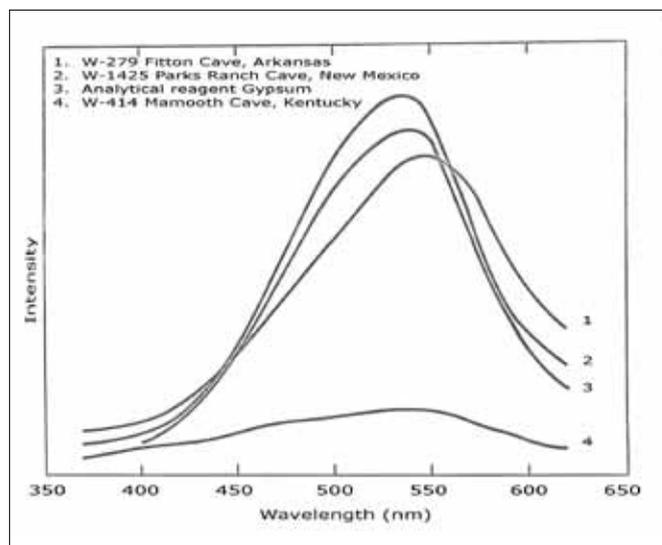


Fig. 2. Candoluminescence spectra for several gypsum specimens. Spectra measured with Cary-14 spectrophotometer; slit = 3 mm. Flame background has been subtracted and photomultiplier response corrected.

1. 279, Fitton Cave, Arkansas
2. 1425, Bedrock from Parks Ranch Cave, New Mexico
3. Laboratory gypsum
4. 414, Turner Avenue, Mammoth Cave, Kentucky

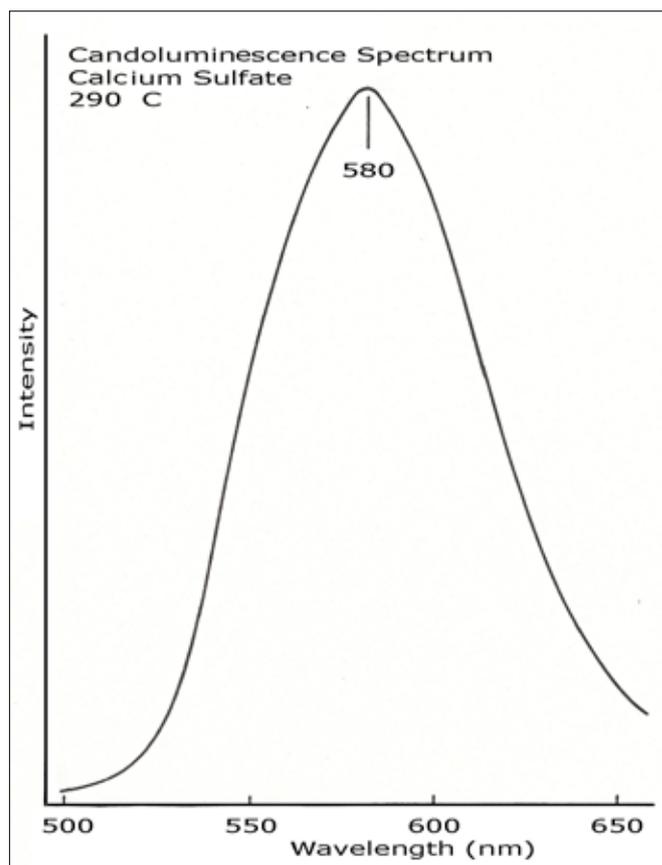


Fig. 3. Emission spectrum of the bright yellow candoluminescence of anhydrite. The spectrum has been smoothed to eliminate noise due to flame flicker. Measurement taken at 290 °C.

DISCUSSION

The results presented above suggest that at least a surface layer of the powdered gypsum dehydrates in the flame to initially produce bassanite which emits the green luminescence. Further heating produces

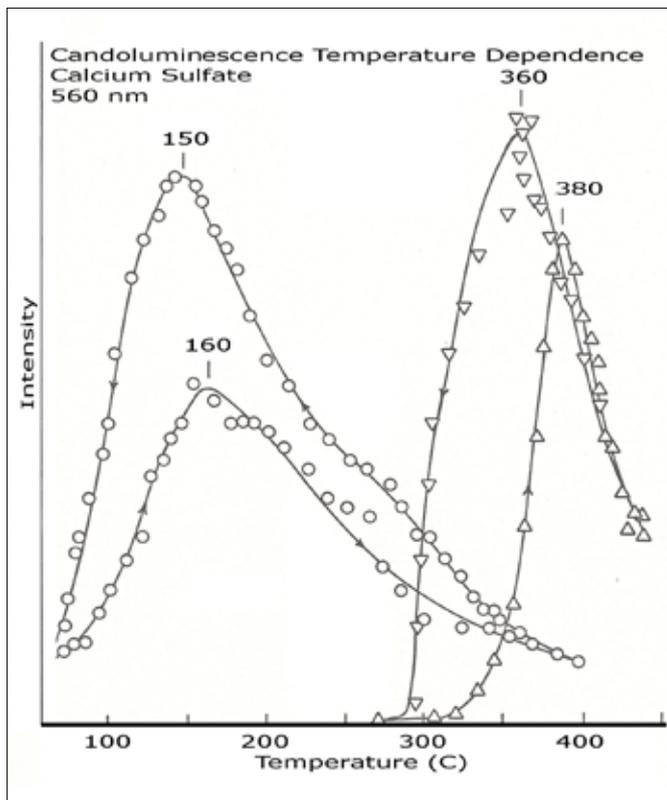
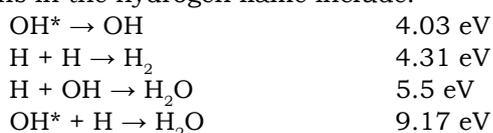


Fig. 4. Temperature dependence of yellow candoluminescence of Mn²⁺-doped anhydrite. Circles are sample A; triangles are sample B. Arrows indicate heat-up and cool-down cycles.

additional dehydration to the anhydrite phase which emits the bright lemon yellow luminescence. The activator ion appears to be Mn²⁺ in spite of its low concentration in the cave gypsum samples.

The photoluminescence due to Mn²⁺ ion is very sensitive to details of the crystallographic site that it occupies and varies from green when it substitutes for Zn²⁺ in willemite (Zn₂SiO₄) to a crimson red in spinel (MgAl₂O₄) (White, 1990). The observed yellow emission at 580 nm in CaSO₄ is close to the 594 nm emission of Mn²⁺ in lime (CaO). In both compounds, Mn²⁺ would have substituted for Ca²⁺ in the host structure. The absence of photoluminescence in any of the samples including those deliberately doped with additional Mn²⁺ is due to the absence of a co-activator that would serve to transfer the UV photons to the Mn²⁺ ion. Calcite, likewise, requires a co-activator for Mn²⁺ photoluminescence.

The energy source for candoluminescence is the recombination of radicals in the flame on the mineral surface. The recombination energy is transferred to the luminescence center where it is emitted as the observed candoluminescence. Possible recombination reactions in the hydrogen flame include:



OH* is an excited state of the OH radical. The energy of short wave UV (253.7 nm) is 4.89 eV. Because the observed bright candoluminescence requires an efficient energy transfer, it seems likely that the 9.17 eV reaction is the excitation source.

The other radical recombinations inject energies similar to that of short wave UV. If they were responsible for the candoluminescence, the absence of photoluminescence becomes difficult to explain.

The maximum in candoluminescence brightness as a function of temperature has been ascribed to the absorption and desorption of the active species from the mineral surface. As the temperature increases, absorbed species are desorbed, exposing fresh surface to the active radicals in the flame. The efficiency of the energy transfer increases until the temperature reaches a value sufficiently high to desorb the active species and thus the emission decreases at higher temperatures. In some systems, thermal quenching of the mineral itself may contribute to the high temperature limb of the brightness curve. Because the adsorption and interaction of flame species is highly dependent on details of the mineral surface, the temperature response of the two synthetic samples, A and B, are quite different.

CONCLUSIONS

After experimenting with a number of cave minerals exposed to hydrogen flames, it was found that gypsum from many cave localities is strongly candoluminescent. At lower temperatures, the emission is a bright green as the gypsum is dehydrated to bassanite. At higher temperatures, a bright lemon yellow candoluminescence appears as the bassanite is further dehydrated to anhydrite. The luminescence is ascribed to tens of mg/kg Mn²⁺ that occurs as an impurity in the gypsum.

ACKNOWLEDGEMENTS

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