THE LUMINESCENCE AND TENEBRESCENCE OF NATURAL AND SYNTHETIC SODALITE

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ABSTRACT

Luminescence emission spectra at 20° C. and at −196° C. of hackmanite, other natural sodalites, and certain synthetic, sulfur-containing sodalites are nearly identical. The luminescence of these sodalites is very closely related to that of scapolite and of a sodium polysulfide-sulfate mixture. From this similarity of the emission spectra and from the known occurrence of sulfur in sodalite and scapolite, it is concluded that the orange-yellow luminescence of sodalite and the yellow luminescence of scapolite are due to the presence of sodium polysulfide.

Hackmanite from Bancroft, Ontario, exhibits, on exposure to 1850 Å ultraviolet, a slow-bleaching blue coloration, in addition to the red-purple coloration described in earlier literature.

INTRODUCTION

Hackmanite, a variety of sodalite, has long been of special interest to mineralogists. First noticed over one hundred years ago, and later the basis for its being classed as a separate variety of sodalite, is the fact that a freshly fractured piece of the mineral has a pink color which fades rapidly on exposure to daylight. The pink color returns when the mineral is kept in the dark for several weeks. References to the early literature on these findings are given by Miser and Glass (1941). Lee (1936) found that a few minutes exposure to an ultraviolet source produced a deep permanganate color, the latter also being rapidly bleached by visible light.

The orange fluorescence of hackmanite and other specimens of sodalite has been noted by many observers; references are recorded by Iwase (1938) and Déribéré (1937–38).[1] Iwase recorded the luminescence of hackmanite photographically and found broad emission bands with maxima at 5800 and 6400 Å. Medved (1953) reported formation of sodalite which colored under 2537 Å ultraviolet by heating synthetic sodalite in hydrogen at 1060° C.

Sodalite has the general formula $6NaAlSiO_4 \cdot 2NaCl$; Na^+ and Cl^- ions are incorporated in the cavities of the open aluminosilicate framework (Bragg, 1937; Pauling, 1945). In synthetic products sodium is replaceable by other alkali metals, NaCl, by a wide variety of other salts (Doelter, 1917, pp. 276–284) with little change in the crystal structure. In the natural minerals, replacement of 2NaCl by Na_2SO_4 is found in noselite;

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[1] Some specimens of sodalite show a blue luminescence; this emission is not treated in this paper.

replacement by other sodium salts and by calcium salts is exemplified by other members of the sodalite and cancrinite groups.

Analyses of hackmanite have shown that it has the crystallographic and chemical constitution of sodalite. The first described analysis (Borgström, 1901) showed the presence of 0.39% sulfur. Haberlandt (1949) found traces of boron, lead, and sulfur. Lee (1936) suspected that the luminescent and photosensitive properties of hackmanite are connected with the presence of manganese, which he found to the extent of 0.001–0.002% in hackmanite from Bancroft, Ontario.

The purpose of the present investigation was to determine, if possible, the nature of the luminescent centers present in hackmanite and other fluorescent sodalites and to synthesize products having the luminescent and coloring properties of hackmanite.

EXPERIMENTAL

Experimental methods employed in the physical measurements and reagents used in the syntheses have been described in an earlier paper (Kirk, 1954).

The first successful synthesis of a substance having the properties of hackmanite involved two steps. The first step was the reduction by hydrogen at 900° C. of all the Na_2SO_4 in a material having the composition $6NaAlSiO_4 \cdot 1.8NaCl \cdot 0.1Na_2SO_4$. The resulting mono-sulfide-containing material was then fired in air at 900° C. for 15 minutes causing a partial oxidation of the sulfur.

The hydrogen-fired product was not luminescent under either 3650 or 2537 Å excitation. It showed strong tenebrescence under a 2537 Å source.[2]

The air-oxidized material had a strong orange-yellow luminescence under a long wave ultraviolet source, colored red-purple within ten seconds on exposure to a 4 watt germicidal lamp (short wave ultraviolet) at a distance of one centimeter, and bleached rapidly on exposure to a tungsten light source. Extended heating of the product in air at 900° C. resulted in a material which exhibited no tenebrescence but which still had a yellow luminescence.

An *x*-ray powder diffraction pattern of this material was identical with that of hackmanite from Bancroft, Ontario, both showing only sodalite lines.

Attempts to duplicate this product showed that the oxidation step is dependent upon such factors as the amount of surface exposed to the air and the amount of air circulation in the furnace. Variation of the firing

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[2] Tenebrescence refers to the property of darkening and bleaching which some nearly colorless solids possess. The darkening may be caused by various types of irradiation; the bleaching, by either heat or irradiation.

temperature or the firing time or both may be necessary to produce a product which is both tenebrescent and luminescent.

A method of synthesis involving firing together of $6NaAlSiO_4 \cdot (2-x) NaCl \cdot (0.5x)Na_2SO_4$ and $6NaAlSiO_4 \cdot (2-x)NaCl \cdot (0.5x)Na_2S$ in helium has been described in the above-mentioned earlier paper by the author. This method allows excellent control of the degree of luminescence and tenebrescence. Products with a large Na_2S/Na_2SO_4 ratio have the best tenebrescence; those with a large Na_2SO_4/Na_2S ratio show the brightest luminescence.

A simpler but more empirical method of preparation consists of the following: the component oxides and salts to give the $6NaAlSiO_4 \cdot 1.8NaCl \cdot 0.1Na_2SO_4$ composition are ball-milled together for three hours in acetone. The filtered cake of reactants is dried for one hour at 100° C., packed into a tall-form silica crucible, and fired for 15 minutes at 800° C. The resulting product has luminescent and tenebrescent properties like those of hackmanite, but to a lesser degree than products made by the above two methods. Milling in acetone is an essential part of this preparative procedure. The same composition prepared by dry mixing is not luminescent after firing.

The products more nearly approaching noselite in composition, e.g. $6NaAlSiO_4 \cdot 1.0NaCl \cdot 0.5Na_2SO_4$[3] show brighter fluorescence and color to a darker shade than those with higher NaCl content. Lowering the silica content to 90% of the theoretical value also improves both the luminescence brightness and the colorability of the synthetic sodalites. Synthetic noselite itself, when prepared by milling the components in acetone and firing, shows an orange luminescence but does not tenebresce. Similarly prepared sodalite with no sulfate neither luminesces under 3650 Å excitation nor tenebresces under 2537 Å ultraviolet.

RESULTS

Luminescence

Emission spectra at room temperature of the partially reduced $1.8 NaCl \cdot 0.1 Na_2SO_4$ sodalite composition and of hackmanite from Kola Peninsula, U.S.S.R. under 3650 Å excitation are given in Fig. 1, which shows the near identity of the spectral distribution. Figure 2 compares the emission spectra of sodalites from various sources, all exhibiting emission maxima at about 6150 and 6350 Å. The luminescence color is thus the same for all the specimens studied.

In observations made by eye some apparent differences in emission color appear which are actually brightness differences, with resulting

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[3] Starting composition. Formulas given hereafter in this paper denote only the starting composition and are not intended to represent the final chemical constitution.

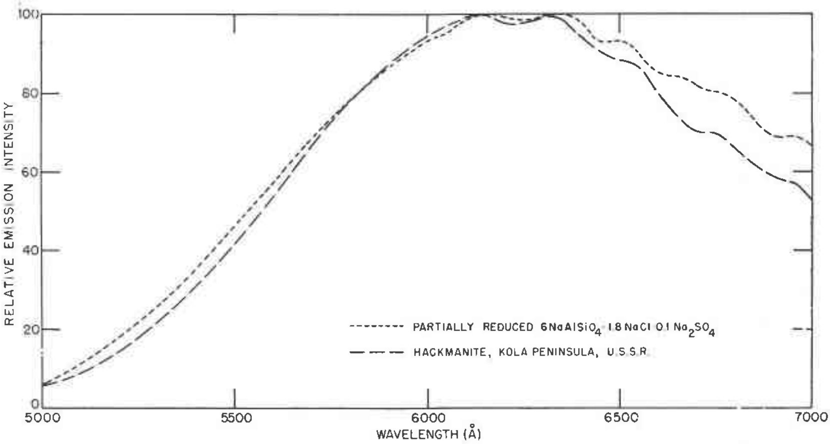

Fig. 1. Luminescence emission of synthetic and natural hackmanite at 20° C. with 3650 Å excitation.

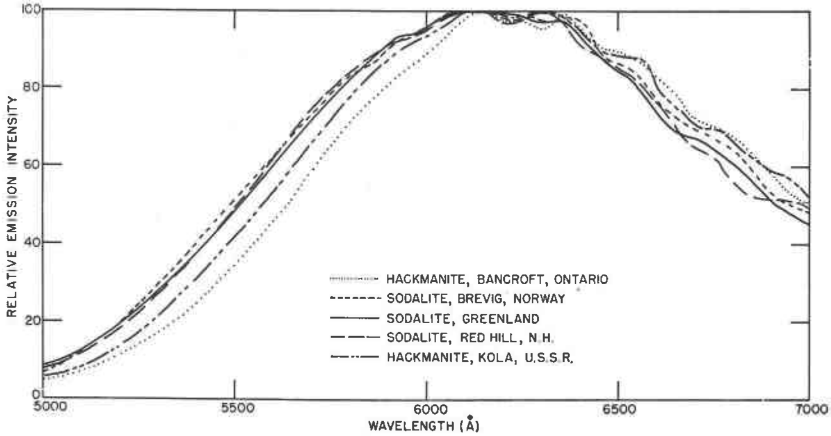

Fig. 2. Luminescence emission of natural sodalite and hackmanite at 20° C. with 3650 Å excitation.

variation in the ratio of luminescence emission to visible light reflected by the specimen; the reflected visible light originates in the ultraviolet source. Insertion of a 5 mm.-thick Corning No. 5860 filter (which passes practically no visible light) between the ultraviolet source and the specimens shows that all the fluorescent sodalites studied luminesce yellow, with a slightly orange tint, rather than red-orange.[4]

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[4] This common subjective error was also demonstrated in a different manner by Schulman et al. (1947), who showed that the fluorescence color of calcite from Franklin, N. J., is actually red-orange, rather than rose or pink as it is often stated to be.

Figure 3 shows the luminescence emission spectra of scapolite from Argenteuil, Quebec, and sodalite from Red Hill, N. H., with long wave ultraviolet excitation. Although the spectral positions are different, the similarity of the emission structure is evident.

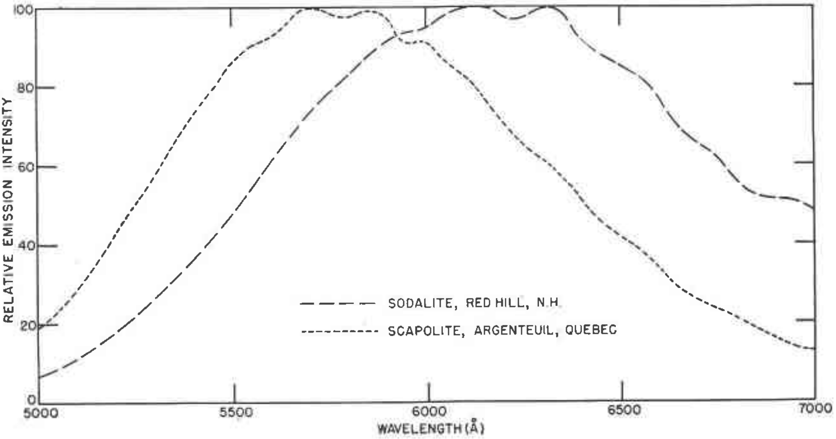

FIG. 3. Luminescence emission spectra of scapolite and sodalite at 20° C. with 3650 Å excitation.

The luminescence emission spectra at −196° C. of hackmanite from Kola, U.S.S.R., scapolite from Argenteuil, Quebec, sodium polysulfide-sulfate mixture prepared by heating thiosulfate as described in the author's earlier paper, and partially reduced $6NaAlSiO_4 \cdot 1.8NaCl \cdot 0.1Na_2SO_4$ are shown in Fig. 4. The near identity of the locations of the

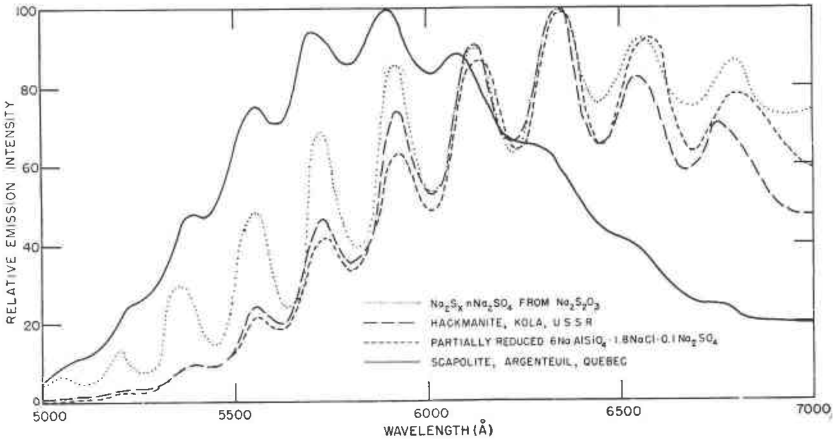

FIG. 4. Luminescence emission at −196° C. with 3650 Å excitation.

emission peaks indicates that the luminescence centers are very likely the same in all the materials given. Exactly the same emission peaks at −196° C. are exhibited by hackmanite from Bancroft, Ontario, and sodalite from Brevig, Norway, Red Hill, N. H., and Greenland, the emission spectra of which are not illustrated.

The excitation spectra of the synthetic sodalite products, of $Na_2S_x \cdot nNa_2SO_4$ prepared by heating $Na_2S_2O_3$, of scapolite from Argenteuil, Quebec, and of sodalite and hackmanite specimens from the localities just mentioned are identical. Maximum emission is produced by an excitation wavelength of 4000 Å, the emission dropping to almost zero under 2500 Å and 5000 Å excitation, as shown for hackmanite from Bancroft, Ontario in Fig. 5.[5]

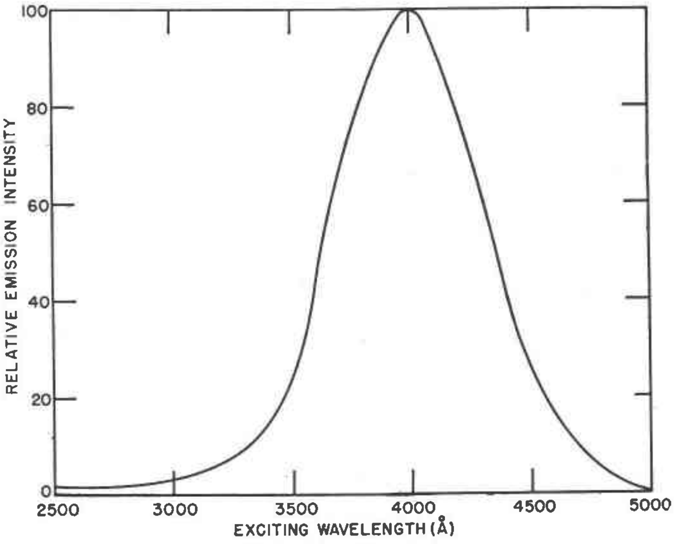

Fig. 5. Excitation spectrum of hackmanite from Bancroft, Ontario.

Tenebrescence

Although the coloration of hackmanite by ultraviolet to a red-purple color is well known, a new tenebrescence color has also been found. Exposure of hackmanite from Bancroft, Ontario, to an unfiltered low-pressure, silica-envelope mercury arc ("Mineralight" Model *R-51*) caused

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[5] The very weak luminescence of scapolite, hackmanite and sodalite under a short wave ultraviolet source (e.g., a "Mineralight" lamp) is due almost entirely to the small amount of long wave ultraviolet emitted by the source. This can be readily demonstrated by the interposition of a Pyrex filter, Corning No. 7740, between the source and the sample, whereby the brightness of this fluorescence is not noticeably diminished. This filter in a 2 mm. thickness cuts off 99.5% of the 2537 Å radiation.

the appearance of the usual magenta color within a few seconds. Exposure of the same sample to this source for a period of several hours produces in addition, a blue coloration. The blue color, like the pink-purple, is scattered in patches and streaks throughout the specimen and is sometimes coincident with the purple areas, but often not. The blue coloration, however, fades out very slowly over a period of several weeks, and does not appear to be affected by visible light. Moreover, unlike the purple color, the blue color is not produced when a Corning No. 9863 filter is placed between the source and the specimen. Since this filter cuts off light below 2300 Å, it is likely that the blue color is produced by 1850 Å radiation. Extended *x*-irradiation also causes formation of the blue color along with the pink-purple. When the specimen is heated at 400° C. for a short period it will no longer color pink but formation of the blue color is not affected. The composition of the mineral at these blue-coloring spots is not known, although it is suspected that it is some variety of sodalite.

Similar extended irradiation of the tenebrescent synthetic products prepared as previously described produces only a deepening of the first-formed magenta color. However, synthetic sodalites with small amounts of Na_2SO_4 (unreduced) replacing NaCl, although not sensitive to 2537 Å, become blue-violet under extended 1850 Å and *x*-irradiation. This color, like the above blue, is very slow to bleach.

Discussion

Haberlandt (1934, 1935) noted the peculiar luminescence emission structure of sodalite and scapolite at room temperature and at low temperatures and suspected the presence of uranium. Iwase (1937) likewise ascribed the band structure of the emission of scapolite to a content of uranium. Haberlandt later showed that these minerals contain no uranium (1949) and mentioned the possibility that the activator is a sulfur compound.

Thugutt notes in Doelter's handbook (1917, p. 247) that a sulfur content in sodalites is of common occurrence. Miser and Glass (1941) reported the presence of sulfur and SO_3 in hackmanite from Magnet Cove, Arkansas, and noted an evolution of H_2S on addition of the mineral to hot, dilute hydrochloric acid, as did Iwase (1938) with hackmanite from Korea. Walker and Parsons (1925) reported no sulfur in the Bancroft, Ontario, hackmanite; however, qualitative tests with sodium plumbite paper showed sulfide to be present in samples of this material available to the author. Haberlandt (1949) noted the formation of H_2S on powdering fluorescent scapolite from Grenville, Canada.

Summarizing these statements and some of the earlier parts of this paper:

1. Many sodalites contain sulfur, often as a sulfide.
2. Synthetic sodalite compositions containing (*a*) no sulfur, or (*b*) sulfur as Na_2SO_4 only, or (*c*) sulfur as Na_2S only, show no luminescence.
3. Synthetic sodalite products containing sulfur partially reduced from sulfate show emission peaks at $-196°$ C. identical in spectral position with the emission peaks of natural hackmanite and other fluorescent sodalites.
4. A sodium polysulfide-sulfate mixture prepared by heating sodium thiosulfate in air at 900° C. also has these same emission peaks.

It is concluded that the orange-yellow luminescence of hackmanite and other fluorescent varieties of sodalite and the yellow luminescence of scapolite (scapolite is related to sodalite in chemical composition) are due to the presence of the polysulfide ion in an environment similar to that present in a sodium polysulfide-sulfate mixture prepared by heating sodium thiosulfate. The author believes by analogy that the orange luminescence with line structure of the closely related haüynite, which was noted by Haberlandt (1935) in specimens from several localities, is likewise due to polysulfide.

Since the luminescence of the non-tenebrescent sodalites is the same as that of the hackmanite varieties and since synthetic sodalites can be prepared which color violet but are non-fluorescent, or which fluoresce but do not color, it is obvious that the luminescence centers of hackmanite are different from its color centers. The color centers, by analogy to those of synthetic products (Kirk, 1954), are believed to be related to the combined presence of sodium chloride and sodium (mono) sulfide in the sodalite-type lattice. The loss of tenebrescence of the synthetic hydrogen-fired sulfur-containing sodalite on extended heating in air at 900° C. would then be attributable to the oxidation of all the monosulfide sulfur to a polysulfide or higher oxidation state.

Thus, the hackmanite variety of sodalite appears to contain small amounts of both sodium mono- and poly-sulfide.

On a few occasions supposedly pure NaCl-sodalites, after hydrogen firing at 900° C., gave an extremely weak coloration on prolonged exposure to a 2537 Å source. The author ascribes this sensitivity to the presence of traces of sulfur in the starting reagents.

Firing of pure synthetic sodalite in hydrogen at 1060° C., in attempts to duplicate the work of Medved, resulted in losses of more than 50% of the contained NaCl. The resulting products, like those fired in hydrogen at 900° C., were very weakly 2537 Å sensitive. However, like pure sodalite fired at 1060° C. in air, they colored red-violet under 1850 Å irradiation.

Ultramarines, which have a composition and structure closely related to that of sodalite (Jaeger, 1930) are not luminescent, nor is a mixture of synthetic sodalite and ultramarine fired together in helium. However, the sodalite-ultramarine product after firing in hydrogen and oxidizing by firing in air shows the typical orange-yellow luminescence of sodalite.

It is usually stated that the blue chromophore in ultramarine (and the blue sodalite minerals) consists of Na_2S_x groups; if this is true, the environment of the groups in ultramarine must be widely different from those in hackmanite and fluorescent sodalite. The possibility that the chromophore is not Na_2S_x alone is shown by the fact that the so-called "primary" ultramarine which contains excess water-soluble sodium polysulfide is a weak, dull pigment (Beardsley and Whiting, 1948). Only after a subsequent oxidation step is true, deep-blue ultramarine formed.

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