

Table 1. Crystallographic data (*I*) for tunellite monoclinic,  $P2_1/a$ :  $a = 14.36 \pm 0.05$  Å;  $b = 8.19_8 \pm 0.02$  Å;  $c = 9.93_0 \pm 0.02$  Å;  $\beta$  (monoclinic angle) =  $113^\circ 55' \pm 10'$ ; cell volume,  $1068$  Å<sup>3</sup>; cell contents  $Z = 4[\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}]$ ; density, calc.  $2.39$  g cm<sup>-3</sup>, obs.  $2.40 \pm 0.01$ .

Atom	Atomic coordinates		
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Sr	0.162	0.056	0.195
O <sub>1</sub>	.194	.025	.952
O <sub>2</sub>	.203	.038	.482
O <sub>3</sub> (OH,*)	.050	.681	.426
O <sub>4</sub> (H <sub>2</sub> O)	.998	.168	.238
O <sub>5</sub> (OH)	.090	.536	.172
O <sub>6</sub>	.242	.799	.399
O <sub>7</sub>	.208	.341	.340
O <sub>8</sub>	.238	.785	.081
O <sub>9</sub>	.194	.350	.101
O <sub>10</sub>	.089	.212	.773
O <sub>11</sub>	.087	.210	.534
O <sub>12</sub> (H <sub>2</sub> O)	.021	.840	.068
O <sub>13</sub> (H <sub>2</sub> O)	.139	.580	.712
O <sub>14</sub> (to 3 B)	.227	.083	.734
B <sub>1</sub>	.194	.151	.849
B <sub>2</sub>	.194	.156	.585
B <sub>3</sub> (*)	.043	.248	.625
B <sub>4</sub>	.187	.455	.220
B <sub>5</sub> (*)	.253	.389	.486
B <sub>6</sub> (*)	.251	.388	.022

\* Atom of B-O triangle.

A study of the crystal structure of tunellite is nearing completion. The crystallographic data and atomic coordinates are listed in Table 1. The residual factor is 0.11 for about 1200 three-dimensional data with  $|F_{\text{obs}}| > 0$ . The structural formula for tunellite is  $\text{SrB}_6\text{O}_{18}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , and the polyanion probably exists, either in the present form or modified according to Christ's rules, in other members of the  $\text{M}^{2+}\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  series. In particular, nobleite (8),  $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ , is isostructural with tunellite and hence must be  $\text{CaB}_6\text{O}_{18}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  (9).

JOAN R. CLARK

U.S. Geological Survey,  
Washington 25

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- I thank my colleagues at the U.S. Geological Survey: R. C. Erd, for crystals of tunellite; D. E. Appleman, who gave much time to solution of associated computer problems and to discussion; M. Ross, who prepared Fig. 1; and C. L. Christ, who suggested the study. Publication was authorized by the director, U.S. Geological Survey.

8 August 1963

20 SEPTEMBER 1963

## Apatite: Origin of Blue Color

**Abstract.** *The optical absorption and emission spectra of natural blue apatite are similar enough to spectra of synthetic compounds containing  $\text{MnO}_4^{2-}$  to conclude that the blue color of natural apatite results from the presence of this ion.*

The origin of the blue color in natural apatites has been the subject of investigation by chemical, optical, and electron-spin resonance techniques. None of this work has resulted in the unambiguous identification of the impurity or defect responsible for the blue color, which has been variously attributed to  $\text{O}^-$  replacing two halide ions (1), to  $\text{Mn}^{2+}$  (2), or to an electron in a halide vacancy (3). In this report we present evidence that the blue color of apatite, obtained from the Hugo mine in Keystone, South Dakota, results from the presence of  $\text{MnO}_4^{2-}$ . The color of these samples is bleached at temperatures above  $500^\circ\text{C}$  as is the color in samples from other sources (4).

Prener and Kingsley (5) have recently found that single crystals of various calcium halophosphates (containing manganese) are blue when grown under suitable conditions. They grew single crystals of calcium chlorospodiosite ( $\text{Ca}_2\text{PO}_4\text{Cl}$ ), calcium chlorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ ], and fluorchlorapatite by slow cooling from a  $\text{CaCl}_2$  melt containing  $\text{MnCl}_2$  in an oxygen-containing atmosphere. Chemical analysis, optical absorption, and fluorescence studies showed that the blue color was due to the presence of  $\text{MnO}_4^{2-}$  ions, probably at  $\text{PO}_4^{3-}$  sites. Similar fluorescence was obtained from some light blue manganese-containing fluorapatite crystals grown by the Czochralski technique by P. D. Johnson (6). The optical absorption spectra of a number of materials containing  $\text{MnO}_4^{2-}$  are shown in Figs. 1 and 2. The marked similarity of the absorption spectra of  $\text{MnO}_4^{2-}$  in various environments to that of the blue natural apatite strongly suggests that  $\text{MnO}_4^{2-}$  ions are responsible for the blue color in the natural mineral. The very strong absorption in Fig. 1a at wavelengths below  $3500$  Å and the fact that the minimum at about  $4500$  Å does not go to zero is probably due to other impurities. The infrared fluorescence at  $78^\circ\text{K}$  observed by excitation in the

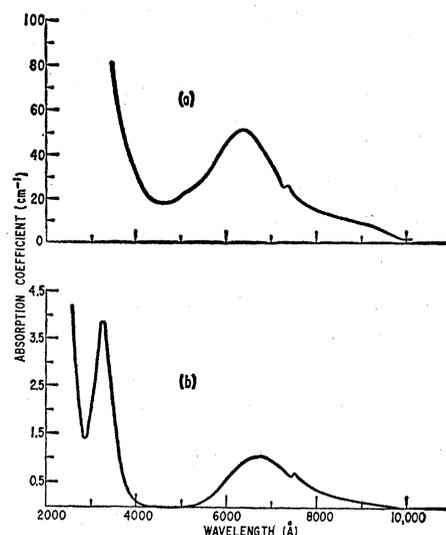


Fig. 1. Absorption spectra at  $298^\circ\text{K}$ . *a*, Blue apatite from Hugo mine in Keystone, South Dakota. *b*, Solution of  $\text{MnO}_4^{2-}$  in  $12\text{M}$  KOH.

visible absorption bands of the various compounds containing  $\text{MnO}_4^{2-}$  is compared with that observed in natural blue apatite in Fig. 3. Phosphors were excited by light from a tungsten lamp filtered by a  $\text{CuSO}_4$  solution. The spectra are not corrected for sensitivity of the detection system. Again the similarity in the infrared fluorescence indicates the presence of  $\text{MnO}_4^{2-}$  in natural blue apatite. Assuming the same oscillator strength for the visible absorption band in the two cases shown in Figs. 1a and 2b, we calculate that the concentration of  $\text{MnO}_4^{2-}$  is ap-

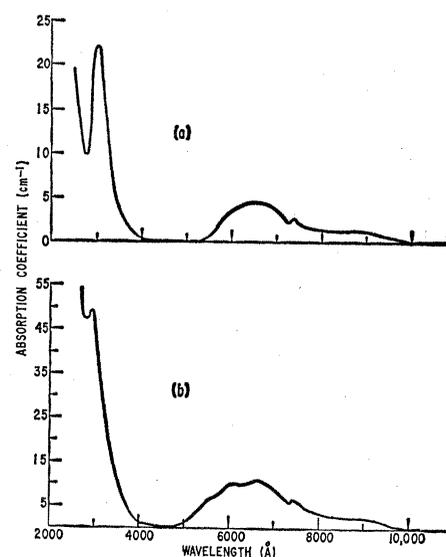


Fig. 2. Absorption spectra at  $298^\circ\text{K}$ . *a*,  $\text{Ca}_5(\text{PO}_4)_3(\text{Cl},\text{F}):\text{MnO}_4^{2-}$ . *b*,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{MnO}_4^{2-}$ ; concentration of  $\text{MnO}_4^{2-}$  is  $1.1 \times 10^{19}$  cm<sup>-3</sup>.

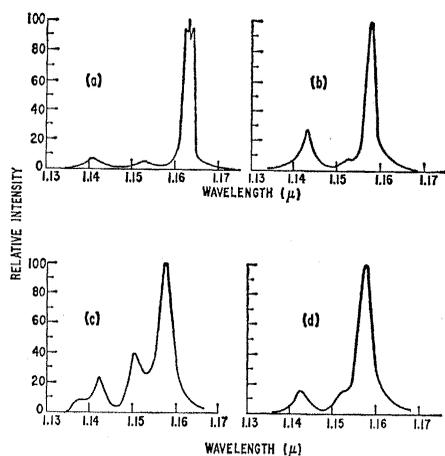


Fig. 3. Fluorescence spectra at 78°K. *a*,  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}:\text{MnO}_4^{2-}$ . *b*,  $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{MnO}_4^{2-}$ . *c*,  $\text{Ca}_5(\text{PO}_4)_3(\text{Cl},\text{F}):\text{MnO}_4^{2-}$ . *d*, Blue apatite from Hugo mine in Keystone, South Dakota.

proximately  $5 \times 10^{19} \text{ cm}^{-3}$ . By chemical analysis the total manganese present is about  $6 \times 10^{20} \text{ cm}^{-3}$ . The difference between these two amounts probably represents the amount of  $\text{Mn}^{2+}$  present in the mineral either incorporated in the apatite or in precipitated phases. Natural blue apatite can be bleached by heating in air for a few minutes at about 600°C. The resulting material has a slightly pink body color. Under 2537 Å ultraviolet excitation it has the luminescence of  $\text{Mn}^{2+}$ , and shows a peak at 5700 Å, which is characteristic of synthetic apatites used in the manufacture of fluorescent lamps.

It is interesting that the synthetic apatites containing  $\text{MnO}_4^{2-}$  are not bleached by heating at 600°C as is the natural crystal. However, after

irradiation of these crystals with  $2 \times 10^7 \text{ r}$  of 1 mev electrons, heating at 600°C does result in an appreciable amount of bleaching of the  $\text{MnO}_4^{2-}$  absorption as well as of the color centers formed on irradiation. The radiation dosage to which the synthetic samples were subjected is typical of that received on the surface of the earth in about  $2 \times 10^8$  years as the result of natural radioactivity (7). We conclude that the thermal bleaching of both the natural apatite and our synthetic crystals requires the presence of other defects. The presence of the blue color in natural crystals requires that either the crystals grew at temperatures much less than 600°C or that those other defects were formed after the crystals cooled below 600°C (8).

P. D. JOHNSON  
J. S. PRENER  
J. D. KINGSLEY

General Electric Research  
Laboratory, Schenectady, New York

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17 June 1963

## Photochemical Production of the Solvated Electron in Ethanol

Abstract. Flash photolysis of several inorganic anions in ethanol gives an absorption spectrum attributed to the solvated electron.

The production of the hydrated electron by flash photolysis of inorganic salts in aqueous solution has been reported recently (1, 2). Comparable results have been obtained in ethanolic solution, giving spectra in good agreement with those obtained by pulse radiolysis (3).

Figure 1 shows the transient spectra that we obtained by flash photolysis of 0.0001M potassium iodide in air-free ethanol. We used the experimental method that was described previously

(2), except that the spectra were taken with Kodak types 103-F and I-N spectroscopic plates and the data reported here are corrected for the spectral sensitivities of the emulsion. The broad, red band of short lifetime is assigned to the solvated electron. The absorption of longer duration is due to the diiodide ion, which was identified in aqueous solution by Grossweiner and Matheson (4) and in ethanolic solution by Edgcombe and Norrish (5). A weak solvated electron spectrum was also

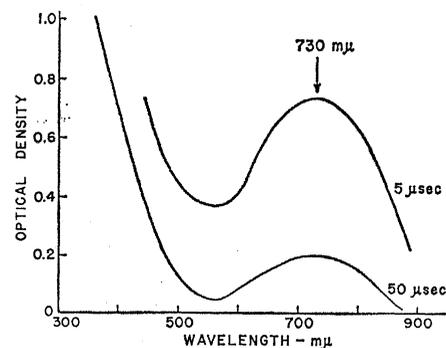


Fig. 1. Transient spectra obtained by flash photolysis of an air-free solution of 0.0001M potassium iodide in ethanol. The band below 500 mμ is due to the di-iodide ion; the shorter-lived red absorption band is attributed to the solvated electron.

obtained from 0.01M potassium bromide in ethanol, but pure ethanol gave a negative result. A strong solvated electron spectrum was obtained by flash photolysis of 0.10M potassium hydroxide in ethanol. The associated longer-lived radical spectrum has a maximum at 380 mμ and has not been identified.

Although the phenol derivatives give strong hydrated electron spectra (2), this is not the case for *p*-cresol in ethanol. Negative results were obtained from 0.001M *p*-cresol and from 0.001M *p*-cresol containing 0.005M potassium hydroxide; for the latter case the 280 mμ band of *p*-cresol was shifted to 299 mμ, indicating that dissociation of the hydroxyl group was almost complete. The strong absorption of the *p*-methyl phenoxyl radical was observed in both cases, showing that the light intensity was adequate for photolysis. The different behavior of the aromatic anion in water and in ethanol remains to be explained (6).

LEONARD I. GROSSWEINER  
EARL F. ZWICKER  
GEORGE W. SWENSON

Department of Physics,  
Illinois Institute of Technology,  
Chicago 16

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6. Supported by U.S. Public Health Service grant GM 10038-01 from the National Institutes of Health.

16 August 1963