

# ON THE COLOUR OF USSINGITE FROM THE ILÍMAUSSAQ (SOUTH GREENLAND) AND LOVOZERO (KOLA PENINSULA) ALKALINE INTRUSIONS

Contribution to the mineralogy of Ilímaussaq, no. 19

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Ussingite  $\text{Na}_2[\text{AlSi}_3\text{O}_8]\text{OH}$  – is a pale violet mineral displaying a distinct thermoluminescence. The spectral absorption curves of the visible region, the thermoluminescence and the electronic paramagnetic resonance of two specimens of ussingite from the Ilímaussaq alkaline massif (South Greenland) and from Lovozero (the Kola Peninsula) have been investigated. It is suggested that the natural and artificial (produced by X-ray irradiation) violet colour of ussingite is connected with radiation centers  $(\text{SO}_4)^-$ , which are typical for the feldspathoids.

Ussingite was first found in the Ilímaussaq intrusion and was described by Bøggild (1913). In the USSR ussingite was detected in 1923 by the Khibina expedition of the USSR Academy of Sciences in the north-western section of the Lovozero tundras (Bonstedt, 1925). Gerassimovsky (1937) gave a detailed description of ussingite from Punkaruav (Lovozero). Ussingite is now known from numerous pegmatitic veins in Ilímaussaq and Lovozero.

## Chemical composition and structure

Ussingite is a basic sodium alumino-silicate formed mainly by hydrothermal alteration of sodalite. Ussingite contains a smaller amount of Al and Na than the latter. The chemical formula is similar to that of albite:  $\text{Na}_2[\text{AlSi}_3\text{O}_8]\text{OH}$ , an excess of sodium being neutralized by hydroxyl.

An isomorphic admixture of S and Cl has been revealed in the Khibina ussingite. These elements may be inherited from the S-containing sodalite of the Lovozero tundras, the so-called hackmanite. The contents of S and Cl are still greater in the ussingite from Ilímaussaq (see table 1).

Table 1. Chemical analyses of ussingite from the Lovozero tundras and Greenland

	Weight percent				
	1	2	3	4	5
SiO <sub>2</sub> .....	59.6	59.225	59.17	57.64	57.25
TiO <sub>2</sub> .....	—	—	—	0.09	0.05
Al <sub>2</sub> O <sub>3</sub> .....	16.9	17.225	17.67	16.05	15.76
Fe <sub>2</sub> O <sub>3</sub> .....	—	—	—	0.00	0.00
FeO.....	—	—	—	1.43	1.43
MnO.....	—	—	—	0.01	0.04
MgO.....	—	—	—	0.57	0.72
CaO.....	—	0.305	—	0.34	0.92
Na <sub>2</sub> O.....	20.5	19.085	19.66	18.00	17.51
K <sub>2</sub> O.....	—	0.865	—	0.80	0.80
P <sub>2</sub> O <sub>5</sub> .....	—	—	—	0.01	tr.
SO <sub>3</sub> .....	—	—	—	0.08	0.03
S.....	—	0.085	—	—	—
F.....	—	—	—	0.09	0.12
Cl.....	—	0.04	—	0.49	0.28
H <sub>2</sub> O <sup>+</sup> .....	3.0	3.40	3.80	3.92	4.47
H <sub>2</sub> O <sup>÷</sup> .....	—	0.30	—	0.34	0.38
	100.0	100.53	100.30	99.89	99.76
—O = S, F <sub>2</sub> , Cl <sub>2</sub> .....	—	0.06	—	0.13	0.10
Total.....	100.0	100.47	100.30	99.76	99.66

1. Ideal composition of ussingite, corresponding to the formula Na<sub>2</sub>[AlSi<sub>3</sub>O<sub>8</sub>]OH.
2. Ussingite from Lovozero tundras (m. Punkaruaiiv). Analyst V. I. Gerassimovsky (1937); average from two analyses.
3. Ussingite from Lovozero tundras (m. Alluauiv). Analyst N. P. Vrevskaya (1937).
4. Ussingite from Greenland (Ilhmausaq). Analyst L. V. Katsnelson (1968), Inst. Geol. Sci. Acad. Sci. Ukrainian SSR.
5. Ussingite from Lovozero tundras (m. Punkaruaiiv). Analyst L. V. Katsnelson (1968), Inst. Geol. Sci. Acad. Sci. Ukrainian SSR.

Ussingite is triclinic; the structure has not yet been determined because of the lack of single crystals. Ilyukhin & Semenov (1959) have determined the unit cell parameters which proved to be as follows:  $a = 8.72$ ;  $b = 7.67$ ;  $c = 10.01$ ;  $\alpha = 110^\circ 30'$ ;  $\beta = 135^\circ 45'$ ;  $\gamma = 91^\circ 31'$ . The space group is  $C_{1h}^1-P1$ ;  $Z = 2$ .

With regard to the main physical properties – density and hardness (which are 2.46 and 6.25, respectively) – ussingite is referred to the framework aluminosilicates, the unit cell volume of which is relatively greater than that of sodic plagioclase or albite. This means that the cavities in the silicium-oxygen framework are large and easily can contain additional ca-

tions and anions as in the minerals of the sodalite group. The supposed low temperature of formation of ussingite indicates that sulphur enters the structure in the form of sulphate-ions ( $\text{SO}_4^{2-}$ ), the charge of which is most probably compensated by the isomorphous admixture of Ca (table 1).

### Optical properties and radiospectroscopy

Ussingite generally displays a violet colour, which ranges from deep violet through pale lilac or pink to practically colourless.

The thermoluminescence, optical absorption spectra and electron paramagnetic resonance of samples of light violet ussingite from Punkaruaiiv, the Lovozero tundras and white, slightly lilac ussingite from the Taseq slope, Ilímaussaq have been studied.

One high-temperature peak of luminescence is observed on the thermoluminescence curve of the light violet Lovozero ussingite at  $400^\circ\text{C}$  (fig. 1 a). The colourless ussingite from Ilímaussaq displays one high-temperature peak of luminescence at  $380^\circ\text{C}$  (fig. 2 a). After heating at  $450^\circ\text{C}$  for one hour the sample of coloured Lovozero ussingite was decolourized.

The investigated samples were also exposed to X-ray action (tube BSV-2, Mo-radiation, 40 kV, 10 mA). The Lovozero ussingite discoloured by heating acquired a more intense light violet colour after X-ray irradiation during 5 hours. On the thermoluminescence curve of the irradiated sample a low-temperature luminescence with the peak near  $180^\circ\text{C}$  appeared. The high-

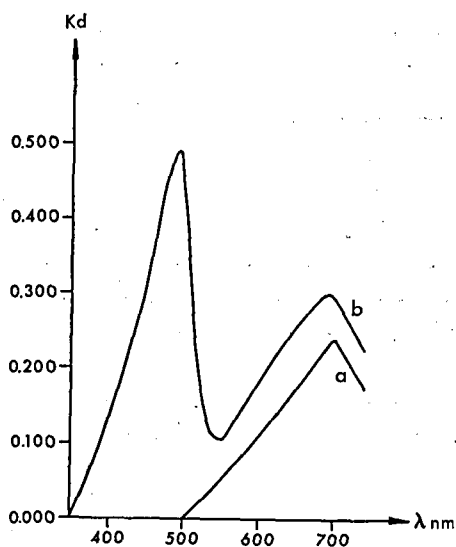
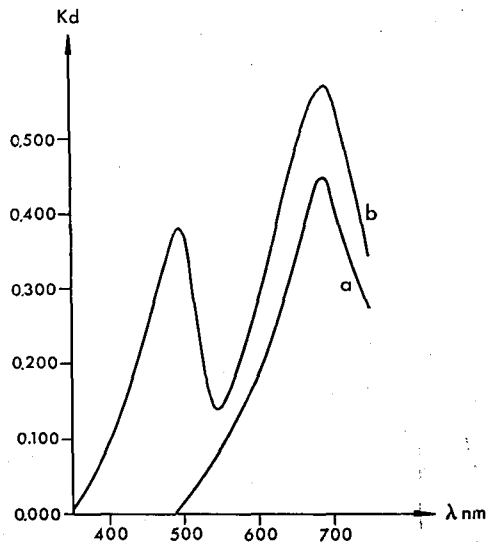


Fig. 1. Thermoluminescence curves of ussingite from the Lovozero tundras (Punkaruaiiv). *a*: naturally coloured. *b*: irradiated with X-rays after heating to  $450^\circ\text{C}$ .

Fig. 2. Thermoluminescence curves of ussingite from Ilímaussaġ. *a*: naturally coloured. *b*: irradiated with X-rays.



temperature peak of luminescence was completely restored at 400°C (fig. 1 b).

The colourless Greenland ussingite acquired a deep lilac colour after irradiation. On the thermoluminescence curve of the irradiated sample an additional peak of luminescence appeared at 180°C and the high-temperature peak was restored at 380°C (fig. 2 b).

The spectral absorption of ussingite was measured on a »SF-4a« spectrophotometer with a special devise for studying powdered samples.

The investigation of the spectral absorption of light violet ussingite from Lovozero showed the presence of a wide absorption band in the range of 460–540 nm with the maximum near 500 nm (fig. 3 a). In the samples heated up to 450°C absorption drops sharply in this range (fig. 3 b). During irradiation of the sample the maximum at 500 nm is restored (fig. 3 c).

On the spectral absorption curve of the pale lilac ussingite from Greenland the absorption band in the range of 460–540 nm is only slightly manifested (fig. 4 a). After X-ray irradiation of this sample the intensity of its colour was noticeably increased. The artificial light violet colour of the ussingite proves to be rather stable and does not disappear during exposure of the samples to day light. A distinct wide absorption band with the maximum 515–520 nm is observed on the spectral absorption curve of the irradiated ussingite (fig. 4 b).

The EPR spectrum was investigated by means of the radiospectrometer »RE-1301« with the klystron frequency 9.4 GHz. This spectrum is characteristic for  $(\text{SO}_4)^{\cdot-}$  centers, which are described by a g-tensor with the

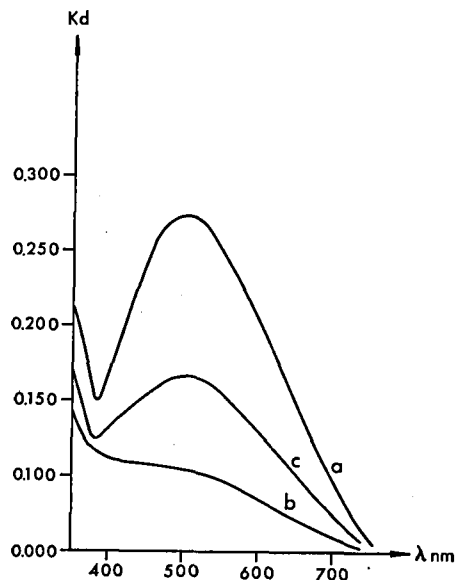


Fig. 3. Spectral absorption curves of ussingite from the Lovozero tundras. *a*: naturally coloured. *b*: decoloured by heating to 450° C. *c*: irradiated with X-rays.

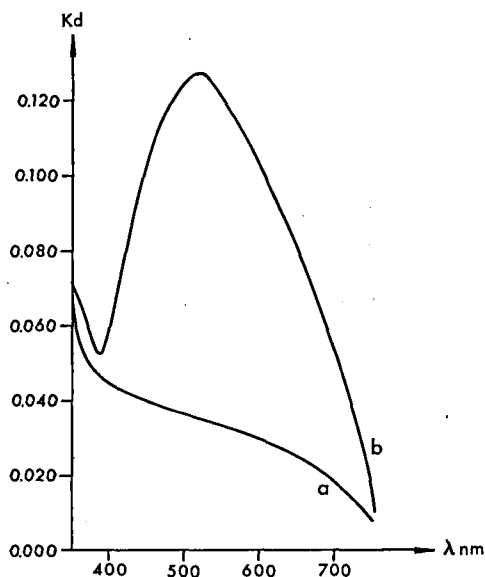
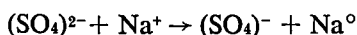


Fig. 4. Spectral absorption curves of ussingite from Greenland. *a*: naturally coloured. *b*: irradiated with X-rays.

following mean values:  $3_1 = 2.0047 \pm 0.0005$ ;  $g_2 = 2.008 \pm 0.001$ ;  $g_3 = 2.024 \pm 0.001$ . Similar centers have been observed in crystals of alkali halogenides (Morton, 1965), sulphates (Medlin, 1963; Morton et al., 1966), and in minerals of the cancrinite group (Novozhilov et al., 1966). They are clearly identified by the *g*-tensor value.

## Discussion

During the thermal decolouration of ussingite the line intensity in the EPR spectrum sharply decreased. It increased again during subsequent X-ray irradiation. This circumstance makes it possible to associate the light violet (and lilac) colour of ussingite with  $(\text{SO}_4)^-$  radiation centers. The origin of these centers may be represented by the following scheme:



The  $(\text{SO}_4)^-$ -groups occupy holes in the structure, and the neighbouring  $\text{Na}^+$  ions capture electrons and »are atomized«.

The violet colour of ussingite induced by the  $(\text{SO}_4)^-$ -centers may, in contrast to the blue colour of cancrinite (Novozhilov et al., 1966) be conditioned by the relatively smaller total mass of atoms (molecular weight) of ussingite, which results in the range of shorter waves. Hydroxyl ions probably play a definite role, the hydrogen bonds of which displace the  $(\text{SO}_4)$  band to the left, as established for many coloured crystalline hydrates. hydrates.

The data presented testify once again to a wide participation of sulphate centers in the radiation colours of mineral.

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## Резюме

Уссингит  $\text{Na}_2[\text{AlSi}_3\text{O}_8]\text{OH}$  - минерал, обладающий бледной-фиолетовой окраской и отчетливой термолюминесценцией. Были изучены кривые спектрального поглощения в видимой области, кривые термолюминесценции и спектры электронного парамагнитного резонанса двух разных образцов уссингита - с г. Пункаруайв /Ловозеро, и из щелочного массива Илимауссак /Южная Гренландия/. В результате было установлено, что природная и искусственная /полученная путем рентгеновского облучения/ фиолетовая окраска уссингита связана с радиационными центрами  $[\text{SO}_4]^-$ , характерными для минералов группы фельдшпатоидов.

## Dansk sammendrag

Ussingit -  $\text{Na}_2[\text{AlSi}_3\text{O}_8]\text{OH}$  - blev først beskrevet af O. B. Bøggild fra Ilímaussaq. Mineraleet er farveløst til violet og viser tydelig termoluminescens. Farven forsvinder ved opvarmning, men kan genfremkaldes ved røntgenbestråling. Den spektrale absorption i det synlige område, termoluminescensen og den paramagnetiske resonans af to

prøver af mineralet fra henholdsvis Ilímaussaq og Lovozero er undersøgt. Det foreslås, at den violette farve skyldes tilstedeværelsen af  $(\text{SO}_4)^{-}$  centre i krystalstrukturen.

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