BLUE SODALITE

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ABSTRACT

ESR, optical spectroscopic and conductivity studies on blue and colorless sodalite have confirmed the attribution of the blue color of sodalite to the presence of colloidal particles of metallic sodium. The colloidal sodium particles give rise to an isotropic resonance line at a *g* value to 2.0112(2) and an absorption line at 580 nm. Experimentally, blue coloration of sodalite was obtained by X-ray irradiation of colorless samples followed by exposure to visible light. The presence of O⁻ radicals in blue sodalite is related to the radiation history of the sample. Colloidal metal particles contribute considerably to the conductivity in blue sodalite. Introduction of excess sodium in sodalite at high temperature is suggested as an additional coloration process in nature.

SOMMAIRE

Nos études de sodalites bleue et incolore, par RSE, spectroscopie optique et conductivité, confirment que la couleur bleue est due à des particules colloïdales de sodium métallique. Ces particules sont à l'origine d'une raie de résonance isotrope, à *g* = 2.0112(2), et d'une raie d'absorption à 580 nm. La coloration bleue a été obtenue dans des sodalites incolores par irradiation X suivie d'un traitement à la lumière visible. La présence de radicaux O⁻ dans la sodalite bleue reflète les épisodes de radiation dans l'évolution d'un échantillon. Les particules métalliques colloïdales contribuent considérablement à la conductivité des sodalites bleues. L'introduction d'un excès de sodium à haute température dans la sodalite pourrait aussi expliquer la coloration de la sodalite naturelle.

(Traduit par la Rédaction)

INTRODUCTION

The sodalite group of minerals is well known for its variety in color. Sodalites may be colorless, white, grey, green, yellow, pink or, most typically, blue. Much interest has also been devoted to their photochromic character; the development of pink color in freshly fractured hackmanite, a variety of sodalite, was the earliest observed photochromic feature of sodalite in nature. The pink color, however, very soon fades away when the mineral is exposed to visible light. The pink color was shown by Medved (1954) to be due to *F* centres, generated by trapped electrons in Cl defect sites. The color developed in hackmanite showed a distinct absorption band at 530 nm when examined optically. Similar properties are also shown by sodalite when subjected to high-energy radiation (UV, X-rays and electron beams), and the colors obtained are bleached when the crystals are exposed to visible light or heated.

Sodalite, $Na_8(Al_6Si_6O_{24})Cl_2$, is cubic; its structure can be described as an aluminosilicate framework with cavities in which sodium and chlorine are situated (Pauling 1930). The color properties of sodalite have been found not to show a relationship with the composition of the mineral. In spite of this, the typical blue color of natural sodalite has been attributed to sulfur bound to the lattice (Kirk 1955, Bershov *et al.* 1969). However, synthetic sulfur-free sodalite shows the same photochromic properties as natural sodalite (Medved 1954) and develops a blue coloration on repeating the photochromic cycle. However, Kirk (1955) attributed the luminescence phenomena to NaS⁻ substituting for NaCl in the sodalite structure.

We have experimentally studied the photochromic properties of natural sodalite by means of ESR, optical spectroscopy, thermoluminescence and conductivity measurements. The behavior of the natural photochromic sodalite investigated by different experimental treatments is shown in Figure 1.

SAMPLES INVESTIGATED

Samples from different localities were used during the course of this study. Most of the results were obtained on blue sodalite from Bancroft, Ontario and a transparent colorless sample from Ice River, British Columbia. The chemical composition, analyzed by microprobe technique, and cell parameters, derived from X-ray diffraction analyses, are shown in Table
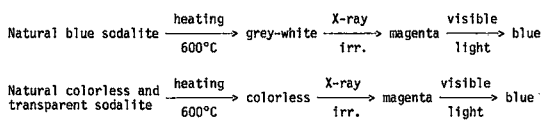
Natural blue sodalite $\xrightarrow[600°C]{\text{heating}}$ grey-white $\xrightarrow[\text{irr.}]{\text{X-ray}}$ magenta $\xrightarrow[\text{light}]{\text{visible}}$ blue

Natural colorless and transparent sodalite $\xrightarrow[600°C]{\text{heating}}$ colorless $\xrightarrow[\text{irr.}]{\text{X-ray}}$ magenta $\xrightarrow[\text{light}]{\text{visible}}$ blue

FIG. 1. Coloration sequences of sodalite under different experimental conditions.

1. Heat-bleaching of the natural blue sodalite decreased the sodium content somewhat, although not as drastically as noted by Bhalla (1974) for synthetic sodalite. After the microprobe analyses of the bleached sodalite, the analyzed spot had turned blue, under the following analytical conditions: beam 15 kV, ~ 50 μA and an analyzed spot 5 μm in diameter.

It is interesting to note that the colorless, transparent sodalite from Ice River contains 0.3 wt.% SO_3, whereas the blue sodalite contains < 0.05% sulfur, the detection limit of the analytical method used. Hence, we cannot directly relate the blue color of sodalite to the presence of sulfur.

EXPERIMENTAL

X-band ESR spectra of single crystals as well as powdered samples were recorded at liquid nitrogen-, room- and elevated temperatures with a Varian V–4500 spectrometer. Optical absorption spectra were measured on polished plates 0.6–0.9 mm thick on a Zeiss PMQ II single-beam spectrophotometer in the range 400–800 nm. Transmission spectra at variable temperatures were measured with a Beckman DK spectrometer equipped with a recorder. Thermoluminescence was measured on natural blue sodalite and luminescence phenomena were investigated by use of an argon-ion laser operating in the UV region between 333.6 to 363.8.

The conductance of sodalite was measured on circular plates of 0.5 cm radius and 0.15 cm thickness. The samples were placed between

TABLE 1. COMPOSITIONS OF SODALITES INVESTIGATED

	Blue Bancroft	Bleached Bancroft	Colorless Ice River
SiO_2 (wt. %)	37.2	37.8	36.2
Al_2O_3	32.5	32.0	32.6
Na_2O	22.8	21.4	25.5
Cl	6.7	6.6	5.8
SO_3	nil	nil	0.25
	99.2*	97.8*	100.35
a (Å)	8.874(2)	8.874(2)	8.885(3)

* Contains K and Ca, not determined

platinum foil electrodes coated with carbon paint and supported on stainless steel contacts in a helium atmosphere. Conductivity measurements were carried out between room temperature and 740°C using a bridge (Wayne Kerr Autobalance Universal Bridge B641) operating at a frequency of 1592 Hz. Temperatures were measured using an iron–constantan thermocouple placed in contact with the sample.

RESULTS AND DISCUSSION

Thermoluminescence

In a thermoluminescence experiment the amount of emitted light is measured while the sample is heated. Electrons trapped at a defect (F centre) site in an insulator are in a metastable condition; they can be liberated by heat to cross the potential barrier at the trap and move to a lower energy state with the emission of light (Townsend & Kelly 1973).

No emission of light was detected in the thermoluminescence experiments on the natural blue sodalite. During the experiment the specimens changed color from blue to white. The results indicate that the blue coloration of sodalite cannot be associated with trapped charges (*e.g.*, F centres) as no emission of light was recorded while the sample changed the color from blue to white.

Although we observed a faint luminescence of our natural heat-bleached sodalites (light blue) during the irradiation by laser, we failed completely to give the sample a color that stayed after the irradiation. We therefore conclude that our samples are not photochromic under UV irradiation in the frequency range of the laser used. Kirk (1955) obtained a pink coloration (F centres) on sulfur-doped sodalite by use of UV radiation. Bershov *et al.* (1969) observed two kinds of luminescence spectra from "sulfur-bearing" natural sodalite. In common with Kirk, they associated one type of the luminescence with sulfur and the second type with O_2^- radicals in the sodalite. They could, by means of ESR measurements, prove the existence of O_2^- ions in the sodalite specimen they examined.

Sodalite doped with S, Se, Te, group VI elements, *etc.*, readily show photochromic behavior under UV. Ballentyne & Bye (1970) proposed that elements of group VI act as donors of the electrons that are transferred under UV irradiation to anion-vacancy traps and later released by exposure to visible light

to be recaptured by the original donors. Photochromic coloration of sodalite by UV light is thus characteristic of S-bearing sodalite (or other group VI elements); active donors are thus needed in the structure to give the characteristic orange-yellow luminescence of sodalite exposed to UV light.

Electron-spin resonance

A portion of a ESR powder spectra obtained on blue sodalite is shown in Figure 2. The intensity *I* of the signal, corresponding to a *g* value of 2.0112(2), is correlated with the decreasing intensity of the blue color of sodalite. Upon heating the blue color disappears; beyond 400°C, the sodalite sample is white-greyish and no resononce signal is observed even when measuring at 77 K. The isotropic nature of this signal was confirmed from measurements on oriented single crystals in agreement with the observation of Bershov *et al.* (1969). The untreated colorless sodalite from Ice River shows no resonance signal. After X-ray irradiation and exposure to visible light, however, this specimen develops the same blue coloration. This coloration corresponds to the same resonance signal at the same *g* value, 2.0112(2). The intensity of the signal increased with increasing irradiation time, resulting in an intensified blue coloration of the sample. At low

temperature (77 K), the intensity of the resonance signal increased many times. A further remarkable effect was the non-saturation behavior of the signal even after using the maximum output from the klystron. ESR signals from trapped electrons (*F* centres) are readily saturable.

We may conclude from our ESR experiments that the isotropic line-resonance signal is linked to the color of sodalite. Bershov *et al.* (1969) suggested that this signal arises from the presence of SO_4^- radicals at a chlorine position, a conclusion that has to be rejected owing to the isotropic nature, the non-saturation behavior and the ability to observe the signal on our sulfur-free blue sodalites. We have recently suggested that the blue color and the observed resonance signal are due to sodium metal particles, experimentally obtained by decay of *F* centres (Hassib *et al.* 1977). The particles are of colloidal nature and are found to exhibit Tyndal scattering when thin sections are studied in a petrographic microscope fitted with a dark-field condenser.

The observed isotropic resonance signal is attributed to conduction electron-spin resonance (CESR). To observe CESR signals from metallic particles, the particles must be small enough for the conduction electrons to be placed in discrete energy levels and not be represented by a continuum as described by band theory
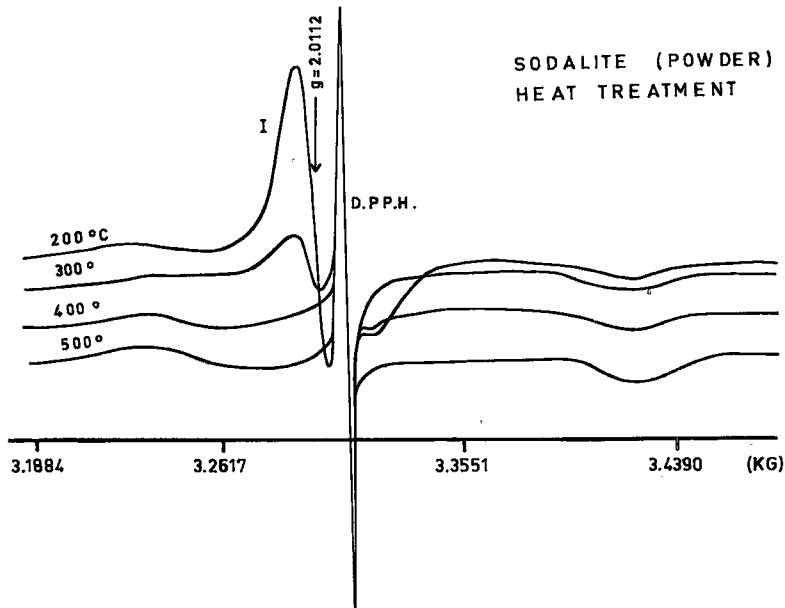

FIG. 2. ESR spectra of blue sodalite powder after heat treatments at different temperatures. DPPH signal was used as a reference.
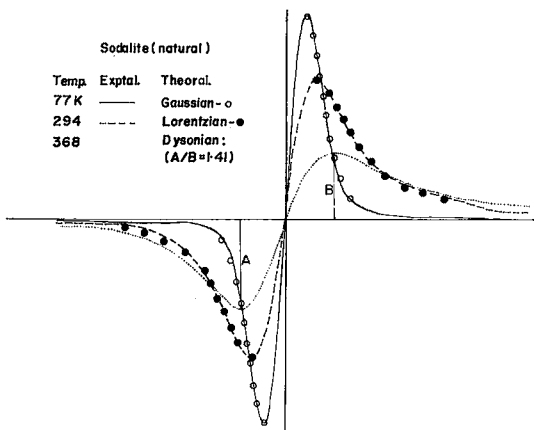
FIG. 3. Line shape of CESR of sodium metal particles in sodalite at different temperatures.

for bulk metal phases (Kawabata 1970). In natural sodalite it is suggested that a wide distribution in size of the colloidal particles is found. A careful study of the isotropic resonance line at different temperatures (Fig. 3) shows a behavior that strongly supports the contention that the signal is arising from colloidal metallic particles.

X irradiation of all the samples resulted in another ESR signal occurring at $g = 1.9978$. This signal was observed by Bershov et al. (1969) in unirradiated natural sodalite. They attributed the signal to an O^- ion at the common apex of a pair of framework tetrahedra; by detailed measurements, they concluded that the central
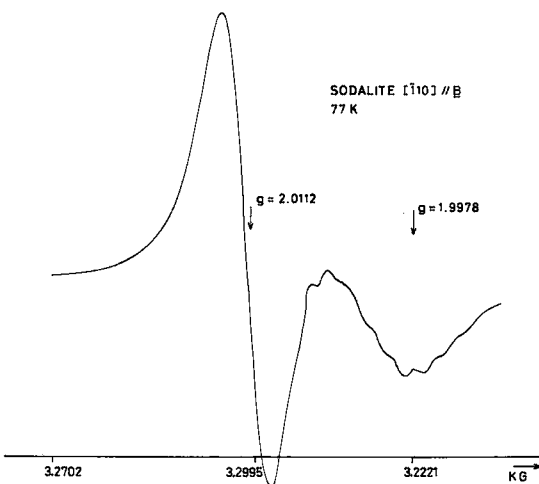

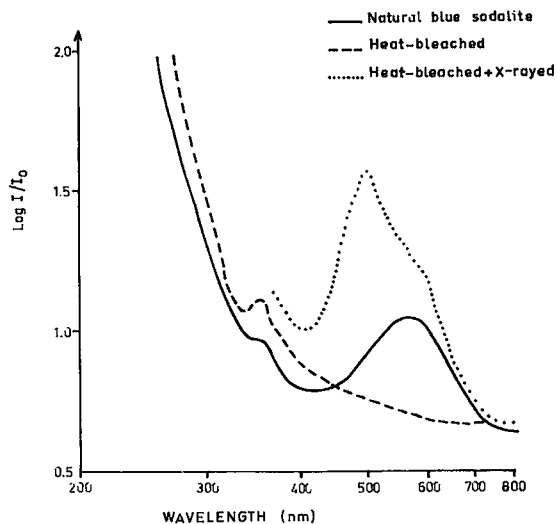FIG. 4. Single-crystal ESR spectrum of X-irradiated white sodalite exposed to light.

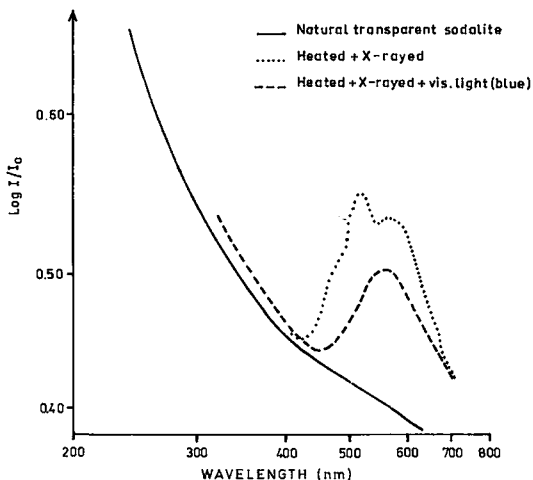FIG. 5. Optical absorption spectra of blue sodalite at different experimental conditions.

FIG. 6 Optical absorption spectra of colorless sodalite at different experimental conditions.

ions of the tetrahedra were both aluminum rather than the usual alternation of aluminum and silicon that occurs in the perfect lattice. The signal we obtained on an irradiated single crystal is shown in Figure 4. This spectrum was anisotropic with maximum resolution of a hyperfine structure along the orientation [110] parallel to the magnetic field. The eleven observed hyperfine lines support the assignment of the O^- ion to a position intermediate with respect to two Al nuclei ($I = 5/2$).

We could not observe the O^- resonance in all of our samples. Transparent sodalite and

blue sodalite from certain localities did not show this resonance until they were irradiated.

Optical spectroscopy

Optical spectra of natural sodalite obtained at room temperature under different experimental conditions are shown in Figures 5 and 6. The natural blue sodalite (Fig. 5) shows a broad absorption band centred at 580 nm; no change occurs in its position when measured at 77 K (Hassib *et al.* 1977). The band gradually disappears upon heating; at above $\sim 400°C$, there is no trace of the absorption band, and the sample has turned grey-white in color. Upon X irradiation the sample develops a magenta color corresponding to a strong absorption band at 520 nm and a shoulder centred at the same position (580 nm) as the blue colored sodalite. Exposure to visible light turns the crystal blue and the absorption peak at 520 nm is no longer observed after 2 hours of exposure to visible light. The absorption spectrum becomes now identical to the spectrum of the natural blue sodalite (Fig. 5). The untreated colorless sodalite (Ice River) shows no absorption band in the measured wavelength region (Fig. 6). Similar properties to those of the blue sodalite, however, are observed in the spectra from the irradiated colorless sodalite. The strong absorption in the UV region arises from *MO* transition in the relatively covalently bonded Si(Al)–O framework in sodalite.

The strong absorption band at 530 nm has been shown earlier to arise from *F* centres (Medved 1954, Ballentyne & Bye 1970). That this absorption was due to *F* centres was further confirmed by Hodgson *et al.* (1967) and McLaughlan & Marshall (1970) who observed a typical 13-line ESR spectrum arising from electrons trapped at a chlorine-ion position and surrounded by four sodium ions. Medved (1954) observed an auxiliary band at 600 nm; we assume that this is the same band we observe at 580 nm and attribute to the presence of metallic sodium colloidal particles, the shift being due to differences in colloidal size. We can now confirm from the temperature-change effects on this band that it cannot be an *F* band. The insensitivity to the decrease of temperature of this absorption band indicates that the spectrum arises from small colloidal particles (Compton 1957). The absorption observed can be explained by Mie extinction (absorption plus scattering) of light by colloidal-size particles. The width and position of the maximum Mie extinction of light by col-
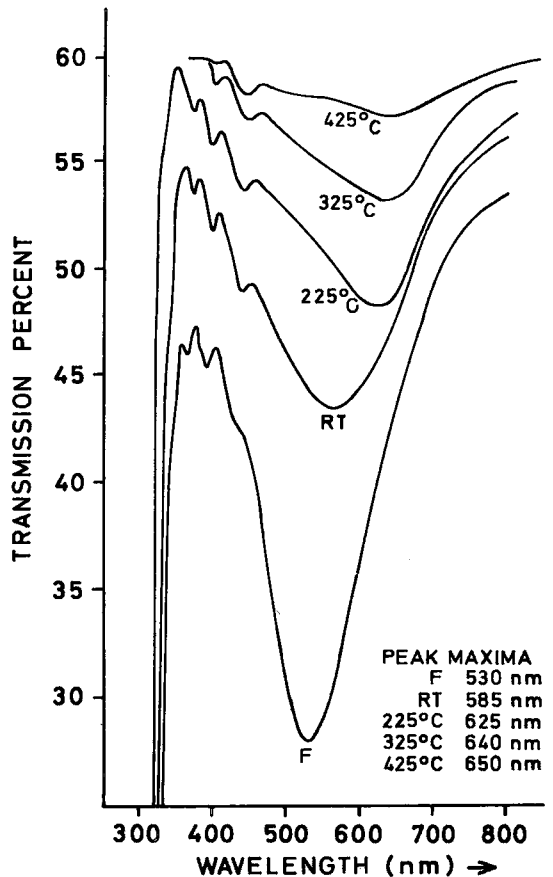

FIG. 7. Shift in optical transmission minima of X-irradiated colorless sodalite after different heat treatments.

loidal particles is strongly dependent on the size of the particles (Karlsson & Beckman 1967). Annealing of the irradiated sodalite at high temperature makes the particles aggregate together and thus the absorption peak maxima are shifted towards longer wavelength. This feature shown experimentally in Figure 7, gives further evidence that the absorption band at 580 nm (RT) arises from colloidal metal particles. In sodalite, sodium metal colloids are responsible for the blue coloration. Bleaching of sodalite upon heating can thus be understood in terms of the lack of particles of suitable size (*i.e.*, too large) to fulfill the requirement for Mie extinction.

Compton (1957) suggested, from optical studies, that the coloration of alkali halide was due to colloidal formations in the crystals. Recently Hassib *et al.* (1977) and Hassib (1979) also suggested from ESR and CESR spectro-
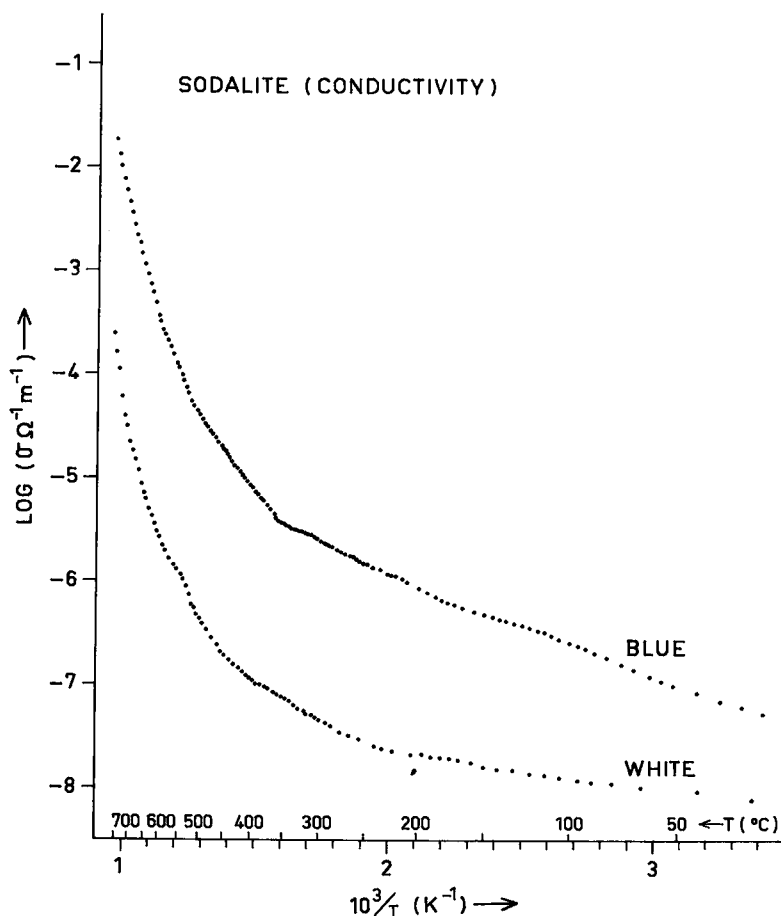
FIG. 8. Conductivity of blue and white sodalite samples at different temperatures.

scopy measurements on natural sodalites that their typical blue color is a result of colloids, formed by annihilation of F centres produced by X-ray irradiation, when exposed to visible light.

Although the samples were kept in dark after X irradiation, there were always traces of the colloidal signals in both the ESR spectra and the optical spectra (cf., Figs. 5 and 6) even at 77 K. This indicates that the stability of the F centres at low temperature is very low, in contrast to the case in common alkali halides (Compton 1957). The energy needed in sodalite for colloidal formation by the reaction $Na^+ + e^- \rightarrow Na^0$ is evidently smaller than that needed in the case of alkali halides.

Conductivity

The results of the conductivity measurements on blue and white sodalite are shown in Fig-

ure 8. The white sodalite sample is the blue sodalite bleached during the first run. The most pronounced feature in the conductivity of sodalite is the rapid increase in the ionic conductivity beyond 400°C. This indicates an increase in ionic mobility at this temperature, at which sodalite loses the blue color. The blue sodalite shows a much higher conductivity than the bleached one, starting from room temperature. This is probably due to the contribution from the colloidal sodium metal particles in blue sodalite. The lower conductivity of the bleached sodalite may be attributed to the loss of sodium in the heat treatment during the first run, in accordance with our chemical analyses (cf., Table 1) and the thermogravimetric analyses of Barrer & Cole (1968).

CONCLUSIONS AND APPLICATION TO PETROLOGY

Our experimental results have demonstrated

the presence of sodium metal particles of colloidal nature in blue sodalite. Experimentally, blue sodalite was produced by annihilation of F centres generated by high-energy radiation. The intensity of the blue color bleached at higher temperature and the bleaching temperature can be regarded as dependent on the amount of colloidal particles and their size. The widths of the optical absorption bands arising from the colloids indicate a wide distribution of metallic-particle size in sodalite. We estimate sizes in natural blue sodalites of around 30 nm, whereas observation of CESR shows that much smaller particle sizes also exist. The large sodium metallic particles are of course too large to be accommodated in the cavities and no expansion of the cell structure is observed in the case of white sodalite exposed to irradiation. Microscopic studies show, however, that intense blue coloration in sodalite is most often found at the grain boundaries and along other well-pronounced crystallographic directions.

The color properties of natural sodalite may therefore give some indication of the thermal history of rocks. We must, however, also consider the process leading to the blue coloration of sodalite and the formation of colloidal phases in sodalite in nature. Sodalite occurs very typically in nepheline syenites and associated rocks. These "residual systems" are commonly characterized by relatively high content of heavy radioactive elements (^{232}Th, ^{238}U and ^{40}K) which would provide the necessary radiation to create electron defects (F centres). We have, however, demonstrated above that colloidal formation through irradiation also gives rise to the presence of O^- radicals in sodalite. The absence of any O^- signals from some of our collected blue sodalite samples from different localities indicate, however, that colloidal formation may proceed through other processes. Barrer & Cole (1968) could color sodalite by interaction of sodium vapor with sodalite and they actually demonstrated the ability of sodalite to store metallic sodium. In the sodium-rich environments in which sodalite forms in nature, we may postulate that a vapor–solid interaction process occurs at elevated temperature and gives rise to colloidal sodium in natural sodalite.

Natural sodalite is found in rocks representing wide differences in genesis; it is reported from phonolites, alkali syenites, volcanic ejecta as well as from metasomatically altered marbles and from pegmatites (Deer *et al.* 1963, Taylor 1967). Our colorless sample from Ice River occurs as well-shaped crystals in a low-temperature hydrothermally altered vein material. In the rare occurrences from volcanic extrusive rocks, sodalites show no color or are white-greyish, as if they had undergone high-temperature bleaching events. Typical blue sodalite, however, does not indicate any temperature of formation. It may form as colorless crystals at a high temperature and later become exposed to high-energy radiation through radioactive decay at lower temperatures, leading to colloidal formation in the crystal.

REFERENCES

BALLENTYNE, D. W. G. & BYE, K. L. (1970): The nature of photochromism in chlorosodalites from optical data. *J. Phys. (D): Appl. Phys.* 3, 1438-1443.

BARRER, R. M. & COLE, J. F. (1968): Interaction of sodium vapour with synthetic sodalite: sorption and formation of colour centres. *J. Phys. Chem. Solids* 29, 1755-1758.

BERSHOV, L. V., MARTIROSYAN, V. O., PLATONOV, A. N. & TARASHCHAN, A. N. (1969): Stable inorganic radicals in sodalite $Na_8(AlSiO_4)_6Cl_2$ single crystals. *Izv. Akad. Nauk SSSR, Neorg. Mater.* 5, 1780-1784 (in Russ.).

BHALLA, R. J. R. S. B. (1974): Electron-beam damage in cathodochromic sodalite. *J. Appl. Phys.* 45, 3703-3709.

COMPTON, W. D. (1957): Production of colloidal sodium in NaCl by ionizing radiation. *Phys. Rev.* 107, 1271-1275.

DEER, W. A., HOWIE, R. A. & ZUSSMAN, J. (1963): *Rock-Forming Minerals* 4. *Framework Silicates.* Longmans, London.

HASSIB, A. (1979): CESR of sodium particles in natural sodalite. *J. Phys. Chem. Solids* (in press).

———, BECKMAN, O. & ANNERSTEN, H. (1977): Photochromic properties of natural sodalite. *J. Phys. (D): Appl. Phys.* 10, 771-777.

HODGSON, W. G., BRINEN, J. S. & WILLIAMS, E. F. (1967): Electron spin resonance investigation of photochromic sodalites. *J. Chem. Phys.* 47, 3719-3723.

KARLSSON, A. V. & BECKMAN, O. (1967): Optical extinction in the colloid system NaCl:Na. *Sol. State Comm.* **5**, 795-798.

KAWABATA, A. (1970): Electronic properties of fine metallic particles. III. E.S.R. absorption line shape. *J. Phys. Soc. Jap.* **29**, 902-911.

KIRK, R. D. (1955): The luminescence and tenebrescence of natural and synthetic sodalite. *Amer. Mineral.* **40**, 22-31.

MCLAUGHLAN, S. D. & MARSHALL, D. J. (1970): Paramagnetic resonance of F-type centres in photochromic sodalites. *Phys. Lett.* **32A**, 343-344.

MEDVED, D. B. (1954): Hackmanite and its tenebrescent properties. *Amer. Mineral.* **39**, 615-629.

PAULING, L. (1930): The structure of sodalite and helvite. *Z. Krist.* **74**, 213-225.

TAYLOR, D. (1967): The sodalite group of minerals. *Contr. Mineral. Petrology* **16**, 172-188.

TOWNSEND, P. D. & KELLY, J. C. (1973): *Colour Centres and Imperfections in Insulators and Semiconductors.* Crane, Russak, Co., New York.