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## FLOOR-NUCLEATED HALITE CRYSTALS FROM WIELICZKA

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**Abstract.** Idiomorphic halite crystals from Wieliczka showing zonal structure have been investigated. The presence of terrigenous and chemical material accumulated in the planes parallel to 001 of these crystals indicates that their nucleation and recrystallization took place on the floor of an evaporational basin. The mineralogical composition of terrigenous and chemical admixtures in halite crystals have been identified and the directions and rate of crystal growth determined.

### INTRODUCTION

During the investigations of the Miocene rocks of the Wieliczka salt deposit in the years 1971—1974, coarse-crystalline rock salts, called green salts, have been noticed. They are a chemico-terrigenous complex made up of alternating rock salt beds and mudstones or sandstones containing anhydrite (Gaweł 1962). In the investigated geological profile, which is on the mining level No VIII in the s.c. bedded part of the deposit, the thicknesses of the consecutive salt beds from the bottom upwards are: 1.2, 3.0, 1.0, 1.0 m. From the bottom they are underlain by mudstones containing anhydrite, while in the top they contact through a thin mudstone layer with the "shaft salt" bed.

Green salts and halite from the Wieliczka mine were investigated by several authors, e.g. Aleugtner and Pawłowska (1961), Gaweł (1962), Charysz (1967), Pawlikowski (in press), Manecki and Pawlikowski (in press). The peculiar form of halite occurring in these salts, as well as the substantial amount of the accompanying anhydrite have induced the present authors to perform more detailed investigations.

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## EXPERIMENTAL PROCEDURE

The analyses were carried out on three samples derived from the lowermost and two successive rock salt beds. They are represented by three large halite crystals that were subjected to microscopic examinations as well as to X-ray diffraction, electron microprobe and infrared absorption spectroscopic analyses. Microscopic (optical) observations were made both in natural samples and thin sections. X-ray diffraction analysis was carried out with the TUR-61 diffractometer in the range of  $\Theta = 0-22^\circ$ , using Fe-filtered  $\text{CoK}_\alpha$  radiation and powder preparations made from the material separated from the halite crystals. Infrared spectroscopic investigations were performed on the UR-10 (Zeiss, Jena) apparatus in the range of  $400-3800\text{ cm}^{-1}$ , with natural halite crystals as preparations. Electron microprobe analysis was made on the MS-46 CAMECA apparatus in the Department of Structural Analyses of the Institute of Metallurgy, the Academy of Mining and Metallurgy in Cracow. The following parameters were selected: accelerating voltage — 10 kV for carbon, 15 kV for sodium and 20 kV for the other elements; sample current — 600 nA for carbon, 50 nA for sodium and 15 nA for the other elements. PET, KAP, OdPb crystals were used as monochromators and  $\text{SiO}_2$ ,  $\text{CaF}_2$ , Al, NaCl, C, potassium glass with 8.4% K as standards. The sample was coated in vacuum with a thin layer of gold.

## EXPERIMENTAL DATA

### Samples 1, 2

Since the samples 1 and 2 represent a similar type of halite crystals, the results of their examinations are given jointly. Their size amounts up to 2.5 cm. They are idiomorphic with a characteristic zonal structure. In dark zones there are substantial amounts of linearly arranged liquid-gaseous inclusions, their size not exceeding  $40-60\ \mu$ . The brine in the inclusions is sometimes slightly turbid, which is readily observable at great magnifications. In halite that makes up these zones single flakes of clay minerals (Phot. 1) with the morphological features similar to those of chlorite are encountered (Lucas 1962). Light zones contain only irregularly distributed liquid-gaseous inclusions about 0.1 mm in size, the brine showing a very high degree of purity. In those crystals, edges of intergrowth of the faces  $100$  and  $010$  with the face  $001$  in the successive stages of growth of the halite crystal have been also examined. Their position (Phot. 2, 3) evidences the varying rate of crystal growth. In the crystal shown on Photograph 2 the trace of intergrowths of faces  $001$  and  $010$  is visible. It may be inferred from its position that the crystallization rate of that crystal did not vary. It should be noted, however, that if a regular halite crystal grows uniformly in all directions, the plane of intergrowth of the faces  $001$  and  $010$  is at an angle of  $45^\circ$  in relation to them. Assuming that the crystallization rate is a function of  $\text{tg } \alpha$ , it equals 1 in all directions. A value of  $\text{tg } \alpha > 1$  indicates a higher rate of crystal growth in one direction. For crystal 1 (Phot. 2) the value of  $\alpha = 75^\circ$ . The crystallization rate in the direction  $\perp 001$  face was 3.73 times higher than in the direction

$\perp 010$ . In the case of crystal 2 (Phot. 3), the rate of growth in the direction  $\perp 001$  varied with time. In the initial stage it was  $\text{tg } \alpha_2 = \text{tg } 70^\circ = 2.74$ , then it decreased to a value of  $\text{tg } 55^\circ = 1.42$ , finally attaining a value of  $\text{tg } 85^\circ = 11.43$  times faster than in the direction  $\perp 010$ . It may be stated then that in the two latter halite crystals the crystallization rate was higher in the direction in which zonal structure is more conspicuous, i.e. in the direction close to the vertical from the bottom of the salt layer.

Infrared spectroscopic analyses. The analyses were performed for two parts of the crystal (sample 1, Fig. 1). One part of the cry-

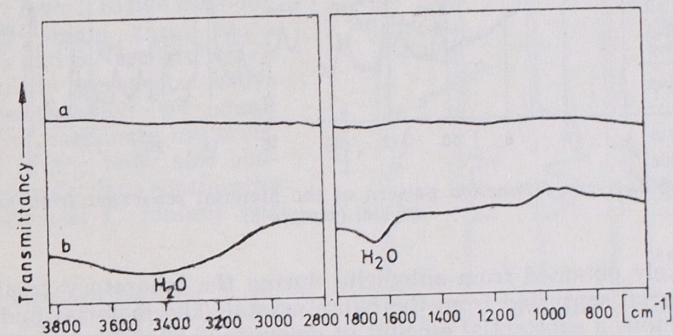


Fig. 1. Infrared absorption spectra  
a — part of halite crystal (sample 1) with indistinct zonal structure, b — part of halite crystal (sample 1) with conspicuous zonal structure

stal, revealing the presence of a few indistinct zones, fails to show absorption bands in the range of  $400-3800\text{ cm}^{-1}$ . It may be inferred therefore that the halite is highly pure, the amount of impurities being lesser than 1% (measurement sensitivity). The other part of the crystal, adjacent to the face  $001$ , has a much better pronounced zonal structure. Its spectrum shows two broad absorption bands about  $800$  and  $1100\text{ cm}^{-1}$  and a band about  $3400\text{ cm}^{-1}$ . It is impossible to identify the admixtures present in the zones on their basis, though it may be noted that this part of the crystal contains a substantial amount of water occluded in the liquid-gaseous inclusions.

### Sample 3

This sample is an idiomorphic halite crystal with an edge length of 4.1 cm, showing distinct zonal structure. Zonality is made more conspicuous by the presence of terrigenous material on the crystal growth surfaces  $\parallel 001$ . Flaky concentrations of clay minerals, accompanied by small anhydrite nodules may be distinguished macroscopically in the zones. X-ray examinations were carried out on the material separated from one half of the crystal (sample 3) whereas the other half was subjected to electron microprobe analysis.

As appears from the X-ray diffraction pattern (Fig. 2), the dominant admixture in halite is anhydrite ( $d_{hkl} = 3.87, 3.50, 2.85, 2.32, 2.19, 2.09\ \text{\AA}$ ). It is accompanied by gypsum ( $d_{hkl} = 6.8, 3.80, 3.07, 2.68\ \text{\AA}$ ), which was



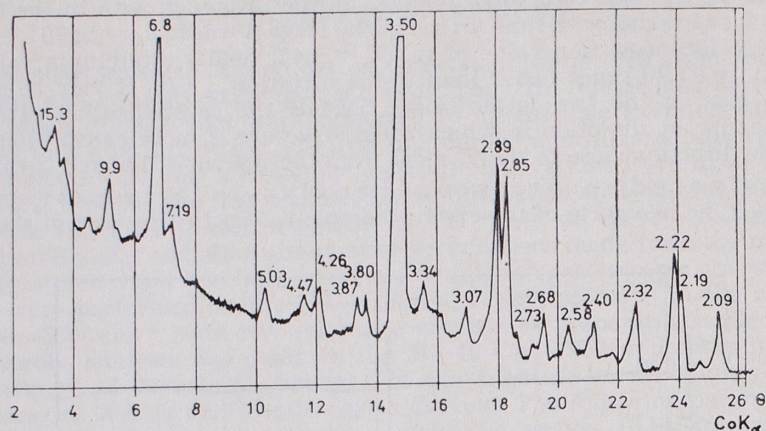


Fig. 2. X-ray diffraction pattern of the material separated from halite crystal (sample 3)

most likely obtained from anhydrite during the laboratory treatment of the material separated from the halite crystal. The material under study also contains a substantial amount of dolomite (2.89, 2.40, 2.19 Å), muscovite (9.9, 5.03, 3.34, 2.85, 2.58 Å), as well as an inconsiderable amount of quartz (4.26, 3.34 Å) and of a mineral from the smectite (15.3 Å) and kaolinite-chlorite (7.19 Å) group. The reflections  $d_{hkl} = 2.68, 2.40, 2.22$  Å may be indicative of the presence of some pyrite. Its occurrence is not, however, quite certain because the above reflections coincide with those of anhydrite and gypsum. The minerals appearing in the amounts lesser than 2–3% failed to be detected by X-ray powder method.

The other part of the crystal was subjected to electron microprobe analysis to determine the distribution of Na, Ca, Mg, S, Fe, K, Ba, Sr, C, Al and Si in three selected microareas of the crystal.

**Microarea 1** ( $200 \times 200 \mu\text{m}$ ). The analyses were carried out on terrigenous minerals distributed in the zones  $\parallel 001$ . Observations of the topographic and absorption electron images have revealed the presence of grains with sharp outlines, standing out in relief against the halite background (Phot. 5). A comparison of Si distribution with the data obtained from linear (Phot. 3) and local analysis has shown that they are quartz grains. In their immediate vicinity Ca and a small amount of C have been noted, this distribution indicating that quartz grains are accompanied mainly by anhydrite and carbonate minerals. Ca and Mg have not been found to co-occur in the analysed microareas, which implies that carbonate minerals are represented mainly by calcite and, subordinately only, by dolomite. The mode of occurrence of Ca and C also indicates that the carbonates concentrate predominantly near quartz grains. Quantitative analyses, as well as the observations of K, Al and Si distribution may point to the presence of potassium aluminosilicate. It is interesting to note the low content of Si, which could have been partly leached from the aluminosilicate under the conditions of the reducing alkaline medium. From the microprobe trace across the area where aluminosilicate and quartz occur in halite (Fig. 3) it appears that they are accompanied by Ca (about 14%). It

is not to be presumed though that Ca enters into the structure of aluminosilicate.

In **microarea 2** ( $200 \times 200 \mu\text{m}$ ), a spherical body about  $120 \mu\text{m}$  in diameter, embedded in halite, has been recorded. The topographic and absorption electron images in this area show that the body stands out distinctly in relief against the surroundings, its interior being heterogeneous. It is evident from the mode of occurrence of C and Na that the rim of the body has a higher content of C, that of Na being simultaneously lower. Inside the body there are single grains with higher Ca and S contents, which attests to the presence of anhydrite accompanied by small amounts of carbonate minerals. The rim of the body also contains a little Ca, but, considering the substantial C content and

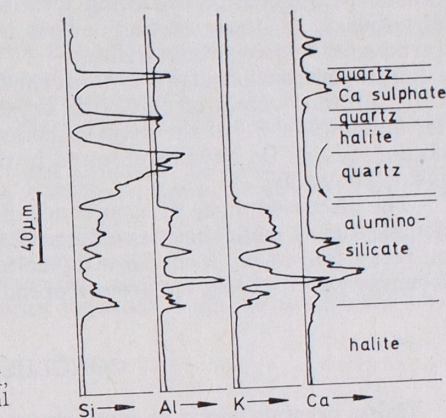


Fig. 3. Microprobe trace for Si, Al, K, Ca across microarea 1 of halite crystal (sample 3)

the insignificant amount of S, this indicates that it is made up almost exclusively of carbon, not of carbonate. This observation has been also confirmed by the distribution of Mg, Si and Fe both in the body and the surrounding halite. The changes in the Na content inside the body and on its boundary which have been noted during analysis along the line are due to micro-irregularities of the surface (Phot. 6 — topographic image) rather than to actual differences in the concentration of Na. The recorded distribution of elements in microarea 2 implies that the spherical body in question is presumably a plant pollen. Its organic matter was decomposed under the reducing conditions, and  $\text{H}_2\text{S}$  thus formed combined with Ca to give calcium sulphate that has been found in its interior. The occurrence of a pollen in a halite monocrystal is most interesting because a component of that type is usually encountered in the intergranular spaces of halite, where it accompanies terrigenous detrital minerals.

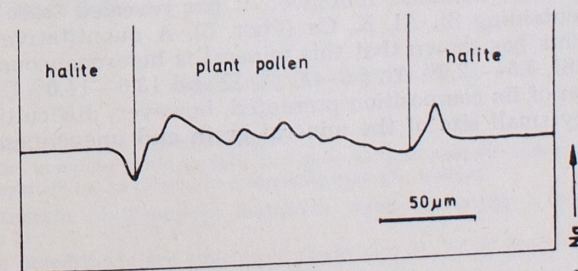


Fig. 4. Microprobe trace for Na across microarea 2 of halite crystal (sample 3)



In the third microarea of the sample ( $300 \times 300 \mu\text{m}$ ), lath-formed anhydrite crystals appear in halite (Phot. 7). Their interiors and contacts with halite were thoroughly investigated. An analysis of the distribution of Ca, S, C and Na shows that Ca is not all bound in anhydrite. It also partly comes from carbonates, which is evidenced by its good correlation with C. In the microarea under study only an insignificant amount of Mg has been detected; it may be therefore presumed that calcite is the carbonate mineral co-occurring with anhydrite. It also appears from the distribution of those elements that anhydrite contains somewhat more carbonate inclusions than halite.

The distribution of Fe is uniform throughout the area. Only sporadically, on the contact of anhydrite crystals with halite, have slightly greater amounts of Fe in the form of concentrations  $1-2 \mu\text{m}$  in size been recorded. Sr and Ba have been found in trace amounts, concentrating mainly inside anhydrite.

The discussed mode of occurrence of anhydrite in the halite crystal evidences that it could not have formed as a result of gypsum dehydration or recrystallization from flowing solutions. It originated authigenically from sea water during the growth of halite crystals.

#### CONCLUSIONS

Halite crystals showing zonal structure have been reported from Wieliczka in earlier mineralogical publications (Gawel 1962; Prochazka *et al.* 1969). In foreign literature a similar type of halite has been described by Wardlow and Schwerdtner (1966). No author, however, has noted so far the presence of terrigenous and chemical material on the crystal growth surfaces. The substantial amount of this material and its distribution on the planes parallel to 001 of halite crystals indicates that nucleation and recrystallization of the green salts took place on the floor of an evaporational basin. Grains of other minerals of chemical origin (anhydrite, dolomite, calcite), terrigenous minerals (quartz, muscovite, minerals of the smectite, kaolinite and chlorite group), as well as plant pollens fell on the partly formed crystals. Observations of zonality of halite crystals also imply that, besides the grains of the above-mentioned minerals, liquid inclusions were the main factor affecting the growth of crystal in a given direction. They are, just like temperature (Honigman 1961), one of the main determinants of the directional development of halite crystals. The electron microprobe analysis has confirmed the presence of the minerals identified by other methods; moreover, it has revealed trace amounts of a mineral containing Si, Al, K, Ca (Phot. 5). A quantitative analysis at different points has shown that this mineral is heterogeneous, containing 12.0—21.0% Si, 8.5—12.0% Al, 6.0—11.0% K and 13.0—14.0% Ca. A precise determination of its composition presented, however, difficulties, considering the very small size of the mineral grain and unevenness of its surface.

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### O PEWNYM TYPIE KRYSZTAŁÓW HALITU Z WIELICZKI

#### Streszczenie

Przedmiotem badań były idiomorficzne kryształy halitu z Wieliczki wykazujące budowę zonalną. Obecność materiału terrygenicznego i chemicznego, skupiającego się na płaszczyznach równoległych do 001, pozwala wnioskować, że krystalizowały one na dnie zbiornika ewaporacyjnego. Rozpoznano charakter mineralogiczny materiału detrytycznego i chemicznego stanowiącego domieszkę w kryształach halitu oraz kierunki i prędkość wzrostu tych kryształów.

#### OBJAŚNIENIA FIGUR

- Fig. 1. Widmo absorpcyjne w podczerwieni  
a — części kryształu halitu (próbka 1) o słabo zaznaczającej się budowie zonalnej, b — części kryształu halitu (próbka 1) o wyraźnej budowie zonalnej
- Fig. 2. Dyfraktogram rentgenowski materiału wyseparowanego z kryształu halitu (próbka 3)
- Fig. 3. Krzywe przedstawiające zmienność zawartości Si, Al, K, Ca w mikroobszarze 1 kryształu halitu (próbka 3)
- Fig. 4. Krzywe przedstawiające zmienność zawartości Na w mikroobszarze 2 kryształu halitu (próbka 3)



## OBJASNIENIA FOTOGRAFII

- Fot. 1. Blaszka minerału ilastego zbliżona pod względem cech morfologicznych do chlorytu, występująca na płaszczyźnie wzrostu 001 kryształu halitu. Próbką 1. Mikroskop elektronowy Tesla BS 613. Pow.  $\times 14\ 000$
- Fot. 2. Kryształ halitu (próbka 1) o zonalności  $\parallel 001$ .  $\alpha_1$  — kąt między śladem krawędzi ścian 001 i 010 oraz śladem płaszczyzny  $\perp 010$ . Pow.  $\times 35$
- Fot. 3. Kryształ halitu (próbka 2) o zonalności  $\parallel 001$ .  $\alpha_2$  — kąt między śladem krawędzi 001 i 010 oraz śladem płaszczyzny  $\perp 010$ . Pow.  $\times 10$
- Fot. 4. Kryształ halitu (próbka 3) zawierający w zonach  $\parallel 001$  minerały trudno rozpuszczalne w wodzie. Pow.  $\times 35$
- Fot. 5. Obrazy elektronowe (topograficzny i absorpcyjny) oraz rozmieszczenia powierzchniowego Si, Na, C i Ca w ziarnach minerałów terygenicznych występujących w kryształach halitu. Próbką 3. Obszar 1. Pow.  $\times 125$
- Fot. 6. Obrazy elektronowe (topograficzny i absorpcyjny) oraz powierzchniowego rozmieszczenia C, Na, Ca i S w pyłku roślinnym występującym w kryształach halitu. Próbką 3. Obszar 2. Pow.  $\times 125$
- Fot. 7. Obrazy elektronowe (topograficzny i absorpcyjny) oraz powierzchniowego rozmieszczenia C, Na, Ca i S w kryształach anhidrytu tkwiących w kryształach halitu. Próbką 3. Obszar 3. Pow.  $\times 125$

Мацей ПАВЛИКОВСКИ, Эва КСЕНЖЕК

## О НЕКОТОРОМ ТИПЕ КРИСТАЛЛОВ ГАЛИТА ИЗ ВЕЛИЧКИ

### Резюме

Предметом исследования были идиоморфные кристаллы галита из месторождения Величка, характеризующиеся зональным строением. По присутствию терригенного и химического материала, скопляющегося на плоскостях параллельных 001, можно предполагать, что кристаллы образовались на дне эвапоритового бассейна. Определен минералогический характер обломочного и химического материала, образующего примесь в кристаллах галита, а также определены направления и скорость роста этих кристаллов.

### ОБЪЯСНЕНИЯ К ФИГУРАМ

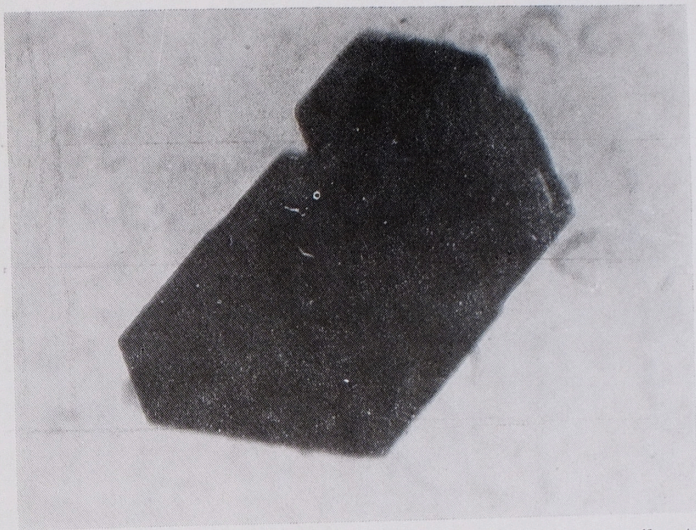
- Фиг. 1. ИК-спектр поглощения  
а — участки кристалла галита (образец 1) со слабо выраженным зональным строением,  
б — участки кристалла галита (образец 1) с отчетливым зональным строением
- Фиг. 2. Рентгеновская дифрактограмма материала, извлеченного из кристалла галита (образец 3)
- Фиг. 3. Графики изменений содержания Al, K, Ca на микроучастке 1 кристалла галита (образец 3)
- Фиг. 4. Графики изменений содержания Na на микроучастке 2 кристалла галита (образец 3)

### ОБЪЯСНЕНИЯ К ФОТОСНИМКАМ

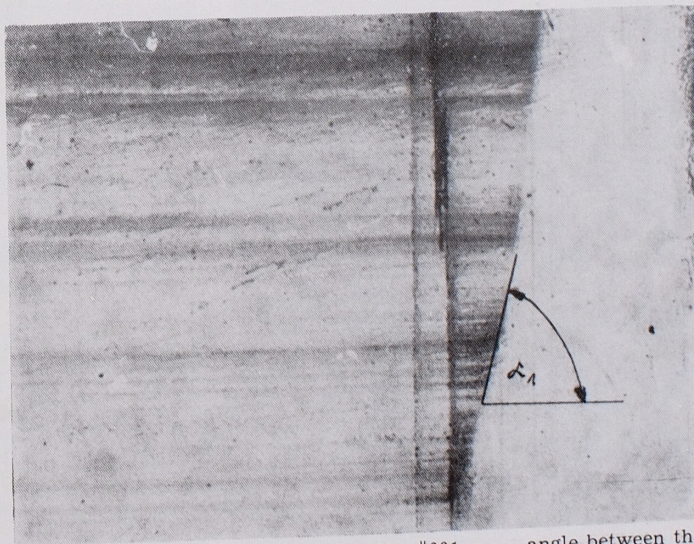
- Фото 1. Чешуйка глинистого минерала, по своим морфологическим признакам напоминающая хлорит, располагающаяся на плоскости роста 001 кристалла галита. Образец 1. Электронный микроскоп Tesla BS 613. Увел.  $\times 14\ 000$

- Фото 2. Кристалл галита (образец 1) с зональностью  $\parallel 001$   
 $\alpha_1$  — угол между следом ребра граней 001 и 010 и следом плоскости  $\perp 010$ . Увел.  $\times 35$
- Фото 3. Кристалл галита (образец 2) с зональностью  $\parallel 001$ .  $\alpha_2$  — угол между следом ребра граней 001 и 010 и следом плоскости  $\perp 010$ . Увел.  $\times 10$
- Фото 4. Кристалл галита (образец 3), содержащий в зонах  $\parallel 001$  минералы трудно растворимые в воде. Увел.  $\times 35$
- Фото 5. Электронные изображения (топографическое и поглощения) и вид поверхностного расположения Si, Na, C и Ca в зернах терригенных минералов, содержащихся в галите. Образец 3. Участок 1. Увел.  $\times 125$
- Фото 6. Электронные изображения (топографическое и поглощения) и вид поверхностного расположения C, Na, Ca и S в растительной пыльце, содержащейся в кристаллах галита. Образец 3. Участок 2. Увел.  $\times 125$
- Фото 7. Электронные изображения (топографическое и поглощения) и вид поверхностного расположения C, Na, Ca и S в кристаллах ангидрита, заключенных в кристаллах галита. Образец 3. Участок 3. Увел.  $\times 125$



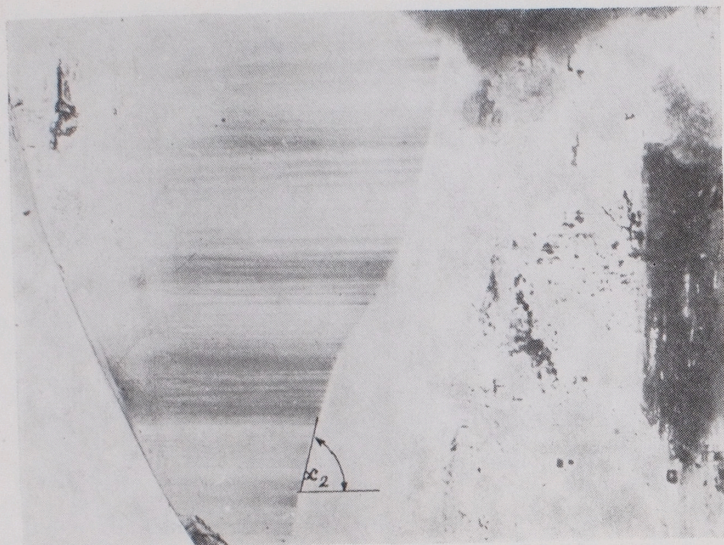


Phot. 1. A flake of clay mineral with the morphological features similar to those of chlorite, appearing on 001 face of halite crystal. Sample 1. Tesla BS 613 electron microscope. Magn.  $\times 14\ 000$



Phot. 2. Halite crystal (sample 1) with zonation  $\parallel 001$ .  $\alpha_1$  — angle between the trace of the edges of 001 and 010 faces and the trace of the face  $\perp 010$ . Magn.  $\times 35$

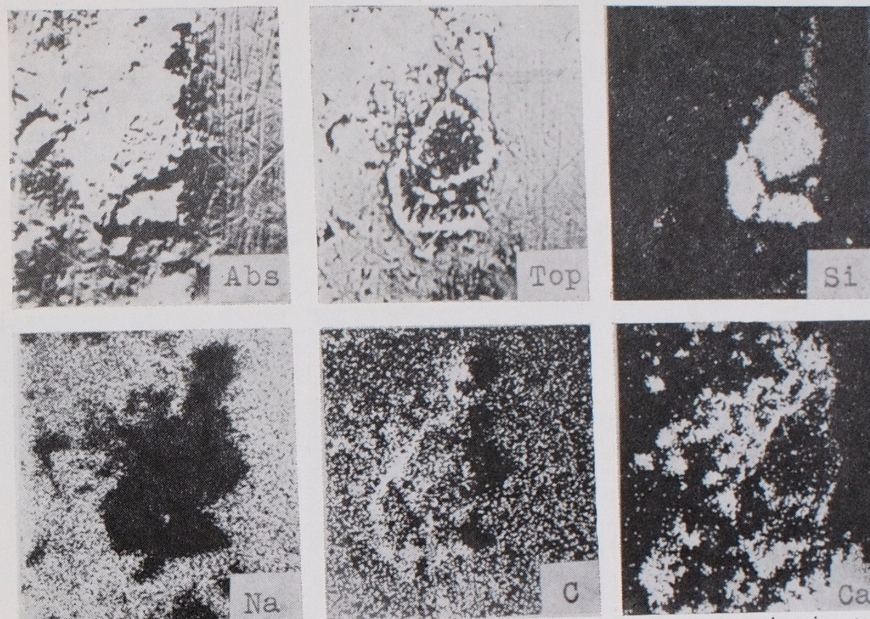




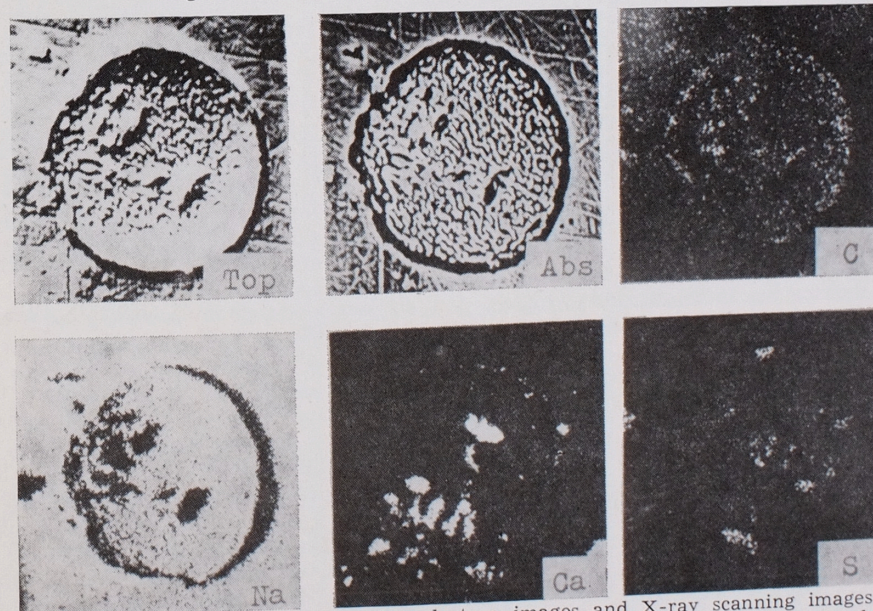
Phot. 3. Halite crystal (sample 2) with zonation  $\parallel 001$ .  $\alpha_2$  — angle between the trace of the edges of  $001$  and  $010$  faces and the trace of the face  $\perp 010$ . Magn.  $\times 10$



Phot. 4. Halite crystal (sample 3) containing sparingly water-soluble minerals in the zones  $\parallel 001$ . Magn.  $\times 35$

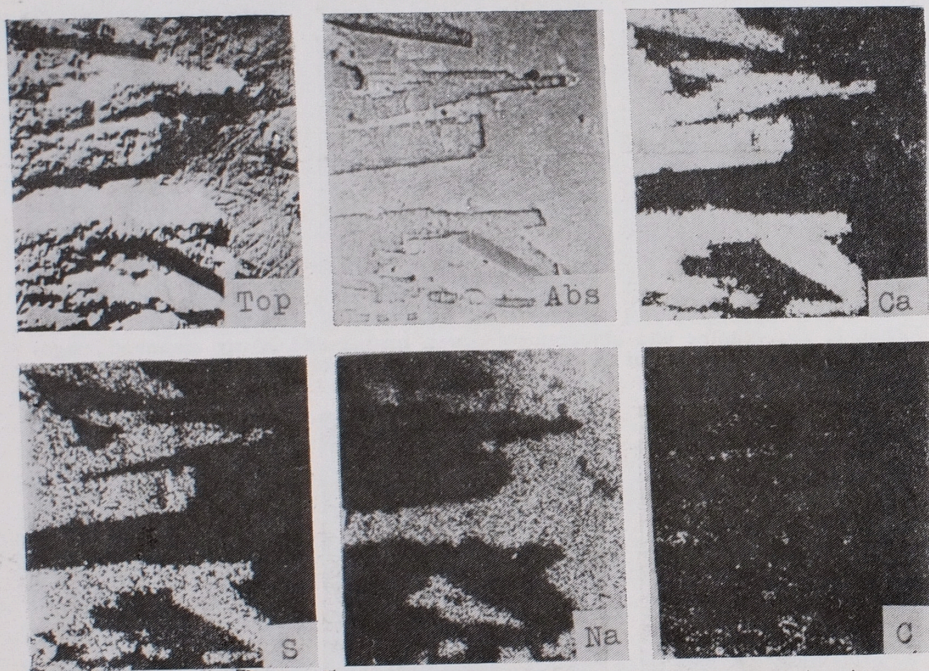


Phot. 5. Topographic and absorption electron images and X-ray scanning images showing the distribution of Si, Na, C, Ca in the grains of terrigenous minerals occurring in halite crystal. Sample 3. Microarea 1. Magn.  $\times 125$



Phot. 6. Topographic and absorption electron images and X-ray scanning images showing the distribution of C, Na, Ca, S in the pollen occurring in halite crystal. Sample 3. Microarea 2. Magn.  $\times 125$





Phot. 7. Topographic and absorption electron images and X-ray scanning images showing the distribution of C, Na, Ca, S in anhydrite crystals embedded in halite crystal. Sample 3. Microarea 3. Magn.  $\times 125$