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THE DISTRIBUTION OF BROMINE IN SOME HALITE ROCK SALTS OF THE WIELICZKA SALT DEPOSIT (POLAND)

(2 Figs.)

Brom w solach kamiennych złoża solnego Wieliczki

(2 fig.)

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Abstract: Miocene salt deposits in the Carpathian foreland area of Poland have been for the first time a subject of a study of bromine. Bromine content 20—221 ppm, are within the range of salt of marine origin and do not indicate any re-solution. In general, the bromine profiles are normally regular or commonly irregular ones. On the ground of distribution of bromine in the Wieliczka profile, three major cycles of salt deposition can be distinguished.

Key words: bromine in salt of Wieliczka, Carpathian foreland, Miocene.

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Treść: Zawartość bromu w mioceńskich osadach solnych Wieliczki wynosi 20—221 ppm i potwierdza ich morskie pochodzenie. Autorzy wyróżniają 3 cykle sedymentacyjne na podstawie rozkładu zawartości bromu w profilu pionowym tych osadów.

INTRODUCTION

Distribution of bromine in the chloride facies of marine evaporites has been a subject of a study of many workers all over the world (Baar 1963, Boeke 1908, Braitsch and Hermann 1962, 1963, d'Ans and Kühn 1940, Hite 1970, 1974, Holser 1966, Kühn 1955a, b, 1968, Raup 1966, Schultze 1960, Schwerdtner and Wardlaw 1963, Valyashko 1956, Zak 1969, 1974, and others. These studies have provided an important geochemical tool in resolving of stratigraphic problems and in prospecting for potash deposits.

In the territory of Poland, the first comprehensive study of bromine distribution was carried by Charysz (1973). The work deals mainly with the Younger Salts of the Zechstein Z 3 stage, but the studies have been extended to the underlying and overlying rock units (Z 2 and Z 4 stages).

Within the Miocene salt deposits in the Carpathian foreland area of Poland, bromine geochemistry has not been carried out so far. The present paper is the first attempt to relate the bromine data to the paleosalinities of the Badenian rock salt beds at the Wieliczka salt deposit.

STRATIGRAPHY AND PETROLOGY

The salt deposit at Wieliczka situated 13 km. south of Kraków, is 1 km. wide, about 10 km. long, over 400 m. deep, and consists of two essential parts. The upper one is developed in the form of coarse breccia composed mainly of salty clays („zuber"), with blocks of coarse-grained salt, called green salt. These blocks of irregular shape and various thickness in some places reach an extension of more than 150 metres. This part is supposed to be the facies equivalent of the lower one. The lower part of the deposit is developed as a complex of salt layers strongly folded, deformed, and thrust over one another, called „stratified" or „bedded" part of the deposit. From the south, flysch sediments in the form of tongue-shaped wedges are squeezed into the inner part of the salt deposit.

Reconstructed normal stratigraphic profile (Fig. 1) of the bedded part of the deposit is as follows (from the bottom):

— anhydritic claystones and siltstones,
— the oldest salts (varigrained salts with admixture and intercalations of clay, silt, and sand),
— salty sandstones and siltstones, partly conglomeratic,

— set of green layered salts (numbered I—V), intercalated with anhydritic claystones,
— shaft salt (coarse-grained salt devoid of mineral admixtures but with traces of gaseous hydrocarbons),
— lower spiza salts
— central intercalation (anhydritic claystone),
— upper spiza salts (both lower and upper spiza salts are coarse-grained, banded, with intercalations of sandy anhydritic clays),
— claystones, siltstones, and sandstones, anhydritic in the upper part.

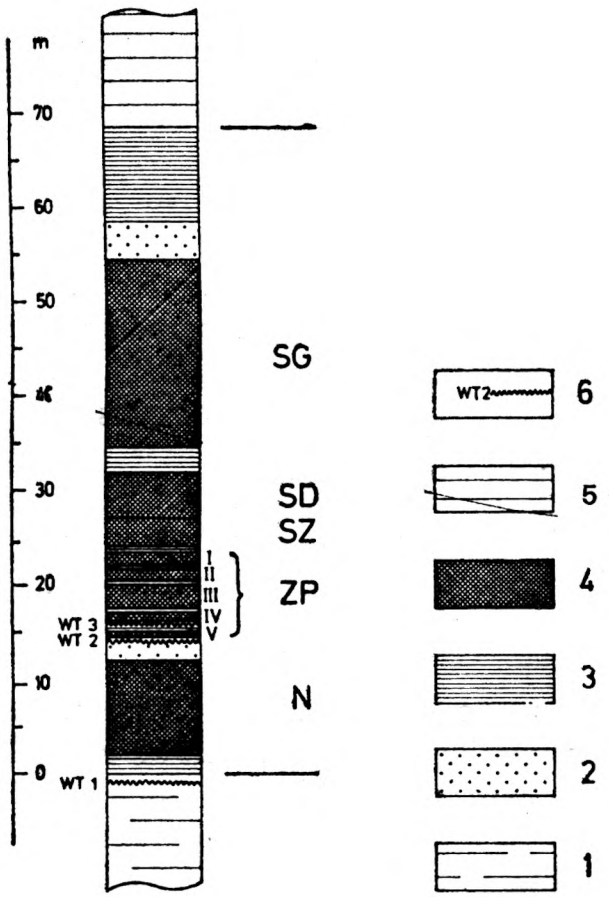

Fig. 1. Schematic columnar section of the Wieliczka salt deposit 1 — marly claystones (Skawina beds), 2 — salty sandstones and siltstones, 3 — anhydritic claystones and siltstones, 4 — rock salt, 5 — claystones and siltstones (Chodenice beds), 6 — distinguished tuffite intercalations. N — oldest salts, ZP — set of green layered salts, numbered I—V, SZ — shaft salt, SD — lower spiza salts, SG — upper spiza salts

Fig. 1. Schematyczny profil litologiczny złoża solnego Wieliczki 1 — iłowce margliste (warstwy skawińskie), 2 — piaskowce i mułowce solne, 3 — iłowce i mułowce anhydrytowe, 4 — sól kamienna, 5 — iłowce i mułowce (warstwy chodenickie), 6 — wyróżnione wkładki tufitowe. N — sole najstarsze, ZP — zespół zielonych soli pokładowych, numery pokładów I—V, SZ — sól szybikowa, SD — sole spizowe dolne, SG — sole spizowe górne

The primary thickness of this sequence was ca. 70 m. At the bottom of evaporites and within the lower part of the green layered salts, three thin tuffite intercalations have been distinguished, being the important marker beds.

METHODS OF SAMPLING AND ANALYSIS

Samples of halite were collected at 0.2—0.5 m intervals through the total thickness of each salt bed. Within the upper spiza salts the spacing varied from 0.5—1.0 m, depending on the uniformity of salt and the position of non-halite intercalations. From the walls of the mine-galleries the material was hand picked to get the purest sample of halite possible from each interval. The total amount of collected samples was — 102.

All samples were analyzed in the Laboratory of the Geological Institute, Warsaw, using colourimetric procedure. As a check on the accuracy of the applied method, 20 samples were also analyzed twice and the results were substantially in agreement with those previous.

BROMINE PROFILES

The variation of bromine content and of bromine-chlorine ratio in relation to the thickness of each salt bed are plotted in Fig. 2.

Within the lowermost part of the profile corresponding to the oldest salts, the bromine content at the base is 18 ppm and increases upward to 40 ppm. The uppermost two metres of the oldest salts display bromine values within the range of 40—50 ppm. The last sample taken from the very top of the oldest salts shows a rapid increase of bromine content, up to 221 ppm. General feature of the profile under discussion is gradual increase in salinity. The rapid increase in salinity in the uppermost part of the profile shows restricted conditions of sea water, which may be sufficient for precipitation of potassium minerals. These conditions were changed abruptly by the inflow of considerable amount of terrestrial material deposited in the form of conglomeratic salty sandstones and siltstones, overlying the oldest salts. This profile may be considered as normally regular profile distinguished by Holser (1966) and resembles those presented by Schultze (1960) for the Zechstein series, and by Raup (1966) for salt bed 3 in Paradox Member.

Green layered salts display fairly uniform bromine content, within the range 24—48 ppm. The profile of salt bed IV shows an increase of the bromine content from the bottom to the top. In the profile of salt bed III, after initial decrease of the bromine content, the upper part of the profile is almost smooth. Salt bed II profile shows slight increase of

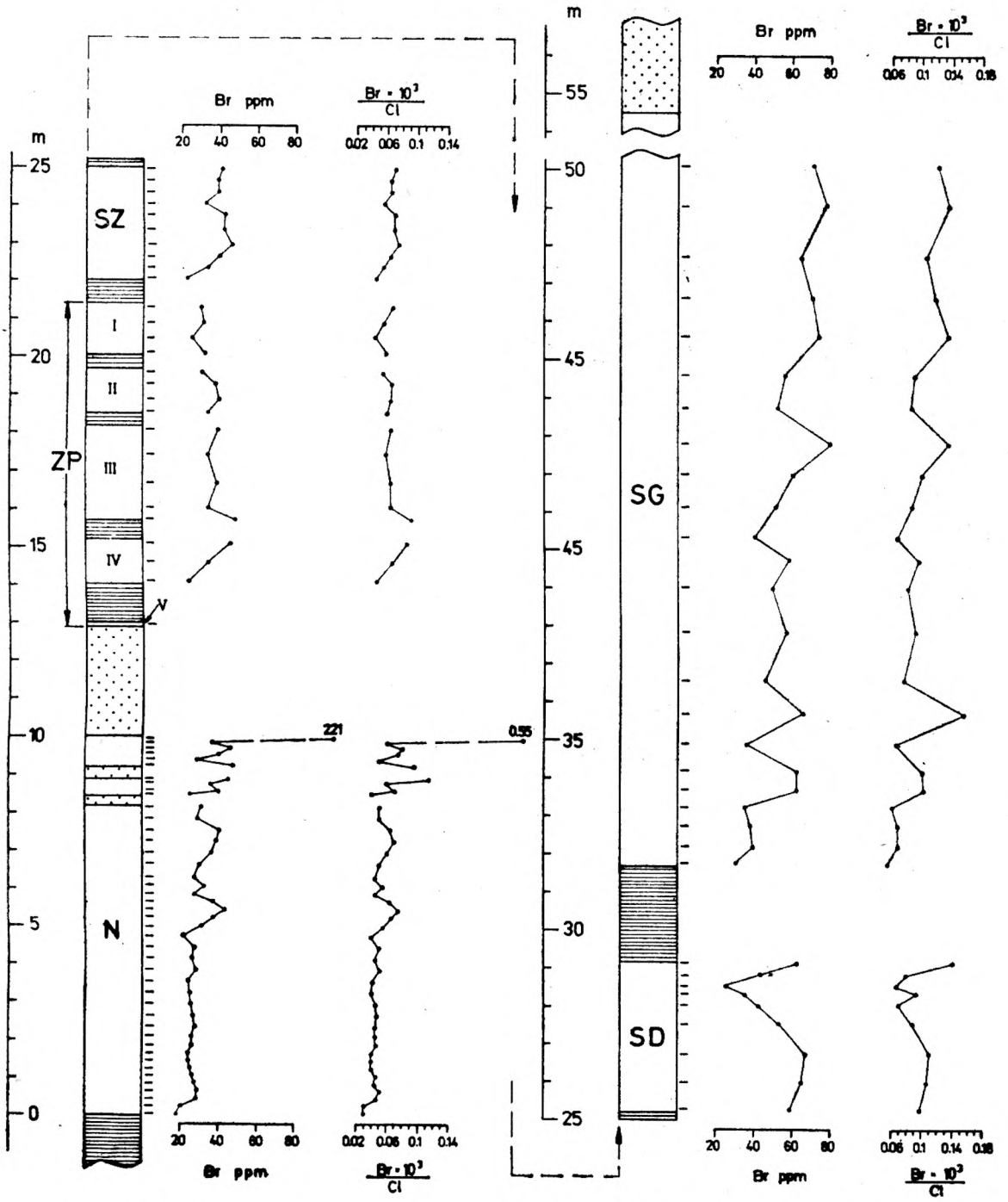

Fig. 2. Bromine profiles of salt beds, Wieliczka salt deposit

Fig. 2. Profile bromowe warstw soli w złożu solnym Wieliczki

bromine content in the middle of the bed. In the profile of salt bed I there are very small irregularities in bromine content, however the bromine-chlorine ratio shows and increasing value in the upper part of the profile. Bromine content in the last sample of each green salt bed shows similar value to that taken from the bottom of the younger bed. This may suggest the continuity of the bromine profile and therefore continous salinity changes in the basin, despite those interrupting episodes during which intercalations of anhydritic claystones were depo-

sited. Bromine profile of the green layered salts, considered as a whole, displays some features of regular one.

Within the next par of the profile being plotted for the shaft salt, the bromine content increases from 22 ppm to 46 ppm, and then gradually decreases to 30 ppm. The last part of this profile shows values about 40 ppm.

Sedimentation of the lower spiza salts started from more concentrated brine, what is indicated by the rise of bromine content from 59 ppm to 67 ppm. Subsequently gradual decrease of bromine content down to 26 ppm takes place, caused by brine dilution that probably resulted from the influx of sea water into the basin. After that period of dilution, the final part of the profile shows steady increase of bromine up to 63 ppm.

Bromine profile of the shaft salt as well as that of the lower spiza salts may be considered as commonly irregular profiles. However, the salinity of brine generally increased from the bottom of the shaft salt to the top of the lower spiza salts, yet some changes in slope of the profile, indicating an increase and decrease of bromine in halite, may reflect few major periods during which the increase in salinity was interrupted by brine dilution.

The last bromine profile corresponding to the upper spiza salts, shows generally increasing bromine content from 30 ppm to 80 ppm. This is normally regular profile. However, the uppermost part of the upper spiza salts could not be sampled due to intense tectonic disturbances. Therefore, there are insufficient data from this section.

CONCLUSIONS

Bromine content in the profile of the Wieliczka salt deposit, 20—221 ppm, is within the range of salt of marine origin.

Generally, the bromine profiles are normally regular or commonly irregular ones. Bromine-chlorine ratio curves are very similar to those plotted for the bromine content.

On the basis of distribution of bromine three major sedimentary cycles can be distinguished, namely: 1. the oldest salts, 2. green layered salts, shaft salt, and the lower spiza salts, 3. the upper spiza salts.

Final stage of the oldest salts sedimentation was the period of the most restricted conditions in the basin, expressed by the highest bromine content, but the inflow of fresh water with terrestrial material abruptly changed these conditions and made impossible precipitation of potassium minerals.

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STRESZCZENIE

Badania zawartości bromu w solach kamiennych były przedmiotem licznych prac geologicznych na świecie. Szczególne znaczenie tych prac polega na ich przydatności w rozwiązywaniu problemów stratygraficznych osadów solnych oraz w poszukiwaniu soli potasowo-magnezowych. Na obszarze Polski badania takie prowadzono dotychczas w osadach cechsztynu, a niniejsza praca jest pierwszą próbą określenia zawartości bromu w mioceńskich osadach solnych. Badaniami objęto profil dolnej, uwarstwionej części złoża solnego Wieliczki, jako najlepiej poznany i umożliwiający rekonstrukcję pierwotnego następstwa i miąższości warstw (fig. 1).

Próbki soli były pobierane w odstępach 0,2—0,5 m z każdej wydzielonej warstwy. W solach spizowych górnych próbki pobierano w odstępach 0,5—1,0 m, w zależności od jednorodności wykształcenia soli i pozycji wkładek ilasto-anhydrytowych. Ogółem w profilu złoża pobrano 102 próbki, które były analizowane w Głównym Laboratorium Instytutu Geologicznego w Warszawie.

Zawartości bromu w próbkach oraz wyliczone wartości współczynnika bromochlorowego przedstawiono graficznie na fig. 2. W solach najstarszych zawartość bromu wzrasta od 18 ppm do 50 ppm, a przy stropie dochodzi nawet do 221 ppm. W solach zielonych pokładowych zawartość bromu mieści się w granicach 24—48 ppm. W soli szybikowej zawartość bromu początkowo wzrasta od 22 ppm do 46 ppm, a następnie utrzymuje się w granicach 30—40 ppm. Sedymentacja soli spizowych dolnych rozpoczęła się z bardziej skoncentrowanych roztworów, na co wskazuje zawartość bromu wzrastająca od 59 ppm do 67 ppm. W dalszej części profilu zawartość ta maleje do 26 ppm i ponownie wzrasta do 63 ppm. Zawartość bromu w solach spizowych górnych stopniowo wzrasta od 30 ppm do 80 ppm.

Zawartość bromu w skałach solnych Wieliczki, mieszcząca się w przedziale 20—221 ppm, wskazuje na ich morskie pochodzenie. Profile bromowe tych soli można zaliczyć do regularnych lub pospolicie występujących nieregularnych. Rozkład zawartości bromu w profilu pionowym osadów solnych złoża Wieliczki pozwala na wydzielenie 3 głównych cykli sedymentacyjnych, obejmujących: 1. sole najstarsze, 2. zielone sole pokładowe, sól szybikową i sole spizowe dolne, 3. sole spizowe górne.

Końcowe stadium sedymentacji soli najstarszych było okresem najbardziej ograniczonej cyrkulacji wód w basenie, czego dowodem jest najwyższa zawartość bromu, jednak napływ słodkich wód niosących materiał z lądu gwałtownie zmienił te warunki i uniemożliwił osadzanie się minerałów potasowo-magnezowych.