Geochemistry and age determination of Badenian evaporites from Wieliczka and Bochnia salt mines (Poland).

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ABSTRACT

This paper presents new geochemical data and results of determination of radiometric age of Badenian salts from the area of Wieliczka and Bochnia (Poland). The determined bromine content in salts as well as distribution of stable isotopes in sulphates are similar to data for other profiles of the Carpathian Foredeep. Preliminary results of absolute dating indicate somewhat younger ages (ca 12.0 - 12.5 Ma) than earlier estimations.

1. GEOLOGICAL SETTING

The first evaporite basin in the area of the Carpathian Foredeep formed during Lower Miocene (Eggenburgian). Salt-bearing and sulphate deposits of this basin, widely developed in Ukraine, are referred to as the Vorotyshcha Suite. Sediments of this series form rock salt and potassium salt deposits (e.g. the Stebnik deposit). In Poland the sediments of the Vorotyshcha Suite have been recognized only in a small area south of Przemycl. These are clay-salt sediments with numerous intercalations of clastic rocks [1-2].

In the Polish part of the Carpathian Foredeep the main salt-bearing series (Wieliczka and Bochnia) formed as late as in Badenian [2]. In the eastern part of the Foredeep, in Ukraine, equivalent sediments are those of the Tiras Suite, developed as rock salts with intercalations of potassium and magnesium salts, anhydrites and gypsums [3]. It should be noted that the evaporites represent only a minor part of the vertical column of marine deposits of the Carpathian Foredeep. They are, however, broadly widespread in sedimentary basin, and therefore form an important marker horizon.

Three facies have been distinguished within the Badenian evaporites (fig. 1):

1) carbonate-littoral facies, comprising organic limestones, mixed carbonate and clastic sediments, with sands, sandstones and gravels;

2) sulphate facies, comprising anhydrite, gypsum and sulphur-bearing deposits;

3) chloride facies, containing rock salt with anydrite and clay-anhydrite sediments.

While sediments of carbonate-littoral and sulphate facies are widespread in the whole Carpathian Foredeep and Foreland, except for the Rzeszów Island, the chloride facies covers only a small area in the Upper Silesia, and extends along the Carpathian northern boundary between Cracow and Przemycl, and further through Ukraine to Romania. Sulphate facies is 10-30 meters thick, chloride facies sediments are 40-50 meters thick, occasionally up to 100 meters.

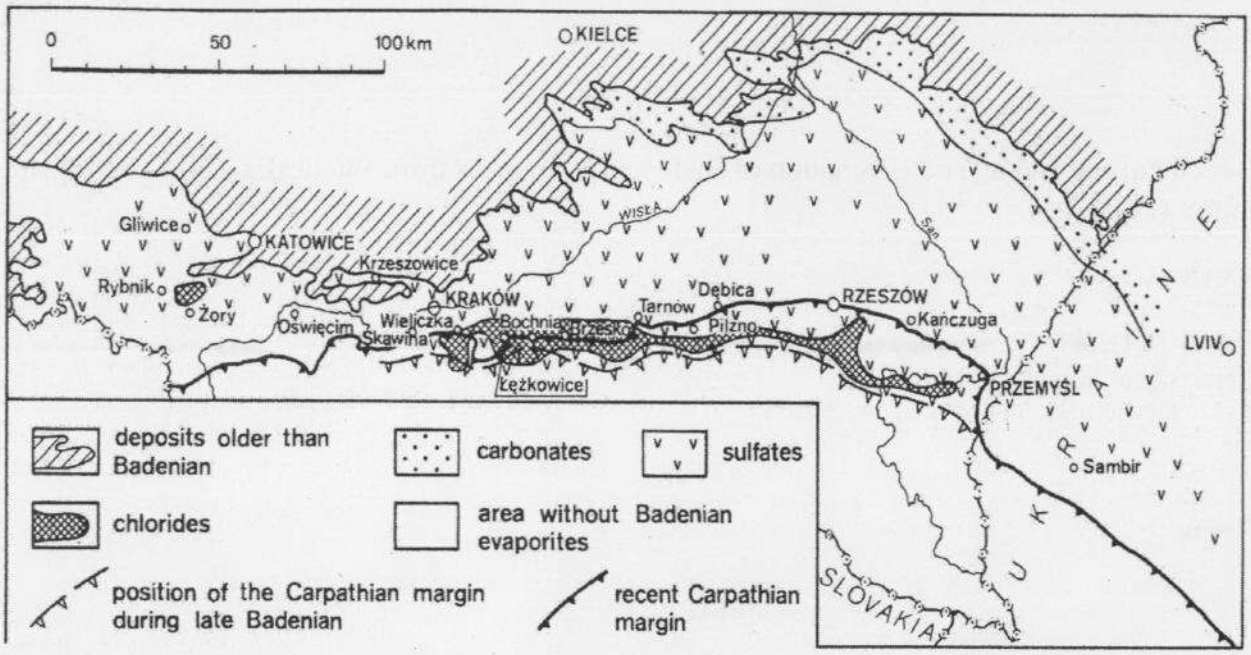

Figure 1. Distribution of the Badenian evaporites in the Polish part of Carpathian Foredeep (after Garlicki, 1979).

2. WIELICZKA SALT DEPOSIT

The geology of the Wieliczka salt mine has been described in numerous papers, of which the most comprehensive is [4]. The salt deposit body is 1 km wide, about 6 km long and more than 300 m thick, and consists of two units. In the lower, bedded part the salt rocks are layered and form elongated structures similar to scales and asymetrical folds. The upper part (boulder deposit) is developed as coarse breccia mainly composed of salt clays (so-called zubers), with blocks of coarse-grained salts. These blocks are of irregular size and shape and range from $1m^3$ to giant blocks of about 100000 m^3 in volume. The lower unit (stratiform deposit) is developed as a complex of strongly folded, deformed and thrust over one another salt layers alternating with anhydrite and anhydritic clays. Tongue-shaped wedges of flysch rocks penetrate inner part of salt deposit from south.

In the stratigraphic profile of the salt deposits the following sediments can be distinguished (from the bottom): base anhydritic claystone and rock salt called the Oldest salts; sandstone and claystone with anhydritic and halite matrix; claystone with anhydrite and the layers of crystalline salt called Green bedded salts; a bed of Shaft salt and a complex of salty banks with layers of claystones and siltstones and admixture of anhydrite called the complex of Spisa salt; sandstone and the top anhydritic claystone. In the upper part of the deposit there are marly claystones and salt zubers (marly claystone with suspended grains of crystalline halite), among which irregular blocks of coarse-grained and crystalline salt, so-called Lumpy Green salt, are placed.

3. BOCHNIA SALT DEPOSIT

The structural configuration of the salt deposits within the Bochnia salt mine was accurately presented by [5]. In this area the salt formation was subjected to folding and considerable uplift while receding before the Carpathians overthrusting border. The main fold dominating in the environs of Bochnia has been called the Bochnia anticline, whereas the parallel one perceivable in southern zone of the said area has been called the Uzbornia anticline. The strongly uplifted folds of the saline formation of Bochnia are generally inverted towards N, but in their upper parts their position is very steep. Flysch deposits lifted up and occur in the cores of these folds.

The salt deposit of Bochnia is situated in the northern wing of the main anticline. Length of the deposits is about 3.5 km, the width from a dozen of meters to 200 m. The salt series is a limited set of beds of rock salt, anhydrite and marly clay whose thickness totals over 70 m.

The following sediments can be distinguished (from the bottom): basal anhydrite, Lower zuber (marly claystone with crystals of halite), the bed of Southern salts, marly claystone with anhydrite, Upper zuber, clayey-anhydritic shale, the layers of crystalline salt called Crystal salt, a body of Middle salts, anhydritic claystone, salts with admixture of anhydrite, claystones and siltstones called Northern salts, top anhydrite. The top anhydrite is connected with the latter by normal succession of sedimentation (The Chodenice Beds).

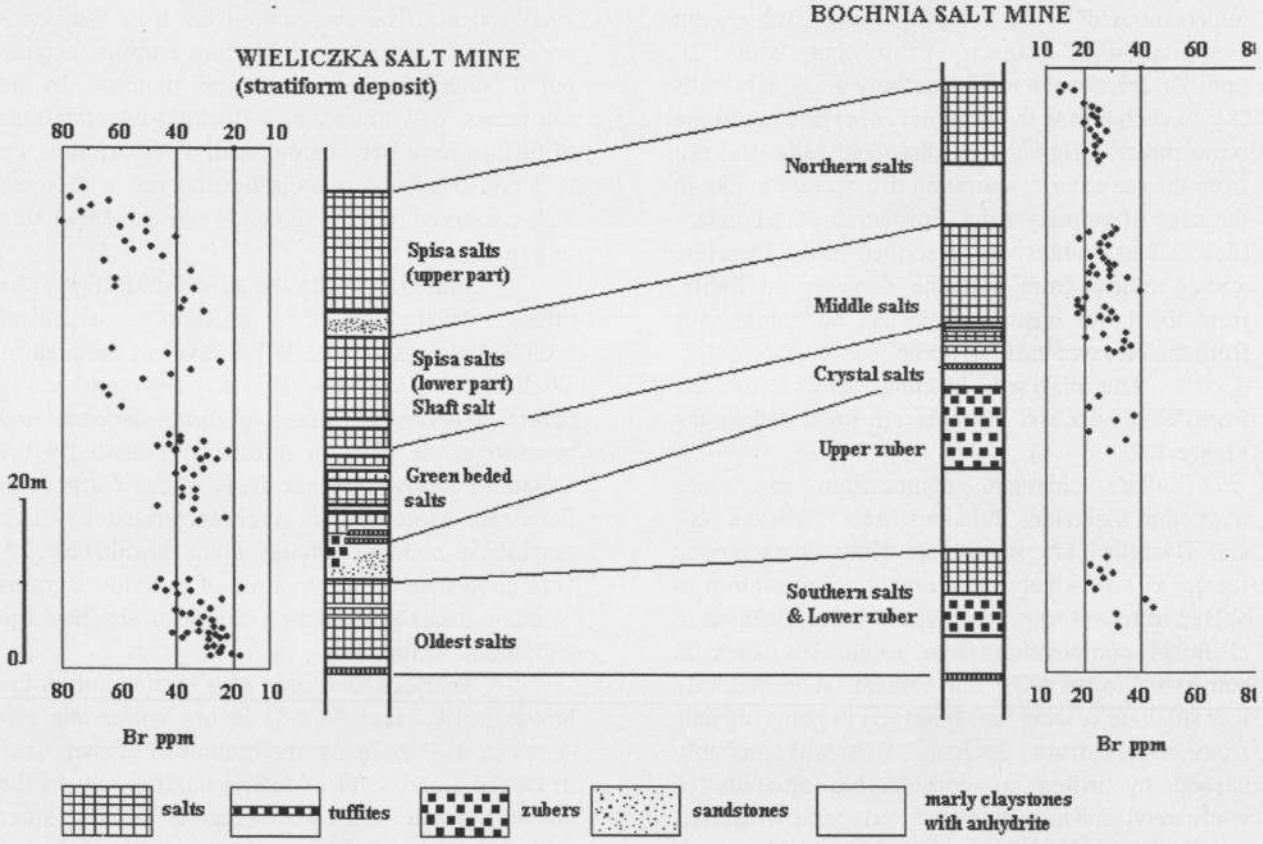

Figure 2. Profile of bromine content in rock salt deposits from Wieliczka and Bochnia, according to (Garlicki & Wiewiórka 1981; Bukowski 1997).

4. GEOCHEMICAL INVESTIGATIONS

Determination of bromine content in rock salts is most frequently carried out in order to infer the degree of maturity of the evaporite cycle (Br content is proportional to the original concentration of the evaporating brine). The bromine content in the Badenian salts from the Polish part of the Carpathian Foredeep was analysed in various parts of the profile of the salt bearing series (the Rybnik-¯ory-Orzesze basin, Wieliczka, Bochnia, Wojnicz). Depending on the lithologic type of salts the bromine content was generally between 15 and 60 ppm [6-7]. Only in a few samples the values of the bromine content were higher (70-100 ppm) or significantly lower (7-15 ppm). The particularly low bromine content (10-20 ppm) may be explained by dissolving of primary salts in waters undersaturated with NaCl, and subsequent precipitation of secondary halite. Salts with 1-20 ppm Br are considered as entirely secondary salts [8]. In such a case the bromine concentration in the brine mostly origins from dissolved salts, and not from the seawater evaporating till saturation, like in the case of primary salts. Formation of secondary (descendent) halites was described in the literature among others from Messine deposits on Sicily, from the Lorca basin and Eocene potassium salts from the Navarra basin in Spain [9].

The analysed bromine contents of salts from Wieliczka and Bochnia are presented in the Figure 2.

The chemical composition of brines trapped in inclusions in halites from Wieliczka [10] and Bochnia [11] is similar. Their characteristic feature is a relatively low content of ions, close to values of recent seawaters. These brines differed in chemical composition from recent seawaters in somewhat lower SO_4^{2-}.ion content. A particularly low sulphate content was observed in halite crystals from zubers from Bochnia. This was probably caused by influx of considerable amounts of continental fresh waters and terrygenic materials into the basin. This action led to impoverishment of brines in the sulphate ion [11].

Analyses of sulphur and oxygen isotopes in anhydrites from Wieliczka and Bochnia also confirmed similarities of both environments of sedimentation. The determined values were generally typical for Miocene sulphates. It should be noted that stable isotopes contents in recent oceanic waters are similar [12].

5. DATING OF TUFFITES FROM BADENIAN SALTS

Evaporites accumulated in the foreland of uplifting mountains, which coincided with increasing tectonic activity in the Carpathians. Contemporaneous recurrent volcanic eruptions produced pyroclastic deposits (tuffites) whose thickness is as much as 1000 m in the Transcarpathian basin of West Ukraine [13].

The accompanying earthquakes caused landslides and submarine slumps, and initiated turbidity currents, which formed deposits characterized by rapid facies changes and relatively small extents. The evaporation basin in Wieliczka and Bochnia was situated far from eruption centers but it contains traces of volcanic material. In the salt mines in Wieliczka and Bochnia intercalations of tuffites have been recognized. They are thin, up to 5 cm, inserts of pyroclastic material with some well-preserved primary minerals cemented by halite or gypsum.

Stratigraphically the most interesting is the tuffite layer directly preceding chemical sedimentation (so-called WT-1 level in the area of Wieliczka - Bochnia). It was distinguished in several outcrops in mines in both deposits and because of its position it can be potentially the easiest to follow in other areas in the Carpathian Foredeep. Moreover, it is characterized by high amphibole content, among them hornblende. A very good state of preservation of individual grains of this mineral enabled first dating of absolute age with the K/Ar method.

Analyses have been also carried out on the biotite tuffite level (WT-3) laying within the salt series ca. 1 -2 m. below the bottom of crystals salts in Bochnia and level of tuffite outcropping in the above evaporite series (Chodenice Beds). The latter is also characteristic for numerous profiles from the area of the Carpathian Foredeep and was also earlier dated with the FT method (zircon) [14].

Ages of the investigated samples have been obtained by K/Ar and $^{40}Ar/^{39}Ar$ methods in Mass Spectrometry Laboratory at Maria Curie-

Sklodowska University in Lublin and K/Ar method in Centre Geochimie de la Surface CRNS in Strasbourg [15-16].

The results of dating are presented in Table 1.

Level	Sample Location	Method - Mineral	Age (m.y.)
WT-1	Wieliczka	K/Ar-amphibole	28.3 ± 1.3
WT-1	Wieliczka	K/Ar-amphibole	18.3 ± 0.8
WT-1	Wieliczka	K/Ar-amphibole	12.5 ± 0.9
WT-1	Wieliczka	K/Ar-amphibole	11.4 ± 0.9
WT-1	Wieliczka	Ar/Ar-amphibole	18.0 ± 1.0
WT-3	Bochnia	Ar/Ar-biotite	12.0 ± 0.3
Chodenice Beds (lower tuff)	Bochnia	Ar/Ar-biotite	12.2 ± 0.4

In spite of some problems with precise determination of the potassium content (what is complicated at contents < 1% in hornblende) the results are interesting (12,5 ± 0,9 MA - the result obtained in Centre de Geochimie de la Surface CNRS in Strasbourg). Also the radiometric dating with the Ar/Ar method of the tuffites from Bochnia (12.0 ± 0.3 Ma - the result obtained in Mass Spectrometry Laboratory at Maria Curie-Sklodowska University in Lublin) confirm similar age of the evaporites.

REFERENCES

1. R. Ney, Prace Geol. PAN, No. 45 (1968) 82 pp.
2. A. Garlicki, Prace Geol. PAN, No. 119 (1979) 67 pp.
3. O.I. Petriczenko, G.M. Panow, T.M. Peryt, B.I. Srebrodolski, A.W. Pobere¿ski, W.M. Kowalewicz, Przegl. Geol., Vol. 42, 9 (1994) 734-737.
4. A. Gawe³, Pr. Inst. Geol., Vol.30, 3 (1962) 305-331.
5. J. Poborski, Biul. Inst. Geol., No. 78 (1952) 160 pp.
6. K. Bukowski, Przegl. Geol., Vol. 45, No. 8 (1997) 819-821.
7. W.T. Holser, Trace elements and isotopes in evaporites [in:] Marine Minerals, R.G. Burns, (ed) Mineral Soc. of Am., Short Course Notes, No. 6 (1979) 295-318.
8. G. Veigas , L. Rossel, A. Garlicki, Slovak Geol. Mag., Vol. 3, No. 3 (1997) 181-186.
9. A. Garlicki & J. Wiewiórka, Rocznik PTG, Vol. 51 No. 3 - 4 (1981) 353 -360.
10. A.R. Galamay, K. Bukowski, J. Przyby³o, Slovak Geol. Mag., Vol. 3, No. 2 (1997) 165-171.
11. W. M. Kowalewicz, Przegl. Geol. Vol., 45, No. 8 (1997) 822-825.
12. K. Bukowski & J. Szaran, Przegl. Geol., Vol. 45, No. 8 (1997) 816-818.
13. W.I. Kityk (ed), Halogennye formacii Ukrainy, Kijev 1983.
14. J.A. Van Couvering, C.W. Neaser, T. Wieser, J.P. Bujak, Paleogeograf. Paleoclim. Paleoecolog., Vol. 36, No. 3-4 (1981) 321-362.
15. K.Bukowski, A. Wójtowicz, T. Durakiewicz, III Ogólnopolska Sesja Naukowa: Datowanie minera ów i ska . UMCS Lublin, (1996) 13-18.
16. K. Bukowski, K. Dudek, A. Wójtowicz, T. Durakiewicz, S. Ha as, IV Ogólnopolska Sesja Naukowa: Datowanie minera ów i ska UMCS Lublin (1997) 22-26.