

# Geochemical Conditions of Deposition in the Upper Devonian Prypiac' and Dnipro-Donets Evaporite Basins (Belarus and Ukraine)

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## ABSTRACT

Earlier studies of individual fluid inclusions in salt minerals of some Devonian evaporite basins showed that the brines in those basins were of chloride type with a high concentration of  $\text{Ca}^{2+}$ . The genetic significance of this occurrence was subject to different interpretations. We have studied in detail samples taken from the East European Dnipro-Donets and Prypiac' evaporite basins aiming to establish the chemical composition of fluid inclusions in studied evaporites and then, using other geochemical information, to establish a geochemical model of the Devonian evaporite basins. Our study showed that salt deposition in the Devonian Dnipro-Donets and Prypiac' evaporite basins was because of intensive evaporation of mainly marine brines of chloride type with a relatively high  $\text{Ca}^{2+}$  content. In turn, the ratios between Na, K, and Mg corresponded to ratios in recent marine brines. Salt minerals precipitated in bottom water conditions. The occurrence of one-phase fluid inclusions indicates the temperatures of halite-precipitating brines  $<43^\circ\text{C}$ . Gas content varied from 10 to 300 g/L and was controlled by the pressures existing at the basin bottom during halite growth. The recorded high  $\text{Ca}^{2+}$  contents, characteristic of brines in the Dnipro-Donets rift basin, is due to intensive discharge of connate highly mineralized  $\text{Ca}^{2+}$ -rich solutions; however, the parent marine water was also  $\text{Ca}^{2+}$  rich.

## Introduction

During the Devonian, evaporites formed in 19 basins in Eurasia. The widespread evaporites occurred in the Middle and Late Devonian. In the Early Devonian, only one evaporite basin existed. Halite was periodically deposited in nine basins and potash in four of them (Zharkov 1984; Vysotskiy et al. 1988). The most intensive salt deposition during the Devonian occurred in the North Siberian, East European, and West Canadian Basins. Other basins were developed locally and lasted for a relatively short period of time. A characteristic feature of the Devonian evaporite deposition was the sylvite-carnallite composition of potash deposits as well as the lack of sulfate potash minerals (Zharkov 1984).

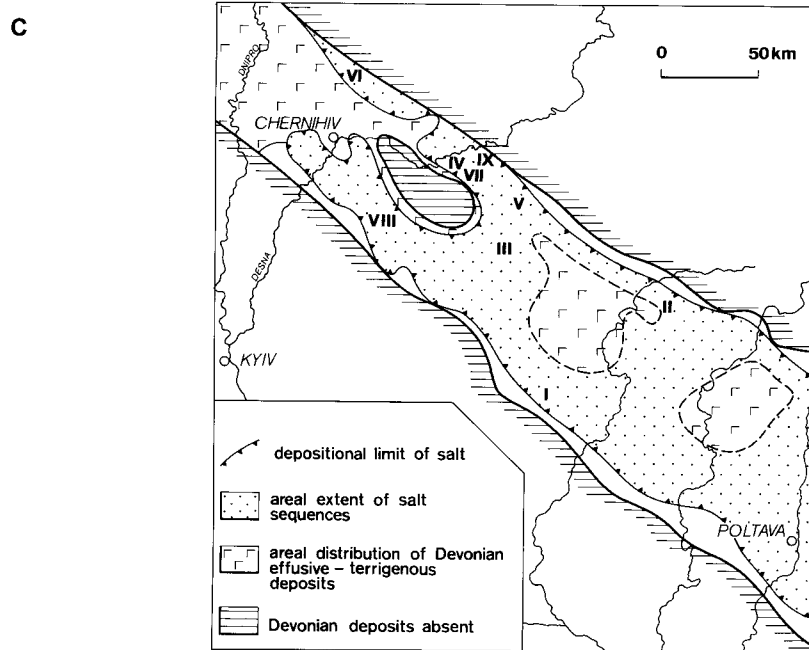
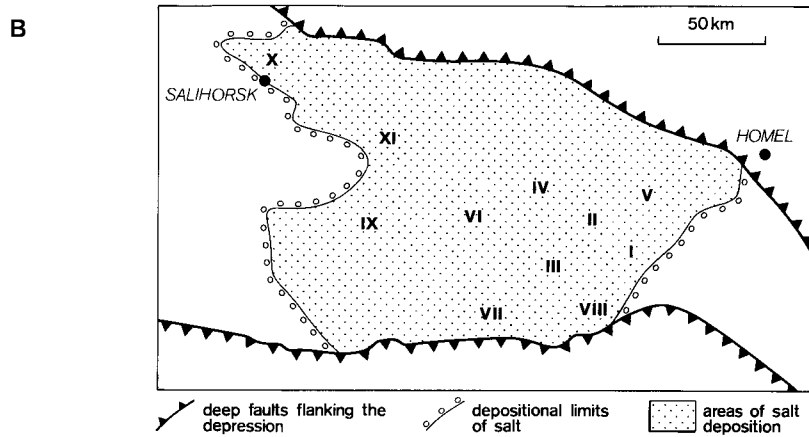
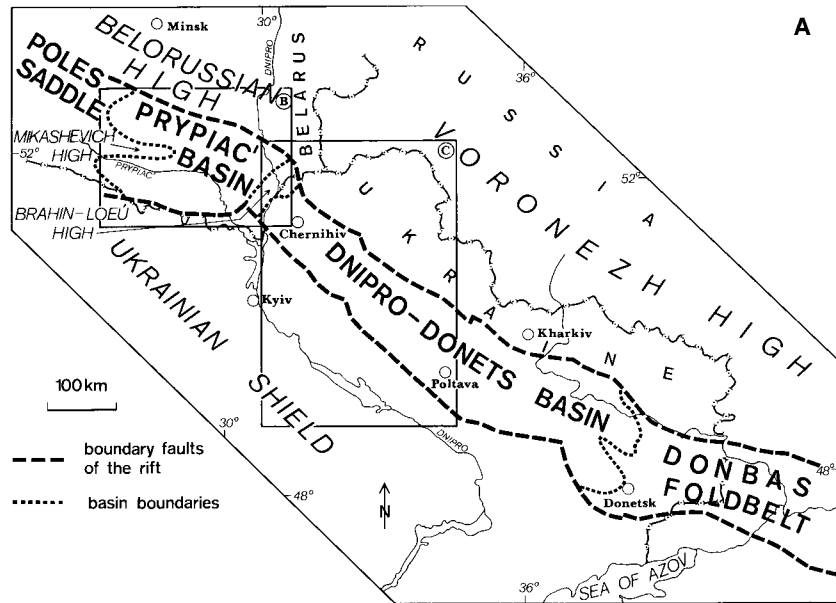
A reconnaissance study of fluid inclusions in evaporite minerals in the Devonian evaporite basin

of the Dnipro-Donets Basin (East European Craton) showed that the brines were of chloride type with a high concentration of  $\text{Ca}^{2+}$  (Petrichenko et al. 1974; Shaidetskaya 1977). Later studies of Devonian evaporite basins of Eurasia (Petrichenko 1989) and North America (Horita et al. 1996) indicated that the presence of  $\text{Ca}^{2+}$  in Devonian brines was global in nature.

The genetic significance of this occurrence was subject to different interpretations (Horita et al. 1996; Horita and Holland 1998; Kovalevich et al. 1998a, 1998b). The importance of seawater as the main supplier of chemical components to brines of evaporite basins remains enigmatic because of the lack of data on chemical composition of ancient seawater. To resolve these problems, we have studied in detail samples taken from Dnipro-Donets and Prypiac' evaporite basins (fig. 1). The aim of the research was to establish the chemical composition of fluid inclusions in studied evaporites and to use this and other information important for the chemical characterization of the sedimentary

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environment, such as pH, Eh, gas content, and temperature, to establish a geochemical model for Devonian evaporite basins.

The importance of information derived from the composition of fluid inclusions in halite for the interpretation of composition of parent seawater is now generally accepted (Zimmermann 2001). Our study demonstrates that another environmental information stored in those fluid inclusions contributes to a better understanding of conditions of evaporite precipitation in the studied basins.

### Geological Setting

The Dnipro-Donets and Prypiac' evaporite basins are related to the Donbas-Prypiac' rift, which is one of the best-studied Paleozoic structures of its type (Ulmishek et al. 1994). The rift is more than 1300 km long and 70–130 km wide and consists of three major parts: the Prypiac' basin on the NW, the Dnipro-Donets basin in its central part, and the Donets basin fold belt on the SE (fig. 1A). Devonian and younger rocks (2 km thick in the western part of the Prypiac' basin to 15 km thick in the SE part of the Dnipro-Donets basin) unconformably overlie the Proterozoic or crystalline basement. The Devonian and younger sedimentary rocks may be divided into prerift platform, synrift, and postrift sag sequences and the overlying platform sequence of post-Early Permian age (Ulmishek et al. 1994; Konishchev et al. 2001).

**Prypiac' Depression.** The synrift sequence of the Prypiac' basin contains two salt formations of late Frasnian (Evlanovsk and Cherninsk horizons) and middle Famennian (Lebedyan, Oressk, and Streshinsk horizons) age (fig. 1B). The salt formations are underlain and separated by mainly carbonate rocks and are overlain by uppermost Famennian shales and carbonates (Kruchek et al. 2001). Every stage of evaporite deposition was terminated by formation of potassium deposits (sylvite, carnallite) a few tens of meters thick. The feeding waters of these evaporite basins derived from the vast epicontinental sea of East European Platform (Zharkov 1984).

The Frasnian evaporite basin was ca. 20,000 km<sup>2</sup>. The cyclic deposition of salts (up to 60 m) and carbonate-sulfate-clayey deposits (20–30 m) led to the sequence up to 1000 m thick that contains 15%–20% of salt at the basin peripheries and up to 60% in the basin center. The rock salt is medium-grained and contains 0.4%–5.1% insoluble residue and 0.75%–1.01% (rarely 1.66%) anhydrite. The bromide content is 60–120 ppm. Primary-sedimentary halite occurs rarely in the form of relics (1–2 mm) in recrystallized transparent halite.

The Famennian evaporite basin was located in almost the entire Prypiac' Depression (area of ca. 23,000 km<sup>2</sup>). In the peripheral part of the basin, 70–200 m of salts occur, and in its northern part up to 3250 m of rock salt with intercalations (up to 100 m) of carbonate, sulfate, and terrigenous deposits occur. The content of salts in the section is 60%–70%. The deposition in the evaporite basin was terminated by the intensive sedimentation of potash of sylvite-carnallite composition (Vysotskiy et al. 1988).

The development of the studied evaporite basins can be subdivided into two phases: halite deposition phase and potash deposition phase. The first was long lasting. Sedimentary halite was studied from deep occurrences of rock salt that correspond to the geochemical conditions characteristic of the beginning of halite precipitation. The bromide content in halite is 60–320 ppm. The deposits of the second phase have been studied in the Starobin deposit (third potash horizon). The studied potash horizon is 30 m thick; the sylvinitic bed (9 m) is overlain by a clay-carnallite bed (15 m) and then by a sylvinitic-carnallite-clay bed (6 m); the latter was not studied by us. The sylvinitic bed is red and contains intercalations (up to 1 m thick) of rock salt that was sampled for fluid inclusion study. In addition, the second potash horizon (2.5 m thick) located 140–150 m above the third potash horizon has been studied. The samples were derived from white sylvite and sedimentary halite. White sylvite forms nests (1–2 cm<sup>2</sup>) in red sylvite. Between the second and third potash horizons, rock salt with intercalations of carbonate-clayey deposits occurs.

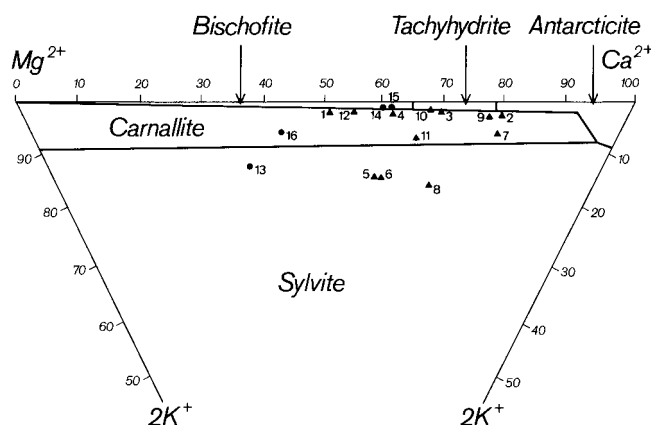
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**Figure 1.** A, Location map of the Prypiac' and Dnipro-Donets basins (after Ulmishek et al. 1994, fig. 1). B, Scheme of distribution of rock salt areas in the Prypiac' Depression (after Zharkov 1984, fig. 45): I, Maladushna; II, Vedrych; III, Zalatukha; IV, Astashkavichy; V, Amelkauschna; VI, Kalinauka; VII, Olkhovka; VIII, Khobnae; IX, Petrykau; X, Starobin; XI, Kapatkevichy. C, Scheme of distribution of rock salt areas in the NW and central parts of the Dnipro-Donets Depression (after Zharkov 1984, fig. 49): I, Solonytsya; II, Romny; III, Ivanhorod; IV, Kholmy; V, Kinashvka; VI, Hrybovo-Rudnya; VII, Adamivka; VIII, Mryn; IX, Borkovka.

**Table 1.** Chemical Composition of Inclusion Brines and Bromine Content in Sedimentary Halite of Frasnian (1–12) and Famennian (13–16) Dnipro-Donets Basin and Frasnian (17–25) and Famennian (26–42) Prypiac' Basin

| Area and no.    | Borehole | Depth (m) | K content (g/L) |         |          | Mg content (g/L) |         |          | Ca content (g/L) |         |          | Br (ppm) |
|-----------------|----------|-----------|-----------------|---------|----------|------------------|---------|----------|------------------|---------|----------|----------|
|                 |          |           | Range           | Average | <i>n</i> | Range            | Average | <i>n</i> | Range            | Average | <i>n</i> |          |
| Solonytsya:     |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 1               | 9        | 203–208   | 1.5–4.5         | 3.2     | 3        | 20.0–45.0        | 31.7    | 3        | 35.5–60.0        | 53.7    | 3        | 60       |
| 2               | 10       | 214–219   | 3.5–5.5         | 4.5     | 4        | 5.0–11.0         | 7.5     | 3        | 31.5–75.0        | 49.0    | 4        |          |
| 3               | 11       | 378–382   |                 | 1.5     | 5        |                  | 18.5    | 4        |                  | 54.0    | 4        | 50       |
| 4               | 12       | 180–186   | 3.0–5.0         | 4.0     | 5        | 26.0–37.0        | 30.4    | 4        | 78.5–89.5        | 82.4    | 5        | 50       |
| Romny:          |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 5               | 6        | 350–355   |                 | 25.5    | 6        |                  | 22.5    | 4        |                  | 62.0    | 6        | 150      |
| 6               | 6072     | 512–518   | 24.5–45.0       | 35.8    | 6        |                  | 27.5    | 3        |                  | 62.0    | 3        | 160      |
| Ivanhorod:      |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 7               | 1        | 3519–3535 | 13.0–17.5       | 14.9    | 5        | 11.0–20.0        | 15.5    | 5        | 80.0–120.0       | 100     | 5        | 140      |
| Kholmy:         |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 8               | 238      | 2415–2425 | 18.5–40.0       | 27.9    | 11       | 16.5–27.0        | 20.9    | 7        | 24.0–49.5        | 36.0    | 8        | 130      |
| 9               | 238      | 4210–4217 | 4.0–9.0         | 6.4     | 5        |                  | 22.0    | 6        |                  | 113.0   | 6        | 110      |
| Kinashevka:     |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 10              | 2        | 2639–2648 | 2.0–4.0         | 3.1     | 4        | 38.0–70.0        | 54.0    | 4        | 43.0–55.0        | 47.5    | 4        | 50       |
| Borkovka:       |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 11              | 12       | 3395–3403 |                 | 13.0    | 5        |                  | 22.0    | 5        |                  | 68.0    | 5        |          |
| Hrybovo-Rudnya: |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 12              | 2        | 1945–1952 | 3.0–7.0         | 5.2     | 5        | 49.0–75.0        | 59.0    | 5        | 70.0–105.0       | 83.3    | 3        | 90       |
| Adamivka:       |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 13              | 2        | 2187–2194 | 9.0–19.0        | 13.6    | 11       |                  | 16.5    | 7        |                  | 32.0    | 7        | 120      |
| Kinashevka:     |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 14              | 1        | 2172–2180 | 2.0–3.0         | 2.5     | 7        | 36.5–47.5        | 42.6    | 7        | 89.0–113.0       | 101.2   | 7        | 60       |
| 15              | 2        | 2231–2240 | 3.0–4.5         | 3.7     | 3        | 44.5, 57.2       | 50.8    | 2        | 105.0–141.5      | 125.9   | 4        | 90       |
| Mryn:           |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 16              | 2        | 3033–3034 | 8.5–9.2         | 8.8     | 3        | 21.4–32.8        | 29.4    | 6        | 28.8–42.2        | 35.9    | 5        | 130      |
| Maladushna:     |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 17              | 4        | 3643–3660 | 5.5–11.5        | 8.5     | 5        | 54.0–65.0        | 59.4    | 3        | 131.0–171.0      | 147.0   | 3        | 160      |
| 18              | 25       | 3638–3641 |                 | 22.5    | 5        |                  | 61.5    | 5        |                  | 120.0   | 4        | 100      |
| Vedrych:        |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 19              | 3        | 3113–3121 |                 | 4.0     | 3        |                  | 26.5    | 3        |                  | 80.0    | 3        | 70       |
| 20              | 2        | 3732–3749 |                 | 4.5     | 5        |                  | 19.0    | 5        |                  | 123     | 6        | 70       |
| Zalatkha:       |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 21              | 2        | 3337–3352 | 2.5–5.5         | 3.9     | 7        | 33.0–58.0        | 43.0    | 5        | 81.0–114.0       | 94.0    | 6        | 60       |
| Astashkavichy:  |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 22              | 13       | 2836–2846 | 2.0–4.0         | 2.8     | 7        | 22.0–39.0        | 31.0    | 4        | 86.0–105.0       | 98.0    | 4        | 70       |
| 23              | 83       | 2570–2580 | 4.5–11.5        | 7.7     | 6        | 17.0–35.0        | 24.8    | 5        | 57.0–105.0       | 78.8    | 6        | 80       |
| Amelkauschyna:  |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 24              | 6        | 3584–3600 | 6.0–12.0        | 8.2     | 4        | 10.5–35.0        | 21.2    | 4        | 36.0–71.5        | 48.4    | 4        | 90       |
| Kalinauka:      |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 25              | 5        | 2920–2945 |                 | 3.5     | 7        |                  | 36.5    | 6        |                  | 94.5    | 5        |          |
| Vedrych:        |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 26              | 3        | 2509–2513 | 3.0–9.5         | 5.5     | 4        | 30.0–54.0        | 40.1    | 4        | 56.0–97.5        | 74.5    | 4        | 70       |
| 27              | 3        | 2726–2742 | 2.5–6.5         | 4.0     | 5        | 18.5–32.0        | 25.2    | 4        | 96.0–104.0       | 97.8    | 4        | 60       |
| Olkhovka:       |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 28              | 1        | 2255–2262 | 19.0–30.0       | 23.0    | 7        | 27.0–66.5        | 44.1    | 6        | 60.0–118.0       | 92.5    | 6        |          |
| 29              | 1        | 2939–2944 | 2.5–4.5         | 3.2     | 3        | 44.5–80.0        | 61.8    | 3        | 120.0–225.0      | 169.0   | 3        | 90       |
| Khobnae:        |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 30              | 2        | 2262–2289 | 28.0–36.5       | 30.5    | 5        | 17.0–35.0        | 22.7    | 5        | 26.5–81.0        | 49.7    | 5        |          |
| Kapatkevichy:   |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 31              | 236      | 1100–1101 | 46.5–64.5       | 56.7    | 3        | 5.0–12.0         | 7.7     | 5        | 2.5–11.5         | 7.5     | 5        | 320      |
| 32              | 236      | 1104–1105 | 50.8, 57.0      | 53.9    | 2        | 9.0–14.5         | 12.0    | 5        | 22.0–26.0        | 24.2    | 5        | 320      |
| 33              | 236      | 1120–1126 | 26.0–49.5       | 36.4    | 9        | 10.0–34.5        | 25.0    | 7        | 40.0–147.0       | 80.9    | 7        |          |
| Petrykau:       |          |           |                 |         |          |                  |         |          |                  |         |          |          |
| 34              | 269      | 1221–1226 | 21.5–46.0       | 30.0    | 3        | 30.0–67.0        | 47.2    | 4        |                  | 73.5    | 5        | 270      |
| 35              | 269      | 1271      |                 | 27.0    | 5        |                  | 39.5    | 3        |                  | 67.5    | 3        |          |
| 36              | 269      | 1344–1350 |                 | 28.5    | 5        |                  | 27.5    | 4        |                  | 54.5    | 4        | 180      |
| 37              | 269      | 1380–1390 | 10.0–14.5       | 12.8    | 4        | 13.5–25.0        | 19.5    | 4        | 23.5–38.0        | 31.8    | 4        | 70       |
| 38              | 269      | 1419–1424 | 19.5–23.5       | 20.8    | 3        |                  | 37.5    | 3        |                  | 36.5    | 3        | 90       |
| 39              | 269      | 1429–1434 | 16.0–19.5       | 17.9    | 5        | 10.0–20.0        | 14.6    | 4        | 13.0–21.5        | 16.1    | 4        | 70       |
| 40              | 269      | 1454–1459 | 6.0–8.0         | 6.9     | 4        | 20.0–28.0        | 24.0    | 3        | 53.5–67.0        | 61.1    | 4        | 70       |
| 41              | 269      | 1465–1470 | 8.0–15.0        | 10.4    | 4        | 10.0–32.0        | 21.0    | 3        | 55.5–99.0        | 81.1    | 4        | 90       |
| 42              | 269      | 1481–1486 | 3.5–8.5         | 6.5     | 5        | 35.5–50.0        | 40.4    | 4        | 49.0–65.5        | 58.5    | 4        | 50       |

Note. Numbers correspond to points showing the composition of inclusion brines as shown in figures 2 and 7. *n* = number of analyses.



**Figure 2.** Brine composition in fluid inclusions from sedimentary halite of the Devonian evaporite basins of the Prypiac' Depression plotted on the Jänecke projection in the  $KCl-CaCl_2-MgCl_2-H_2O$  system saturated with respect to halite at 25°C. Triangles, Frasnian basin; circles, Famennian basin. Location of points is explained in table 1.

In the rock salt, sedimentary halite forms abound, and they have been sampled and studied.

The history of the Famennian evaporite basin was not terminated with the potash precipitation. Considering the occurrence of relatively thick (up to 130 m) rock salt with carbonate-clayey intercalations above the potash deposits, the basin existed until terrigenous deposits ended its development. The rock salt contains many preserved forms of sedimentary halite with zoned arrangements of fluid inclusions.

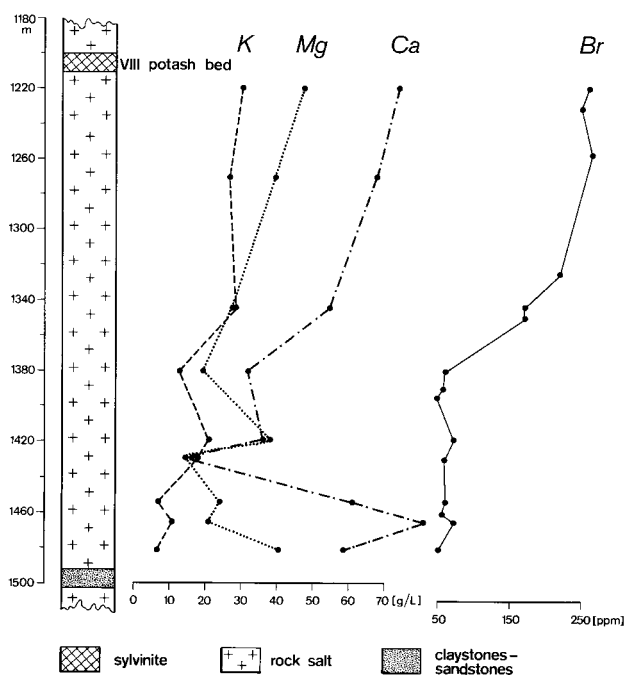
**Dnipro-Donets Depression.** Two evaporite basins with an area of ca. 40,000 km<sup>2</sup> existed during late Frasnian and Famennian (fig. 1A; Petrichenko and Shaidetska 1998). The thickness of evaporite deposits reaches a few hundred meters, and the thickness of the synrift sequence in the Dnipro-Donets basin seems to be generally similar to that of the Prypiac' basin (Ulmishek et al. 1994).

The late Frasnian evaporite deposition terminated with potash salts of sylvite composition. Although evaporites occur in the entire area of the depression, in its SE part they are located at considerable depth (>3000 m) and are arranged in diapirs so the primary-sedimentary halite forms are not preserved. We studied 70 samples of sedimentary halite with fluid inclusions from the NW and central part of the depression, from diapirs (<500 m) and bedded salts (located at a depth >2500 m).

The Famennian evaporite basin was restricted to the NW part of the depression. Thick (up to 300 m) rock salt deposits with marls, anhydrites, and sandstones are located between anhydrite-dolomite series at a depth >2000 m with an area <10,000 km<sup>2</sup>.

### Methods of Study of Fluid Inclusions in Sedimentary Halite

This article is based on a study of ca. 300 samples of rock salt from the Prypiac' and Dnipro-Donets Depressions. The weight of each sample was 50–



**Figure 3.** Changes of K, Mg, and Ca contents in inclusion brines in sedimentary halite that occurs below the eighth potash horizon (Petrykau deposit, borehole 269) and Br content in sedimentary halite forms.

**Table 2.** Chemical Composition of Inclusion Brines in Sedimentary Halite from the Famennian of Prypiac' Basin, Lower Sylvinite Bed, Potash Bed 3, Starobin Deposit, Mine 2

| Location of sample | Content (g/L) |           |         |          |             |         |          | Number in figure 4 |
|--------------------|---------------|-----------|---------|----------|-------------|---------|----------|--------------------|
|                    | K             | Mg        |         |          | Ca          |         |          |                    |
|                    |               | Range     | Average | <i>n</i> | Range       | Average | <i>n</i> |                    |
| Bed 4–5            | 45            | 23.9–50.5 | 32.3    | 5        | 48.8–69.8   | 60.4    | 6        | 43                 |
| Bed 3–4            | 30            | 24.0–35.4 | 30.6    | 3        | 109.5–121.9 | 116.1   | 3        | 44                 |
| Bed 3              | 35            | 28.7–32.8 | 29.1    | 3        | 64.0–102.7  | 81.0    | 4        | 45                 |
| Bed 2–3            | 25            | 26.5–46.7 | 35.1    | 4        | 116.1–149.1 | 131.3   | 4        | 46                 |
| Bed 2              | 25            | 27.4–32.0 | 30.2    | 3        | 108.5–152.8 | 128.6   | 5        | 47                 |
| Bed 1–2            | 40            | 24.2–34.4 | 31.2    | 4        | 76.9–106.2  | 96.8    | 5        | 48                 |

Note. *n* = number of analyses.

700 g. A good preservation of sedimentary halite is characteristic of the Prypiac' Depression. More rare relics of sedimentary halite have been encountered in the NW part of Dnipro-Donets Depression. The central and SE parts of the Dnipro-Donets Depression are characterized by deep (down to 10 km) occurrences of rock salt, formation of abundant salt diapirs, and the manifestations of endogenous processes that led to the complete recrystallization of salt at elevated (>120°C) temperature conditions. In total, relics of sedimentary halite were recorded in 57 samples from the Dnipro-Donets Depression and in 35 samples from the Prypiac' Depression. In every sample, three to seven plates of sedimentary halite have been studied.

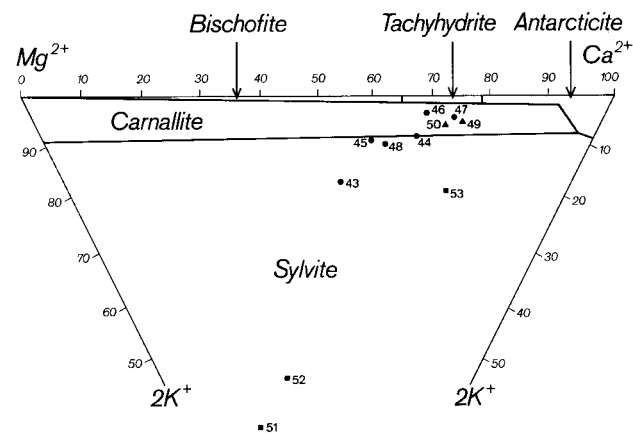
Fluid inclusions in Devonian sedimentary halite occur in zones that are tens to hundreds of microns thick. In some cases, microzones (<10 μm thick) occur, and their arrangement is cloudy.

The total volume of inclusions in individual zones is 10%–28%, and between these zones the inclusions are practically lacking. The inclusions are cubic in shape (they have negative crystal form); they are a fraction of a micron to 80 μm (rarely up to 100 μm) wide and are one-phase fluid; only near to potash zones are the inclusions two-phase (with sylvite or carnallite).

**Chemical Analysis.** All brine inclusions in the studied samples were analyzed by the use of the ultramicrochemical analysis method introduced by Petrichenko (1973). This method allows us to determine the content of major ions in brine inclusions, except for Na and Cl (i.e., K, Mg, Ca, and SO<sub>4</sub> ions). During the last decade, several techniques have become available for the analysis of individual fluid inclusions in halite (Horita et al. 2002), but the ultramicrochemical analysis method is the only one—considering the size of fluid inclusions occurring in the studied rocks—that allows us to observe the behavior of inclusions during their opening by a needle under the microscope, to establish the approximate pressure in inclusions

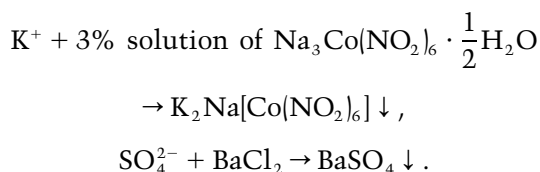
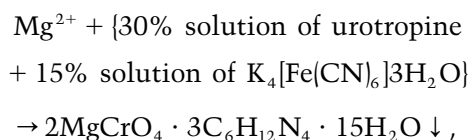
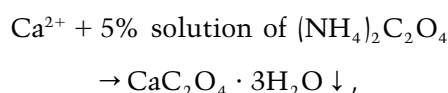
(high or low), and to establish the approximate degree of gas concentration in the brines. These features of brine inclusions are very important for a genetic characterization of types of inclusions (Kovalevych et al. 2002b). A recent comparative study of the same samples realized with both methods (energy dispersive spectroscopy and ultramicrochemical analysis) showed that the results of both methods fit well, considering the potential errors for both techniques (Kovalevych et al., in press).

In his method, Petrichenko (1973) applied ultramicroanalytical techniques (Lazar and Holland 1988, p. 485). The halite is dissolved with a thin jet of water within a few tens of micrometers of the inclusion walls, and then, after the halite crystal is dried, the inclusion is opened. The inclusion fluid is extracted with a conical capillary tube (3–



**Figure 4.** Brine composition in fluid inclusions from halite in the potash series of the Starobin Deposit (Prypiac' Depression) plotted on the Jänecke projection in the KCl–CaCl<sub>2</sub>–MgCl<sub>2</sub>–H<sub>2</sub>O system saturated with respect to halite at 25°C. Circles, lower sylvinite bed of the third horizon; triangles, second potash horizon; squares, rock salt between the third and second potash horizons. Location of points is explained in tables 2–4.

5  $\mu\text{m}$  in diameter at the sharp end of the cone), and a reagent is then added to determine the solutes in the inclusion fluid, following the recommendations by Korenman (1955): 30% solution of  $\text{BaCl}_2$  for determination of the  $\text{SO}_4$  ion, 3% solution of  $\text{Na}_3\text{Co}(\text{NO}_2)_6 \cdot (1/2)\text{H}_2\text{O}$  for the K ion, 5% solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  for the Ca ion, and one part of a 30% solution of urotropine and one part of a 15% solution of  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  for the Mg ion (assuming that its content is  $<6$  g/L) or 15% solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  (if its content is higher). The reagent is added until the process of precipitation is completed according to the reactions (Korenman 1955)



The capillary is then sealed and centrifuged. For determination of each element, separate aliquots of solution are used for each titration and then centrifugation, and the amount of the reagent added is controlled visually under the microscope by the moment of termination of chemical reaction. The amount of reagent added depends on the concentration of the element studied, and usually it is double to triple the volume of the parent inclusion fluid; it always exceeds the amount of the element to be precipitated. The volumes of precipitate and solution formed during this process are measured and then compared with those formed from a standard solution, according to formulas published by Petrichenko (1973, table 4). The contents of K, Mg, Ca, and  $\text{SO}_4$  can be determined with this method. The analytical error of the applied method is 15%–23% (for Mg and K) and 37%–43% (for  $\text{SO}_4$  and Ca) when a single measurement is done. The sources of errors are different density of the precipitates in capillaries that depends on the speed of reactive solution (which in turn depends on the temperature) and the size of the precipitating crystals that are forming. To decrease the error of determination, a number of analyses of each component in inclusion brines of each sample were carried out; two to

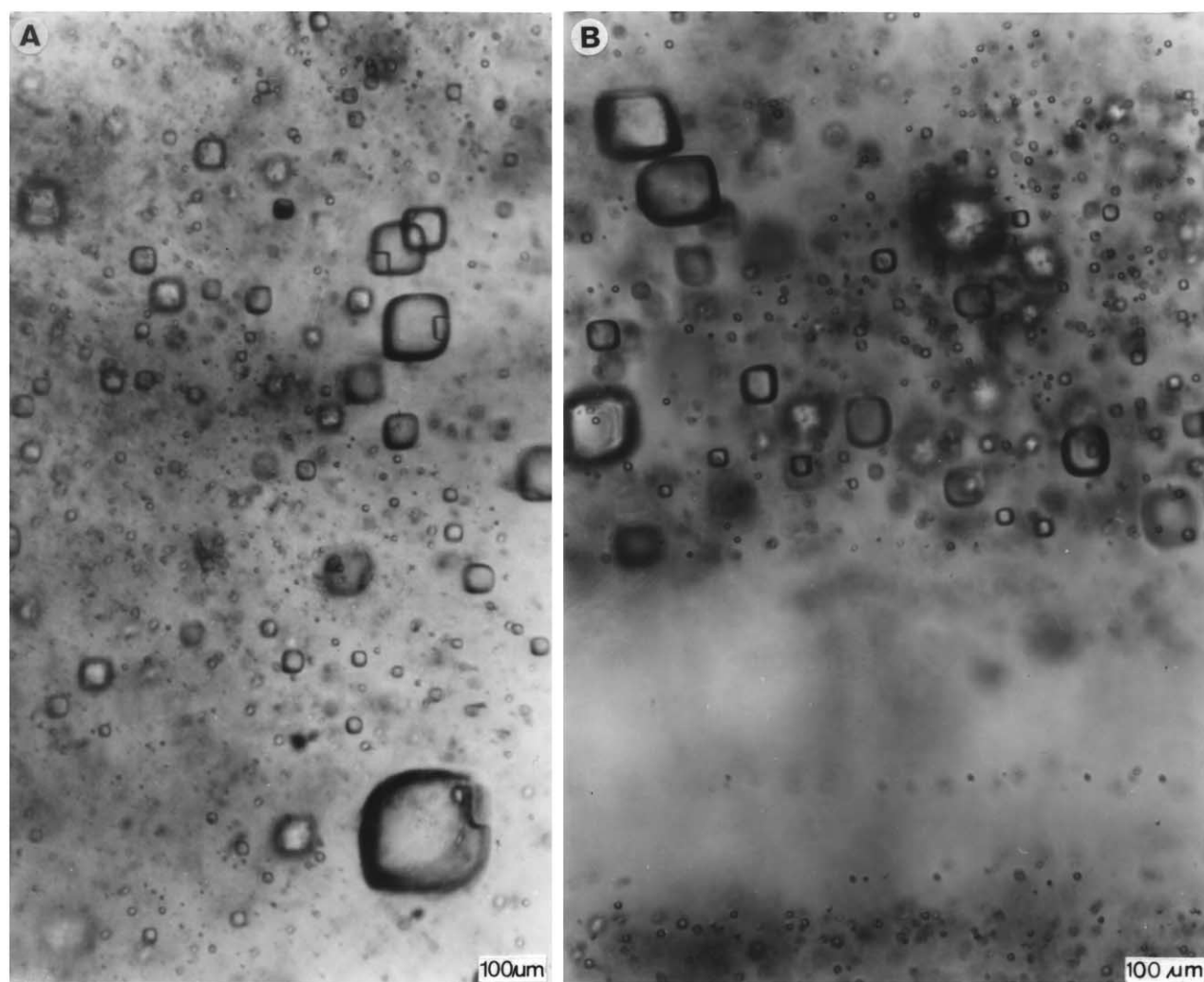
three parallel analyses decrease the error to 16%–17% (see Petrichenko 1973, table 4). The minimum quantities of the studied ions needed for such an error are (in g/L) 0.8 for K, 1.0 for Mg, 0.9 for Ca, and 0.5 for the sulfate ion, and the lower values are semiquantitative. It should be mentioned that initially, the concentration of particular ions in the standard solutions has been given in g/L, and thus it seems not useful to change this approach since this would lead to difficulty in comparisons with the earlier published results.

It is preferable to use average values of ion contents in inclusion brines of each sample for interpretations because the analytical error can be larger than possible changes of brine composition in different inclusions from the same sample. We used inclusions  $>40$   $\mu\text{m}$  for chemical analyses.

**Gas Content.** Gas content was measured using the following procedure that was earlier tested on samples taken from modern halite formed in salt lakes of Crimea and the Dead Sea. The sample with fluid inclusions was heated for 6–8 h at a temperature of 110°–120°C that led to overheating of fluid inclusions and to the formation of microcracks around the individual inclusions and their filling by fluid. During the cooling of the sample to room temperature, the volume of solution that went into the microcracks was compensated by the dissolved gases and water vapor, which had a similar pressure to that during the mineral crystallization; thus, this method is semiquantitative.

Subsequently, the slide was gradually dissolved in a 30%–40% water solution of glycerine that contained  $\text{CO}_2$  absorbent, i.e.,  $\text{Ba}(\text{OH})_2$ . The examination of the gas fraction was carried out under the microscope in plain light. The diameter of gas bubble was measured before and after the inclusion opening as well as after  $\text{CO}_2$  reagent absorption, and then the gas pressure was calculated applying the Henry principle. For simplicity, it was assumed that the average gas (nitrogen + methane) saturation in NaCl-saturated brines is 2  $\text{cm}^3/\text{L}$ . Accordingly, if the measured gas saturation is 20  $\text{cm}^3$ , the pressure necessary to dissolve such a quantity of gas is about 10 atmospheres, which corresponds to the basin depth of ca. 80 m. The chemical composition of gases was established with the use of the mass spectrometric method (Kaluzhny et al. 1974). For measurements of gas content, we used inclusions  $<50$   $\mu\text{m}$ .

The approach applied by us deals with the one-phase fluid inclusions in sedimentary halite, so initially there was no gas as a separate phase. The gas phase in such inclusions appears during the heating of inclusions to 80°C that leads to the origin of



**Figure 5.** A, Sedimentary halite with fluid inclusions in which sylvite daughter crystals occur only in big ( $>40\ \mu\text{m}$ ) inclusions. Prypiac' Basin, Starobin deposit, Potash Bed 3. B, Sharp change from zone with inclusions to zone without inclusions. Prypiac' Basin, Starobin deposit, Potash Bed 2.

micropores (because of the fact that the coefficient of fluid expansion is greater than the coefficient of halite expansion), which are filled by the solution. Because this process is one-way only during the cooling down to  $20^{\circ}$ – $25^{\circ}\text{C}$ , in the inclusions there appears a vacuum that is filled by water vapor or dissolved gases ( $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and others). The gas phase that originated is preserving the pressure that exists during the mineral crystallization, although those results are semiquantitative. The value of gas pressure in the inclusions is approximately equal to the ratio of gas volume after the inclusion opening to its original volume (Boyle principle).

**Temperature Measurement.** For study of fluid inclusions with sylvite or carnallite daughter crystal in sedimentary halite below the potash zones, a

thermo-chamber with the temperature accuracy  $\pm 0.5^{\circ}\text{C}$  and the heating rate  $0.5^{\circ}$ – $1.0^{\circ}\text{C}/1\ \text{min}$  was used. The size of inclusions used for this was  $>30\ \mu\text{m}$ .

### Composition of Fluid Inclusions

**Prypiac' Depression.** In the Frasnian, primary-sedimentary halite in rock salt occurs very rarely in the form of relics (1–2 mm across) in recrystallized halite. The recrystallization of rock salt is controlled first by its deep (1000–4000 m) occurrence and relatively elevated temperatures as recorded by data on homogenization of gas-fluid inclusions in this series (Petrichenko 1988), which gave values of  $45^{\circ}$ – $115^{\circ}\text{C}$  (the values increase with



**Table 3.** Chemical Composition of Inclusion Brines in Sedimentary Halite and Sylvine from the Famennian of Prypiac' Basin, Starobin Deposit, Potash Bed 2, Bed 4

| Mineral | Content (g/L) |          |           | Number in figure 5 |
|---------|---------------|----------|-----------|--------------------|
|         | K             | Mg       | Ca        |                    |
| Halite  | 10.1 (7)      | 20.3 (4) | 112.0 (5) | 49                 |
| Halite  | 15.0 (3)      | 20.7 (4) | 93.8 (5)  | 50                 |
| Sylvine | 23.6 (5)      | 10.8 (5) | 83.4 (7)  |                    |
| Sylvine | ...           | 27.2 (3) | 108.8 (3) |                    |

Note. Number of analyses is shown in parentheses.

the increasing depth). In relics of sedimentary halite, inclusions are mostly two-phase (liquid and gas). The origin of the latter is related to overheating of  $>70^{\circ}\text{C}$ . The gas is under a pressure of 7–27 atmospheres. The size of individual inclusions varies widely from a few to 90  $\mu\text{m}$ . In most cases, there is no rhythmic zonation in the inclusions, which suggests relatively great depths of evaporite basin in its center.

The chemical analyses of brine inclusions  $>40\ \mu\text{m}$  are shown in table 1 and figure 2. All studied samples are from cores of deep holes that are relatively evenly distributed throughout the Prypiac' Depression. Systematic changes in chemical composition of brines throughout the basin were not revealed. Most data indicate very high Ca concentrations in basin brines. The highest values are related to the earliest stages of evaporite sedimentation. The content of K is 3–9 g/L (rarely up to 22 g/L).

In the Famennian, inclusions (mostly liquid and rarely gas-liquid) in sedimentary halite rarely reach 100  $\mu\text{m}$ . At the beginning of halite precipitation, the K content was 4 g/L, which is characteristic of the initial stages of halite precipitation from modern marine water. With time the K content increased, and the Ca content first decreased and then increased (fig. 3).

In borehole 2 in the area of Khobnae at the depth of ca. 2300 m, cubic halite crystals (0.5–1.5 mm) contain fluid inclusions up to 50  $\mu\text{m}$  wide. These inclusions contain 7.5–80.9 g/L of Ca. In the Ka-

patkevichy 236 borehole, in the inclusion brines 0.5–0.7 g/L of  $\text{SO}_4$  ion were recorded (these results are not shown in table 1).

The fluid inclusions in sedimentary halite of the third potash horizon of the Starobin Deposit (table 2; fig. 4) are mostly two-phase, with sylvite daughter crystal (fig. 5A). Considering the sylvite presence, in the inclusions brine the K content was not recorded (at the temperature  $20^{\circ}\text{--}25^{\circ}\text{C}$ ). Its possible concentrations before sylvite precipitation at the temperature  $>50^{\circ}\text{C}$  are calculated (table 2) considering the solubility of KCl in brines that contain high contents of Ca and Mg chlorides (Kafarov 1969). In the second potash horizon, fluid inclusions are mostly zoned, two- and three-phase, isometric, and up to 100  $\mu\text{m}$  across (fig. 5B). The composition of the inclusion brines is shown in table 3 and figure 4. These inclusions contain cubes of allogenic halite and gas (under a pressure of  $>5$  atmospheres). Inclusions in sedimentary halite from between the second and third potash horizons have relatively low contents of Mg and Ca and a high content of K (table 4; fig. 4). Such a composition of fluid inclusions corresponds to the exclusively sylvinitic composition of the second potash horizon and the lack of carnallite deposits (Vysotskiy et al. 1988). Fluid inclusions above the potash complex are characterized by low concentrations of Ca ( $<6$  g/L) and Mg ( $<5$  g/L) and high content of K (up to 50 g/L). In some cases, because of low contents of Ca and Mg, the presence of  $\text{SO}_4$  (up to 1.5 g/L) within the limits of anhydrite solubility was recorded.

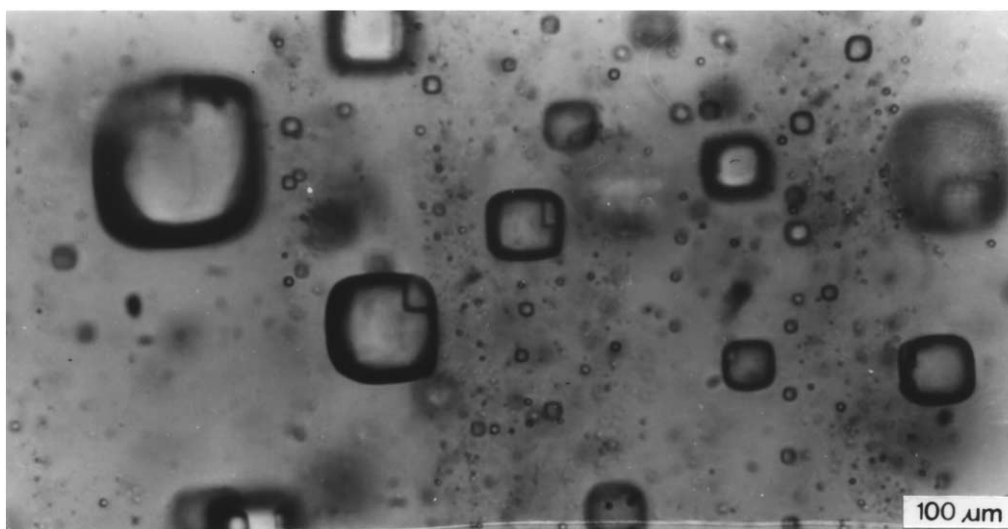
**Dnipro-Donets Depression.** In the Frasnian evaporite basin, sedimentary halite occurs rarely in the form of relics (up to 1 mm) of sedimentary halite within recrystallized halite. The width of zones with fluid inclusions is 120–430  $\mu\text{m}$ . Fluid inclusions are one-phase, up to 80  $\mu\text{m}$ , and rarely contain solid phase (sylvite; fig. 6). A good preservation of relics of sedimentary halite is characteristic only for the Solonytsya structure.

Bromide content in halite is 50–150 ppm. The

**Table 4.** Chemical Composition of Inclusion Brines in Sedimentary Halite from between Third and Second Potash Bed (Starobin Deposit, Famennian of Prypiac' Basin)

| Area and borehole | Depth (m) | Content (g/L) |          |          | Number in figure 4 |
|-------------------|-----------|---------------|----------|----------|--------------------|
|                   |           | K             | Mg       | Ca       |                    |
| Rachytsa:         |           |               |          |          |                    |
| 213               | 487–488   | 33.9 (8)      | 4.1 (10) | 4.1 (10) | 51                 |
| 213               | 490–492   | ...           | 5.7 (7)  | 13.0 (5) |                    |
| 213               | 516–524   | 19.0 (6)      | 6.5 (6)  | 35.0 (5) | 53                 |
| Starobin:         |           |               |          |          |                    |
| 136               | 450–456   | 33.6 (6)      | 8.8 (7)  | 7.6 (10) | 52                 |

Note. Number of analyses is shown in parentheses.



**Figure 6.** Two-phase fluid inclusions with sylvite daughter crystal within the day and night zone of sedimentary halite of the Upper Devonian evaporites from the Dnipro-Donets basin (Romny area, borehole 6072, depth 518.0 m).

results shown in table 1 and published data (Shaidetskaya 1990) indicate the constant, elevated content of Ca and its small variation in fluid inclusions. In contrast, the contents of K and Mg vary considerably (1.5–36.5 g/L and 7.0–59.5 g/L, respectively). The average content of all mentioned elements corresponds to the location of the corresponding point on the diagram within the sylvite field (fig. 7) that is characteristic of marine solutions with a decreased Mg content. During sylvite precipitation (Romny area), the K content reaches considerable concentration along with decreased contents of Mg and Ca in solutions; the reason for this remains enigmatic. During the deposition of thick halite sequences (Kholmy area; cf. fig. 8), the K content in solution was regularly increasing, and Mg and Ca contents were decreasing.

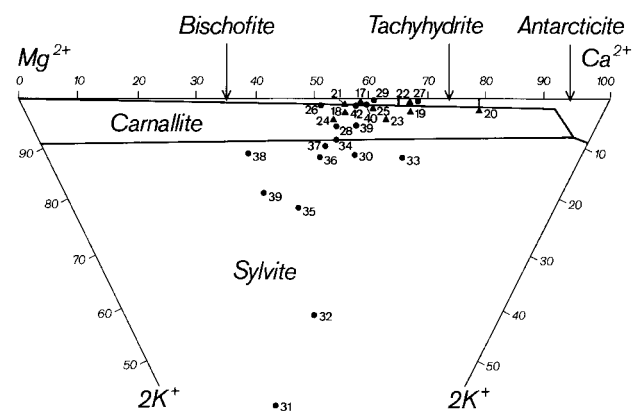
In Famennian evaporites, fluid inclusions are usually  $<60 \mu\text{m}$ , and the width of zones with inclusions is 350–400  $\mu\text{m}$ . The Br content is 60–130 ppm. Data on inclusions in sedimentary halite are fragmentary, but they indicate that the solutions contained considerable Ca content, while Mg content was higher compared with the Frasnian brines (table 1; fig. 7).

#### Interpretation of Seawater Composition

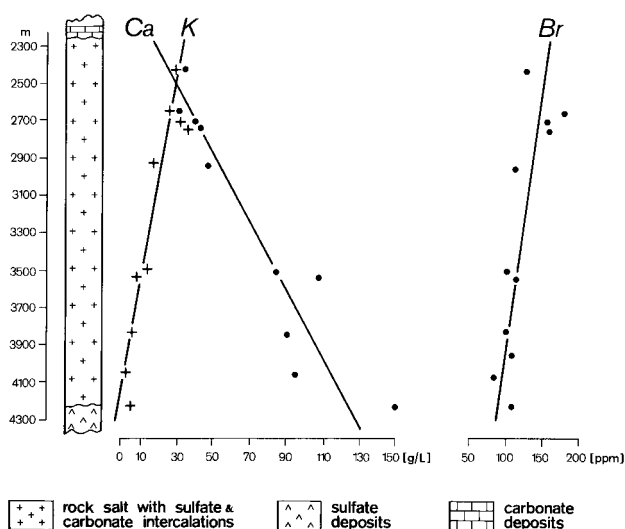
Our data suggest that in the Devonian Prypiac' and Dnipro-Donets evaporite basins, anomalously high Ca contents (100–200 g/L) are characteristic of brines at the stage of halite precipitation. Consid-

ering the data on solubility of  $\text{NaCl-MgCl}_2\text{-CaCl}_2$  in water at the normal temperature and at a total chloride concentration of 200–400 g/L (Kafarov 1969), halite precipitation in those basins could begin when the NaCl content of the brines was  $<100$  g/L. For comparison, in recent marine brines, halite starts to precipitate when the NaCl content is 260–270 g/L.

Assuming that the K content of the Devonian water was similar to that in modern water (about



**Figure 7.** Brine composition in fluid inclusions from sedimentary halite of the Dnipro-Donets evaporite basins plotted on the Jänecke projection in the  $\text{KCl-CaCl}_2\text{-MgCl}_2\text{-H}_2\text{O}$  system saturated with respect to halite at  $25^\circ\text{C}$ . Triangles, Frasnian basin; circles, Famennian basin. Location of points is explained in table 1.



**Figure 8.** Changes of Ca and K contents in inclusion brines in sedimentary halite and of Br in halite of the Frasnian rock salt of the Dnipro-Donets Trough (Kholmy area, borehole 238; after Kityk et al. 1980).

0.4 g/L K; McCaffrey et al. 1987, table 2), it can be calculated, by the Ca/K ratio in fluid inclusions at the onset of halite precipitation, that the Ca content in Devonian water was, on average, 0.2 g/L and 0.51 g/L, as found in the Pripyat Basin (table 4, Starobin) and the NW part of the Dnipro-Donets Basin (table 1, Adamivka area), respectively.

In modern seawater, during its natural evaporation, the ratio Mg/K at the onset of gypsum precipitation is 4.5, at the onset of halite precipitation is 4.7, and at the onset of epsomite precipitation is 4.8 (Valiashko 1962). Thus, during halite precipitation, the Mg/K ratio was almost constant. This conclusion was supported by evaporation of seawater in laboratory conditions (McCaffrey et al. 1987), although the ratio was found to be slightly <3.4. This difference is explained by different experimental conditions. Accordingly, the brine inclusions in Devonian halite may be used to evaluate the Mg/K ratio in parent seawater, although

it should be remembered that in contrast to the modern seawater (that was used in the previously mentioned experiments), which is of sulfate-rich type, the Devonian seawater was Ca rich. The Mg/K values in individual samples from the Frasnian of Prypiac' Basin and Famennian of the Dnipro-Donets Basin (table 1) vary from 3 to 16 (taking into account samples of basal halites with the K content in fluid inclusions <10 g/L), but the average values are 5.4 and 7.1 for the Frasnian of Prypiac' Basin and Famennian of the Dnipro-Donets Basin, respectively (table 1), and those values are reasonably close to the value of 4.7 given by Valiashko (1962).

Our method of studying fluid inclusions allows the measurement of the sodium content. However, the experiments on evaporation of modern seawater (Valiashko 1962; McCaffrey et al. 1987) indicate that at the onset of halite precipitation, the K content in brine is 3.3–3.9 g/L. The samples taken from basal halites (2–10 m above the base of halite) contain 3.0–8.8 g/L (average 5.6 g/L) of K in fluid inclusions, and thus it seems that the Na/K ratio in Devonian seawater was close to the ratio in modern seawater. The higher values of K in fluid inclusions can be because of the provenance of samples not from the very base of halite precipitation and/or decreased Na content in seawater, as suggested by Brennan and Lowenstein (2002).

The studied salts have precipitated from mainly marine brines of chloride chemical type with a relatively high  $\text{Ca}^{2+}$  content. Our data thus support the recent concept that marine water was Ca rich throughout the early and middle Paleozoic (Kovalovich et al. 1998a; Lowenstein et al. 2001; Brennan and Lowenstein 2002; Horita et al. 2002) till the Viséan (Petrychenko et al. 2002), in contrast to the sulfate-rich chemical type prevailing in the Permian (Kovalevych et al. 2002a) and Triassic (Kovalevych et al. 2002b).

Table 5 shows a comparison of Ca content in solutions of different inclusions occurring within one small (1 × 2 cm) halite plate. All data indicate a sharp increase of Ca concentration in buried

**Table 5.** Comparison of Ca Content in Brine Inclusions in Sedimentary and Diagenetic Halite

| Basin and area | Borehole | Depth (m) | Ca (g/L)    |            |
|----------------|----------|-----------|-------------|------------|
|                |          |           | Sedimentary | Diagenetic |
| Dnipro-Donets: |          |           |             |            |
| Solonytsya     | 9        | 422.7     | 46.8 (4)    | 71.1 (4)   |
| Kholmy         | 238      | 2420.0    | 37.0 (6)    | 77.7 (3)   |
| Prypiac':      |          |           |             |            |
| Starobin       | 136      | 450.0     | 7.6 (8)     | 18.1 (3)   |
| Kapatkevichy   | 236      | 1112.0    | 23.5 (5)    | 144.5 (3)  |

Note. Number of analyses is shown in parentheses.

**Table 6.** Homogenization Temperature of Inclusions (with Sylvine or Carnallite Daughter Crystal) in Sedimentary Halite of Potash Deposits

| Basin, area, and composition of deposit | Homogenization temperature (°C) |
|---|---------------------------------|
| Dnipro-Donets:                          |                                 |
| Romny:                                  |                                 |
| Sylvinite                               | 57–69                           |
| Rock salt                               | 48–53                           |
| Prypiac':                               |                                 |
| Starobin:                               |                                 |
| Carnallite                              | 67–75                           |
| Sylvinite                               | 77–83                           |
| Rock salt                               | 50–64                           |
| Petrykau:                               |                                 |
| Rock salt                               | 48–52                           |
| Rock salt                               | 47–57                           |

brines that have taken part during overgrowth of sedimentary halite during lithification of chemical deposits. Accordingly, results of Ca determinations in inclusion solutions in diagenetic halite support an important role of  $\text{Ca}^{2+}$  in buried deposits (cf. Sadykov et al. 1981; Vlasova 1981; Petrichenko 1989).

The maximum concentration of Ca in solutions at the beginning of halite sedimentation and its gradual decrease along with the salt accumulation, by the reciprocal relation of Ca behavior regarding other elements (K, Mg, Br) in the process of chemical sedimentation, and a considerable variation (between 0.1 and 45) of Ca/K ratio indicate that there existed another source of  $\text{Ca}^{2+}$  that was supplied to the evaporite basin (cf. Sadykov et al. 1981; Vlasova 1981). Hardie (1990) has suggested that rift basins, especially during their early developmental stages, are fed, partly or entirely, by nonmarine waters. We assume that the additional supply of  $\text{Ca}^{2+}$  to the Devonian evaporite basin was because of discharge of connate highly mineralized subsurface brines (cf. Petrichenko 1989).

### Environmental Data and Their Interpretation

**Temperature of Salt-Forming Brines.** The occurrence of one-phase fluid inclusions indicates the temperatures of salt-forming brines  $<43^\circ\text{C}$  as indicated by experimental data on growth of artificial crystals in different temperatures within the range of  $20^\circ\text{--}100^\circ\text{C}$  (Kovalevich 1978). The study of inclusions from sedimentary halite of the Prypiac' Depression (Petrykau area, borehole 269, depth 1481–1486 m) with the use of the method described by Roberts and Spencer (1995) showed that the homogenization temperatures of artificial gas-fluid

inclusions were  $20^\circ\text{--}27^\circ\text{C}$ . However, it should be noticed that the temperatures of homogenization of gas-fluid inclusions are slightly decreased compared with the real temperatures (Arcos and Ayora 1997).

The study of homogenization temperatures of inclusions with sylvite and carnallite daughter crystals in sedimentary halite occurring below the potash deposits and in halite from sylvinite deposits of the Dnipro-Donets and Prypiac' Basins indicate high temperatures in which potash minerals have precipitated (table 6). This physical parameter influenced evaporation and halite precipitation rates. In the Prypiac' Basin, a correlation between the width of halite growth zones (interpreted as daily; cf. Dellwig 1955; Valiashko 1962) and brine temperature was recorded. Considering that the present daily growth of halite in marine lagoons of Crimea is  $120\text{--}470\ \mu\text{m}$  at the maximum brine temperature of  $30^\circ\text{C}$  (O. I. Petrychenko, unpublished data), at the temperature  $>65^\circ\text{C}$  the rate of Devonian halite growth could reach 1.2 mm/d.

Carnallite precipitation, characteristic of the Prypiac' Basin, could have resulted from precipitation from brines of chloride type with  $\text{CaCl}_2$  in high temperatures (cf. Braitsch 1971).

**Gas Content and Composition of Dissolved Gases.** Many measurements of gas content show a great spread of values (10–300 g/L) what was evidently controlled by the pressures existing at the basin bottom during halite growth. High (50–300 g/L) gas content is accompanied by high (50–70 vol%)  $\text{CO}_2$  share among gases.

In some cases, patterns of changes of gas content have been recorded. In the Prypiac' Depression, series (about 100 m thick) characterized by gradual decrease of this value upward from  $6\ \text{cm}^3/\text{L}$  to  $3\ \text{cm}^3/\text{L}$  are recorded in the Petrykau area (borehole 269). In the Dnipro-Donets Depression, an opposite trend was recorded as the gas content increases upward from 4 to  $50\ \text{cm}^3/\text{L}$  (Kholmy area, borehole 238).

The measurements of gas content of inclusion brines in sedimentary halite indicate that the onset of halite precipitation in the Prypiac' Basin (Olkhovka area) occurred at a depth of 360–400 m, which is compatible with paleogeographic data (Khomenko 1966; Makhnach 1966; Kudelskiy 1982; Petrichenko and Shaidetska 1998; Kruchek et al. 2001), and in the NW part of the Dnipro-Donets Basin (Kholmy area) at a depth of 90–100 m. The most common depths for all studied basins were 20–50 m. Accordingly, our data support the theoretical concepts (Yanshin 1961; Schmalz 1969) of deepwater evaporite basins.

**Table 7.** Chemical Composition (in Vol%) of Gases from Brine Inclusions in Sedimentary Halite

| Basin         | N <sub>2</sub> |         | CO <sub>2</sub> |         | CH <sub>4</sub> |         | n  |
|---------------|----------------|---------|-----------------|---------|-----------------|---------|----|
|               | Range          | Average | Range           | Average | Range           | Average |    |
| Dnipro-Donets | 14–81          | 39      | 4–70            | 47      | 10–40           | 14      | 11 |
| Prypiac'      | 23–93          | 55      | 6–34            | 26      | 4–43            | 19      | 17 |

Note. MS analysis after method of Kaluzhny et al. (1974). *n* = number of analyses.

In inclusion brines, N<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> were recorded (table 7; fig. 9), whereas H<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, and heavy hydrocarbons are lacking. CO<sub>2</sub> could react with water-forming anion HCO<sub>3</sub> and thus additionally influence the carbonate precipitation. CO<sub>2</sub> could be also supplied by endogenic processes as indicated by the occurrence of fluid CO<sub>2</sub> in vein halite (Petrichenko 1989). It is possible that this is the cause of high content of dolomite in insoluble residue of halite from the Prypiac' and Dnipro-Donets Depressions.

### Geochemical Model of the Devonian Evaporite Basin

Our results are summarized in figure 10, which shows the model of the Frasnian Prypiac' and Dnipro-Donets Basins at the stage of halite and potash deposition. We used the data on paleogeography and sedimentation in the basins, given by other authors and indicating a marine provenance of Devonian salt deposits (Khomenko 1966; Makhnach 1966; Kityk and Galabuda 1981; Kudelskiy 1982; Petrichenko and Shaidetska 1998; Kruchek et al. 2001), for the model construction.

The graphic presentation of the model is along two lines (fig. 10) although in different horizontal scales (see distances shown in the upper part of fig. 10). As already mentioned, toward the SE, the detailed data on conditions of chemical sedimentation are lacking, and therefore the graphic presentation is restricted only to that part of the basin from which the data come. The vertical scale is schematically discretionary because of considerable differences between thicknesses of sedimentary series and the probable basin depth.

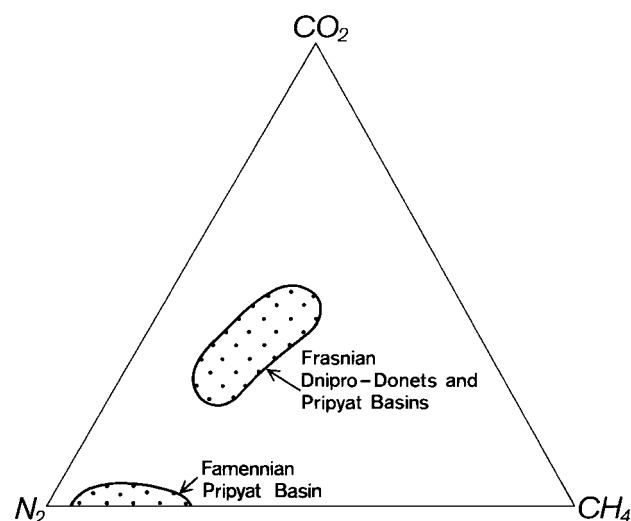
The marine basins originated at the Middle-Late Devonian boundary because of the origin of rift structure. The feeding of the Dnipro-Donets Basin by seawater was from the SE, whereas seawater was inflowing from the NW into the Prypiac' Basin. It is possible that both basins could be temporarily connected during high sea level but not during the evaporite sedimentation.

The formation of the large rift valley was associated with endogenous processes and active vol-

canism (Lashkevich and Marushkin 1982), which undoubtedly had an influence on evaporite basins, as indicated by the presence of tuff material among the rock salt, influence of thermal solutions on the rock salt, high content of CO<sub>2</sub>, and slightly lighter (0.95–1.06) δ<sup>13</sup>C values in calcite and dolomite occurring in the Frasnian rock salt (Shaidetskaya 1992).

Because of endogenous processes and the shallow depth (<500 m) of the Precambrian crystalline basement, the entire area of the Prypiac'-Dnipro-Donets Depression was characterized by a high geothermal gradient (Bogomolov et al. 1981). The common occurrence of increased temperature (up to 90°C) is supported by our data on homogenization of gas-fluid inclusions in late diagenetic halite of the Frasnian salt-bearing series. The most active influence of endogenous processes was typical for the areas that are located on both sides of the Chernihiv Horst, in the area of Romny area, and in other places (cf. Skachedub 1986).

We have not recorded any features that suggest an influence of deep-seated processes on conditions



**Figure 9.** Composition of dissolved gases occurring in fluid inclusions of sedimentary halite of evaporite basins of the Prypiac' and Dnipro-Donets depressions.

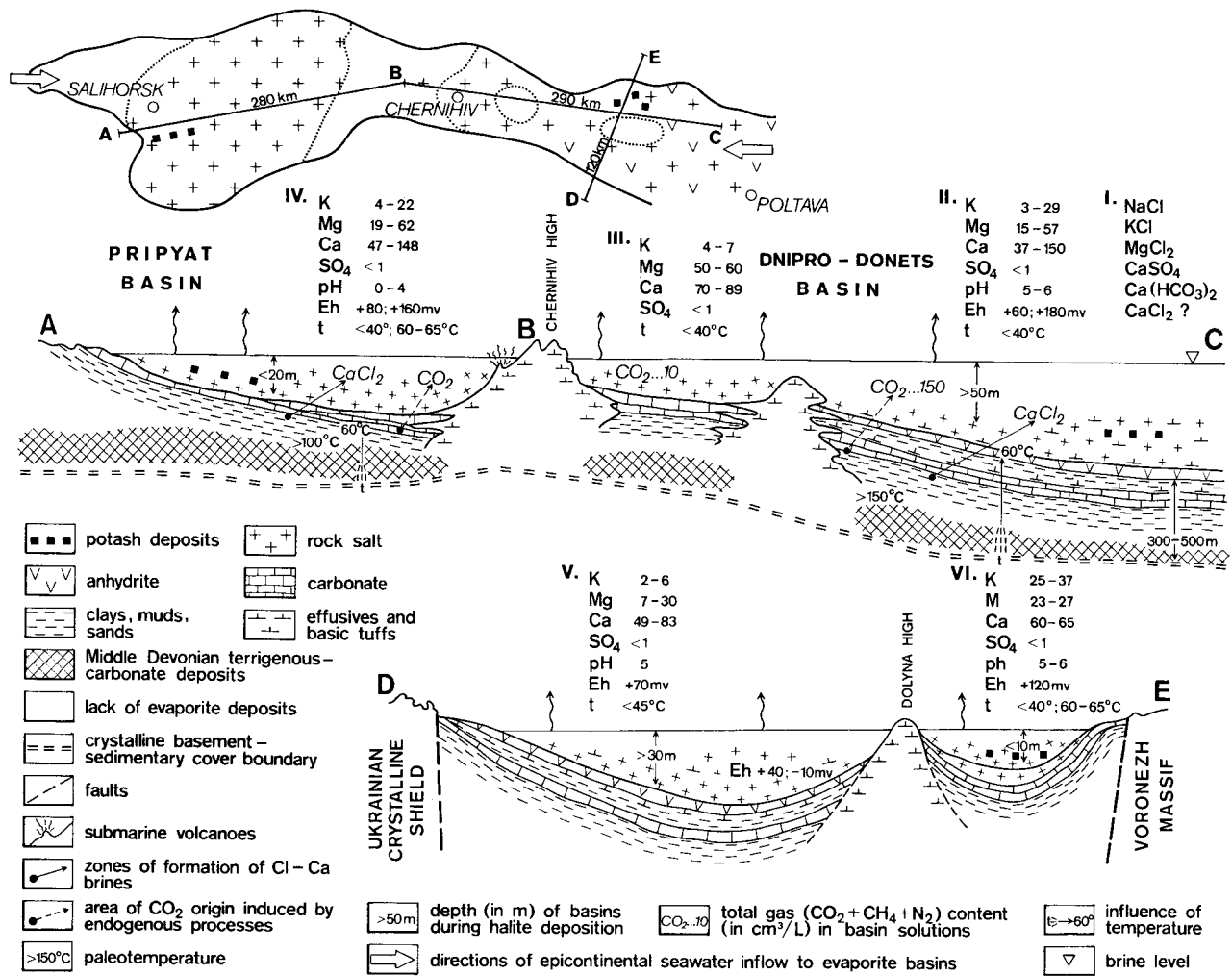


Figure 10. Geochemical model of the Frasnian evaporite basin of the Prypiac'-Dnipro-Donets rift trough

of salt deposition. The temperatures of salt-forming solutions did not exceed 43°C, and the daily growth of zoned sedimentary halite (up to 400 μm) and the seasonal growth rate (4–7 cm) are within the usual values. Taking into account the sylvinite distribution, it can be concluded that the maximum density of brine was related to the basin parts, which were isolated from the main basin. For example, the greatest occurrence of sylvinites of the Romny area was controlled by the presence of elongated Dolyna Horst.

Although the geochemical model of the Devonian evaporite basin shown in figure 10 is based on observations and interpretations of conditions that prevailed in the Frasnian Prypiac' and Dnipro-Donets Basins at the stage of halite and potash deposition, it can be applied to other rift depressions as well, especially to rifts in which evaporites have

been precipitated from marine brines that were Ca rich (cf. Kovalevich et al. 1998a; Lowenstein et al. 2001).

### Conclusions

1. Salt sedimentation in the Devonian in the upper Devonian Prypiac' and Dnipro-Donets evaporite basins was due to the intensive precipitation of marine brines of chloride chemical type with a relatively high Ca<sup>2+</sup> content. The Devonian marine brines thus differed from the recent brines of marine origin.

2. Salt minerals precipitated in bottom water conditions. Sedimentary halite precipitated in the temperature <43°C and before precipitation of potassium minerals brines have been heated up to 50–60°C. During sylvite and carnallite deposition,

the temperature increased to 70°–80°C. Brines have been gas saturated (mostly CO<sub>2</sub> and minor N<sub>2</sub> and CH<sub>4</sub>).

3. Relations between Na, K, and Mg in brines of Devonian basins corresponded to the relations in recent marine brines. However, important Ca<sup>2+</sup> concentration was the cause of the more intensive deposition of halite and potash minerals.

4. The combined geochemical data made it possible to present the geochemical model of the Devonian rift basin during evaporite deposition.

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#### REFERENCES CITED

- Arcos, D., and Ayora, C. 1997. The use of fluid inclusion in halite as environmental thermometer: an experimental study. *In* Boiron, M. C., and Pironon, J., eds. Volume des résumés. Proc. 14th ECROFI (Nancy, 1997), p. 10–11.
- Bogomolov, G. V.; Panov, V. V.; and Bogomolov, Y. G. 1981. O paleotemperaturnykh usloviyakh formirovaniya Pripyatsko-Donetskogo avlakogena. *In* Lubimova, E. A., and Khlebovitskiy, V. A., eds. Geotermometry i paleotemperaturnyye gradienty. Moskva, Nauka, p. 42–49.
- Braitsch, O. 1971. Salt deposits: their origin and composition. Berlin, Springer, 297 p.
- Brennan, S. T., and Lowenstein, T. K. 2002. The major ion composition of Silurian seawater. *Geochim. Cosmochim. Acta* 66:2683–2700.
- Dellwig, L. F. 1955. Origin of Salina salt of Michigan. *J. Sediment. Petrol.* 25:83–110.
- Hardie, L. A. 1990. The roles of rifting and hydrothermal CaCl<sub>2</sub> brines in the origin of potash evaporites: an hypothesis. *Am. J. Sci.* 290:43–106.
- Horita, J., and Holland, H. D. 1998. Brine inclusions in halite and the origin of the Middle Devonian Prairie Evaporites of western Canada: reply. *J. Sediment. Res.* 68:230–231.
- Horita, J.; Weinberg, A.; Das, N.; and Holland, H. D. 1996. Brine inclusions in halite and the origin of the Middle Devonian Prairie Evaporites of western Canada. *J. Sediment. Res.* 66:956–964.
- Horita, J.; Zimmermann, H.; and Holland, H. D. 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. *Geochim. Cosmochim. Acta* 66:3733–3756.
- Kafarov, V. V., ed. 1969. Spravochnik po rastvorimosti (Vol. 3, Part 2). Leningrad, Nauka, 1170 p.
- Kaluzhny, V. A.; Svoren, I. M.; and Platonova, E. L. 1974. Sostav gaza fluidnykh vklucheniyy i voprosy obnaruzheniya vodoroda v nikh. *Dokl. Akad. Nauk. SSSR* 219:973–975.
- Khomenko, V. A. 1966. Devon Dneprovsko-Donetskoy vpadiny. Kiev, Naukova Dumka, 113 p.
- Kityk, V. I., and Galabuda, N. I. 1981. Paleogeografiya periodov devonskogo solenakopleniya v Dneprovsko-Donetskoy vpadine. *In* Yanshin, A. L., and Zharkov, M. A., eds. Stroyeniye i usloviya obrazovaniya solenosnykh formatsiy. Novosibirsk, Nauka, p. 74–82.
- Kityk, V. I.; Galabuda, N. I.; Petrichenko, O. I.; and Shaidetskaya, V. S. 1980. K izucheniyu pozdnedevonskogo solenakopleniya v Pripyatskom progibe i Dneprovsko-Donetskoy vpadine. *In* Kityk, V. I., and Petrichenko, O. I., eds. Litologiya i geokhimiya osadochnykh tolschch. Kiev, Naukova Dumka, p. 77–95.
- Konishchev, V. S.; Garetskiy, R. G.; and Ayzberg, R. E. 2001. Plitnyye ortoplatformennyye etapy: gertsinskiy etap. *In* Makhnach, A. S.; Garetskiy, R. G.; et al., eds. Geologiya Belarusi. Minsk, Institut Geologicheskikh Nauk NAN Belarusi, p. 591–629.
- Korenman, I. M. 1955. Mikrokrystalloskopiya. Moskva, Goskhimizdat, 431 p.
- Kovalevich, V. M. 1978. Fiziko-khimicheskiye usloviya formirovaniya soley Stebnikskogo kaliynogo mestorozhdeniya. Kiev, Naukova Dumka, 98 p.
- Kovalevich, V. M.; Peryt, T. M.; and Petrichenko, O. I. 1998a. Brine inclusions in halite and the origin of the Middle Devonian Prairie Evaporites of western Canada: discussion. *J. Sediment. Res.* 68:228–229.
- . 1998b. Secular variation in seawater chemistry during the Phanerozoic as indicated by brine inclusions in halite. *J. Geol.* 106:695–712.
- Kovalevych, V.; Peryt, T. M.; Beer, W.; Geluk, M.; and Halas, S. 2002a. Geochemistry of Early Triassic seawater as indicated by study of the Röt halite in the Netherlands, Germany, and Poland. *Chem. Geol.* 182: 549–563.
- Kovalevych, V. M.; Carmona, V.; Pueyo, J. J.; and Peryt, T. M. In press. A comparative study of ultramicrochemical analysis and cryogenic SEM-EDS analysis of brines in fluid inclusions in halite. *Geochem. Int.*
- Kovalevych, V. M.; Peryt, T. M.; Carmona, V.; Sydor, D. V.; Vovnyuk, S. V.; and Halas, S. 2002b. Evolution of Permian seawater: evidence from fluid inclusions in halite. *Neues Jahrb. Miner. Abh.* 178:27–62.
- Kruchek, S. A.; Makhnach, A. S.; Golubtsov, V. K.; and Obukhovskaya, T. G. 2001. Devonskaya sistema. *In* Makhnach, A. S.; Garetskiy, R. G.; et al., eds. Geologiya Belarusi. Minsk, Institut Geologicheskikh Nauk NAN Belarusi, p. 186–239.
- Kudelskiy, A. V., ed. 1982. Devonskiye solenosnyye for-

- matsii Pripyatskogo progiba. Minsk, Nauka i Tekhnika, 207 p.
- Lashkevich, Z. M., and Marushkin, A. I. 1982. Vulkanicheskiye formatsii Dneprovsko-Donetskoy vpadiny. Kiev, Naukova Dumka, 179 p.
- Lazar, B., and Holland, H. 1988. The analysis of fluid inclusions in halite. *Geochim. Cosmochim. Acta* 52: 485–490.
- Lowenstein, T. K.; Timofeeff, M. N.; Brennan, S. T.; Hardie, L. A.; and Demicco, R. V. 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. *Science* 294:1086–1088.
- Makhnach, A. S. 1966. Litologiya i geokhimiya devonskikh otlozheniy Pripyatskogo progiba v svyazi s ikh neftegazonosnostyu. Minsk, Nauka i Tekhnika, 315 p.
- McCaffrey, M. A.; Lazar, B.; and Holland, H. D. 1987. The evaporation path of seawater and the coprecipitation of  $\text{Br}^-$  and  $\text{K}^+$  with halite. *J. Sediment. Petrol.* 57:928–937.
- Petrychenko, O. I. 1973. Metody doslidzhennya u mineralakh galogenykh porid. Kyiv, Naukova Dumka, 91 p.
- . 1988. Fiziko-khimicheskiye usloviya osadkoobrazovaniya v drevnikh solerodnykh basseynakh. Kiev, Naukova Dumka, 125 p.
- . 1989. Epigenez evaporitov. Kiev, Naukova Dumka, 62 p.
- Petrychenko, O. I., and Shaidetska, V. S. 1998. Chlorek wapnia w solankach górnodewonskich basenów ewaporatowych ryftogenu prypecko-dnieprowsko-donieckiego w swietle badan inkluzji w halicie. *Przeegl. Geol.* 46:689–699.
- Petrychenko, O. I.; Slivko, E. P.; and Shaidetskaya, V. S. 1974. Ob usloviakh formirovaniya devonskoy kamennoy soli Dneprovsko-Donetskoy vpadiny. In Lazarenko, E. K., ed. *Perspektivy poiskov poleznykh iskopaemykh v Dneprovsko-Donetskoy vpadine*. Kiev, Naukova Dumka, p. 110–123.
- Petrychenko, O.; Peryt, T. M.; and Roulston, B. 2002. Seawater composition during deposition of Viséan evaporates in the Moncton Subbasin of New Brunswick as inferred from the fluid inclusion study of halite. *Can. J. Earth Sci.* 39:157–167.
- Roberts, S., and Spencer, R. 1995. Paleotemperatures preserved in fluid inclusions in halite. *Geochim. Cosmochim. Acta* 59:3929–3942.
- Sadykov, L. Z.; Borisenkov, V. I.; and Bogashova, L. G. 1981. Porovyye rastvory solenosnykh glin. In Valiashko, M. G., ed. *Zakonomernosti formirovaniya khimicheskogo sostava prirodnykh vod*. Moskva, Moskovskiy Universitet, p. 128–141.
- Schmalz, R. F. 1969. Deep-water evaporite deposition: a genetic model. *Am. Assoc. Petrol. Geol. Bull.* 53:798–823.
- Shaidetskaya, V. S. 1977. Zakonomernosti izmeneniy khimicheskogo sostava rastvorov vklucheniyy v galite iz kamennoy soli Kholmnskoy struktury Dneprovsko-Donetskoy vpadiny. In Kityk, V. I., ed. *Geologiya i geokhimiya solenosnykh formatsiy Ukrainy*. Kiev, Naukova Dumka, p. 100–104.
- . 1990. Usloviya khemogennoy sedimentatsii v pozdne-devonskikh solerodnykh basseynakh Dneprovsko-Donetskoy vpadiny. In Kityk, V. I., ed. *Geologiya i geokhimiya solenosnykh otlozheniy neftegazonosnykh povintsiy*. Kiev, Naukova Dumka, p. 101–106.
- . 1992. Izotopnyi sostav ugleroda karbonatov devonskoy kamennoy soli Dneprovsko-Donetskoy vpadiny i Pripyatskogo progiba. *Geol. Geokhimiya Goryuchykh Kopalyn* 2:58–63.
- Skachedub, E. A. 1986. Ispolzovaniye dannykh o sostave porod keprokov solanykh struktur dlya rekonstruktsii usloviy formirovaniya Dneprovsko-Donetskoy vpadiny v pozdnem devone. In Yanshin, A. L., ed. *Novyye dannye po geologii solenosnykh basseynov Sovetskogo Soyuza*. Moskva, Nauka, p. 154–158.
- Ulmishek, G. F.; Bogino, V. A.; Keller, M. B.; and Poznyakevich, Z. L. 1994. Structure, stratigraphy, and petroleum geology of the Pripyat and Dnieper-Donets basins, Byelarus and Ukraine. In Landon, S. M., ed. *Interior rift basins*. *Am. Assoc. Petrol. Geol. Mem.* 59: 125–156.
- Valiashko, M. G. 1962. Zakonomernosti formirovaniya mestorozhdeniy soley. Moskva, Moskovskiy Universitet, 397 p.
- Vlasova, N. K. 1981. Eksperimentalnoye izucheniye protsessov metamorfizatsii rastvorov morskogo galogeneza karbonatami i silikatami. In Valiashko, M. G., ed. *Zakonomernosti formirovaniya khimicheskogo sostava prirodnykh vod*. Moskva, Moskovskiy Universitet, p. 65–82.
- Vysotskiy, E. A.; Goretskiy, R. G.; and Kislik, V. Z. 1988. Kalienosnye basseyny mira. Minsk, Nauka i Tekhnika, 385 p.
- Yanshin, A. L. 1961. O glubine solerodnykh basseynov i voprosy formirovaniya solanykh tolshch. *Geol. Geof.* 1:3–16.
- Zharkov, M. A. 1984. Paleozoic salt bearing formations of the world. Berlin, Springer, 427 p.
- Zimmermann, H. 2001. On the origin of fluids included in Phanerozoic marine halite-Basic interpretation strategies. *Geochim. Cosmochim. Acta* 65:35–45.