Generation of primary sylvite: the fluid inclusion data from the Upper Permian (Zechstein) evaporites, SW Poland

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Abstract: The chemical composition of primary inclusions in sedimentary halite from the Polish Zechstein salt deposits (Upper Permian), which represent deposition in salt lagoon to salt pan-salina conditions of two evaporitic units of the Stassfurt and Leine cyclothems, contains evidence that the included brines belong to the Na–K–Mg–Cl–SO_4 (SO_4-rich) type. They differ from the brines typical for other Zechstein salts by having an elevated potassium content, which produced primary sylvite (daughter crystals in inclusions), caused by redeposition of locally generated potassium salts during inflow of fresh seawater into the sedimentary basin. The homogenization temperature of primary inclusions in halite with sylvite daughter crystals reflects the increased temperature (53–60 °C) of basin brines, caused by a greenhouse effect due to density stratification of the brines. Isotopic composition of the anhydrite (sulphur: 9.4–13.30‰ Canyon Diablo Troilite (CDT); oxygen: 9.44–10.4‰ Standard Middle Ocean Water (SMOW), as well as the bromine content in halite (49–77 ppm) indicated that these salts had a marine origin and were deposited at an elevated temperature, from concentrated seawater with a high potassium content, that favoured precipitation of primary sylvite.

Fluid inclusions in primary halite record the chemical composition of basin brines; however the primary origin of sylvite, present in these deposits, still remains controversial. Syndepositional origin of sylvite from most of ancient evaporitic basins is doubtful because of the lack of primary structures in sylvite crystals. The presence of such fluid inclusion structures (chevrons) in halite serves as evidence that the crystals have grown on the floor of the basin. These structures are known only in halite. Commonly crystals of sylvite contain high-pressure gas inclusions, the presence of which is unambiguous evidence for sylvite crystal growth (or recrystallization) during a postsedimentary (diagenetic) stage of the development of a salt deposit. The incongruent dissolution of carnallite has been suggested as the possible mechanism of sylvite formation (Borchert & Muir 1964; Braitsch 1971; Sonnenfeld 1984). On the other hand, Valyashko (1962), after a series of experiments in artificial solutions, showed that primary deposition of sylvite is possible in the case of a metastable pathway of evaporite crystallization. Lowenstein & Spencer (1990) reported apparent primary formation of sylvite in three deposits (Oligocene Rhine Graben, Alsace, France; Permian Salado Formation, New Mexico, USA; and the Devonian Prairie Formation, Saskatchewan, Canada). In Lowenstein's study, fluid inclusions in primary halite crystals contain daughter crystals of sylvite. Halite in these deposits crystallized from relatively hot brines, the cooling of which permits supersaturation with respect to KCl (Lowenstein & Spencer 1990).

Inclusions containing daughter crystals of sylvite within halite from the Polish Zechstein have been noted and studied. These inclusions form primary sedimentary structures. As a rule, these structures have the shape of chevrons or sometimes appear as cubic hopper crystals. Geochemical and fluid inclusion studies suggested a primary sylvite formation in the deposit. Dissolution of earlier formed potassium salts is the most probable origin of an elevated KCl content within the basin. Similar inclusions have also been noted in halite from the German Zechstein and the Devonian Starobinsk deposits of the Pripyat of Belarus (Petrychenko 1977) and the Permian Upper Kama Potash Deposit, Uralian Foredeep, Russia (unpublished author data). Taking into consideration the data from all these deposits, we can conclude that sylvite crystallization took place by cooling during deposition from brines, supersaturated with respect to KCl, and that this was the general mechanism of sylvite formation in most ancient potash-bearing deposits. During diagenesis many deposits of sylvite also may undergo significant recrystallization.

Geological setting

The Zechstein (Upper Permian) evaporites are present across more than half of Poland (Fig. 1),

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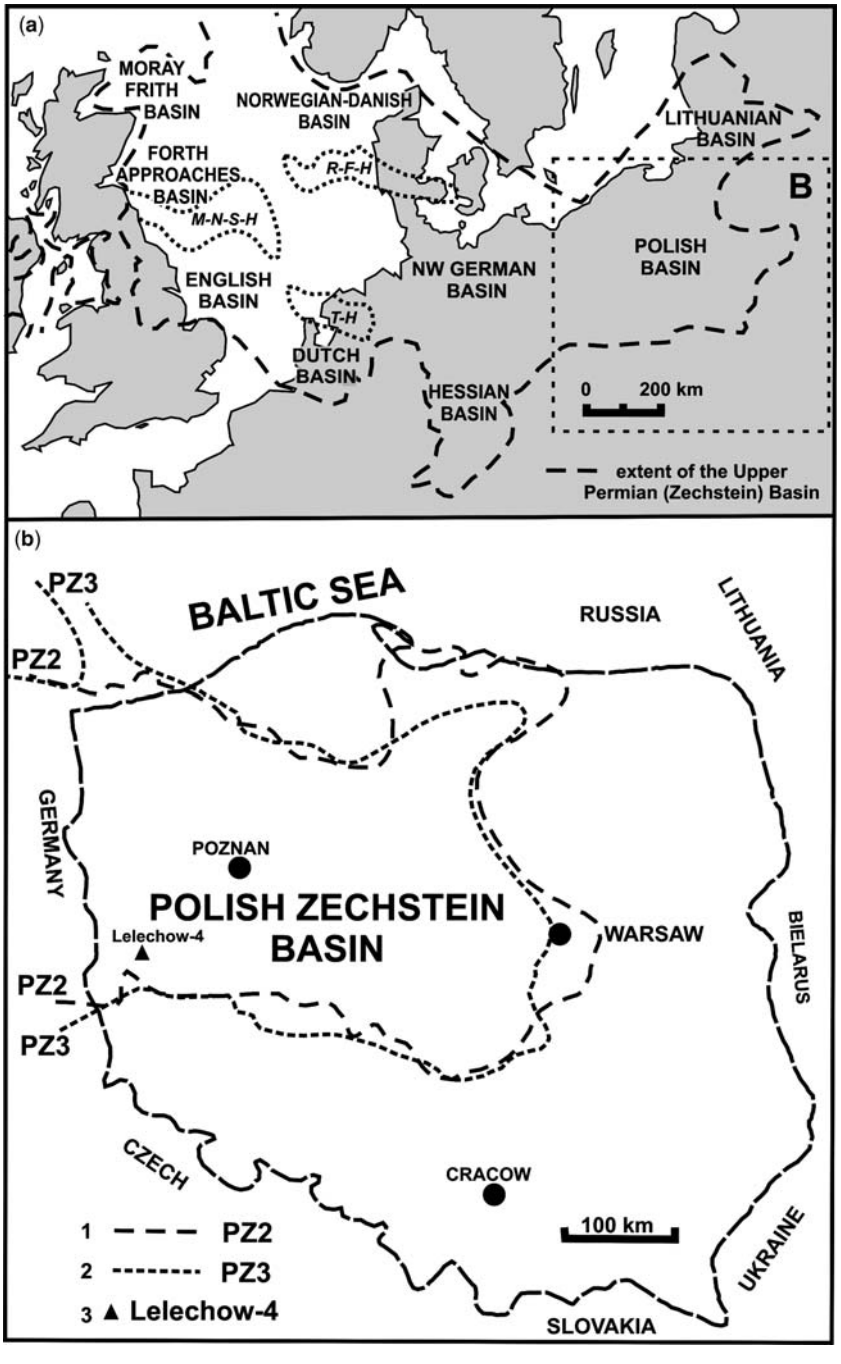

Fig. 1. Location of studied section with Zechstein (Upper Permian) evaporite units in Poland (**b**), belonging to the Zechstein Basin of Europe (**a**; basin contour after Smith 1980). 1, Present limit of PZ2 (with Older Halite unit) deposits; 2, present extent of PZ2 (with Younger Halite unit) deposits; 3, studied borehole Lelechow-4; M-N-S-H, Mid North Sea High; R-F-H, Ringkøbing-Fyn High; T-H, Texel High.

within the Polish sub-basin portion of the giant Zechstein Basin that stretched across much of Europe (Kiersnowski *et al.* 1995). It is made up of four major stratigraphic units, composed of sulphates, halite and potassium salts, separated by carbonates and siliciclastics, which together comprise four cyclothems: PZ1–PZ4 (Wagner *et al.* 1981; Wagner 1987), and are equivalent to the German stratigraphic cycles Z1 (Werra) to Z7 (Möln: Wagner & Peryt 1997).

Salts of the PZ2 cyclothem are divided into two rock salt members: the Older Halite (Na2; Czapowski *et al.* 1991; Czapowski 1995), and the locally developed Screening Older Halite (Na2r; Wagner 1994), separated by the potash salt member – Older Potash (K2; Wagner *et al.* 1981). The Older Halite member was initially deposited in relatively deep water conditions in the basin centre and in more shallow lagoons and salt pans of its margin, but that environmental pattern was subjected to successive shallowing phases and eventually separated into numerous salt pans and salinas during accumulation of the Older Potash and Screening Older Halite units (Czapowski 1991; Czapowski *et al.* 1991).

The rock salt member of PZ3 cyclothem is called the Younger Halite (Na3), and is subdivided by the potash salt member – Younger Potash (K3; Wagner 1994; Wagner *et al.* 1981) – into two units: the Lower Younger Halite (Na2a) and the Upper Younger Halite (Na3b), with thickness ranging from a few up to 240 m (Czapowski 1993). Locally the uppermost part of Upper Younger Halite contains dispersed clay matter and it is distinguished as a separate unit, the Younger Clayey Halite (Na3t). Salts were deposited initially in the relatively shallow open basin, framed by lagoons and salt pans along its margins, but due to a successive brine level drop (and/or sediment infill) salinas, salt pans and shallow lagoons predominated during accumulation of potash and upper rock salt members (Czapowski 1991, 1993). Studied halite samples of both Na2 and Na3 rock salt members were taken from the borehole Lelechow-4, located in the SW margin of the Polish Zechstein Basin (Fig. 1).

The Older Halite (Na2) member is sharply underlain by the laminated to nodular anhydrite of the Basal Anhydrite (A2) member and overlain by nodular anhydrite of the Screening Anhydrite member (A2r) topped with the claystone bed of the Grey Pelite (T3). Rock salt is semitransparent to opaque, red, pink and orange in the lower part but grey and orange in the upper portion, it contains dispersed clay matter and fine aggregates of anhydrite and carnallite. The halite is heteromorphic, with crystal size from 3 to 20 mm, cloudy (having partial, inclusion-rich zonation), and hopper crystals are relatively frequent and locally occur in clusters as 3 cm 'nests' of secondary giant halite as well as displaying solution/erosion scours lined with sulphates and clay matter. In the whole member there are sections observed as horizontal to gently undulating fine anhydrite laminae, present in groupings from 1 to 10 cm in thickness. This salt unit apparently was deposited in the shallow salt lagoon and pan environments as defined by the salt facies criteria in Table 1 (Czapowski 1995). The bromine content in equivalent salts of pan facies from nearby wells varies from 119 ppm to 160 ppm (Kovalevych *et al.* 2000).

The Older Potash (K2) member, absent in the studied well, is present in many boreholes located just to the north of this study area and consists of halite + anhydrite + polyhalite and halite + sylvite interbeds decimetres to metres thick (Podemski 1972).

The next salt bed in the borehole Lelechow-4 is the lower unit of the Younger Halite (Na3) member, called the Lower Younger Halite (Na3a) unit (22.5 m thick). It is underlain with a 15 m thick Main Anhydrite (A3) member and is overlain by Younger Potash (K3) member, composed of halite + anhydrite + polyhalite and sylvite + kieserite + polyhalite beds (Podemski 1972). These apparently originated in the shallow lagoon to salina environments. The bottom part of the Na3a unit is made up of beige to pink, semitransparent, almost monomorphic halite, with an average crystal size 2–3 mm and common fine parallel laminae of anhydrite. This part of Younger Halite member was deposited in the shallow open salt basin but features of the upper portion one include heteromorphic and secondary giant halites, cloudy crystals indicative of accumulation in a progressively shallowing lagoonal conditions. Bromine content in equivalent salts of shallow salt lagoons, analysed in nearby wells, varies from 45 to 60 ppm, suggesting frequent dissolution/erosion events in less saline waters (Kovalevych *et al.* 2000). Also the shallow lagoon to salt pan conditions, with erosion of Older Potash sediments at the beginning, is evidenced by inclusion composition data in a nearby well (Kovalevych *et al.* 2000), characterizing deposition of the Upper Younger Halite (Na3b) member, topping the evaporitic succession of the PZ3 cyclothem. Discussed units are presented in the profile of rocks of the Lower Red Pelite (T4a) and Youngest Halite (Na4a) members (Fig. 2).

Fluid inclusions

Primary sedimentary structures were revealed in halite from six samples (Fig. 2). The fluid inclusions that form these structures are of negative crystal

Table 1. *Features of fossil salt facies from the Upper Permian (Zechstein) rock salt deposits in Poland (after Czapowski 1995)*

Facies	Lithology	Structures	Br content (ppm)
Deep salt basin (I)	Common primary banded halite (C) and salt rhythmites; dominant salt sequences: A + C, A + B + C; sulphates as laminae; sporadic K–Mg salt	Common 'internal lamination' in primary banded halite (LC) and fine sulphate lamination, rare hopper, raft halite and halite intraclasts	30–250, sporadically >300
Shallow salt basin (II)	Rare C-halite, sporadic secondary giant halite (D) and salt rhythmites; dominant salt sequences: A + B, A + C, B + C; sulphates as laminae and nodules; sporadic terrigenous material (T)	Rare LC and fine sulphate lamination; common hopper halite, halite intraclasts and erosion boundaries; rare raft and chevron halite	40–200
Deep salt lagoon (IIIA)	Frequent C-halite, rare salt rhythmites; dominant salt sequences: B + C, A + B; sulphates as laminae; locally K–Mg salt; sporadic T	Frequent LC and fine sulphate lamination; common hopper and raft halite; rare halite intraclasts, chevron halite and erosion boundaries	20–330
Shallow salt lagoon (IIIB)	Rare C-halite, D-halite and salt rhythmites; dominant salt sequences: B + A, B + C; sulphates as laminae and nodules; common T	Rare LC, fine sulphate lamination, raft and hopper halite; frequent halite intraclasts, chevron halite and erosion boundaries	40–100
Salt pan (IV)	Absent C-halite and salt rhythmites, common D-halite; dominant salt sequences: A + B, B + D; sulphates as laminae and nodules; common T; sporadic K–Mg salt	Structures as in facies IIIB, absent LC	10–80 (sporadic 260)
Salina (IVs)	Lithology as in IIIB and IV facies, common K–Mg salt	Structures as in facies IV	>300

A, Monomorphic halite; B, polymorphic halite.

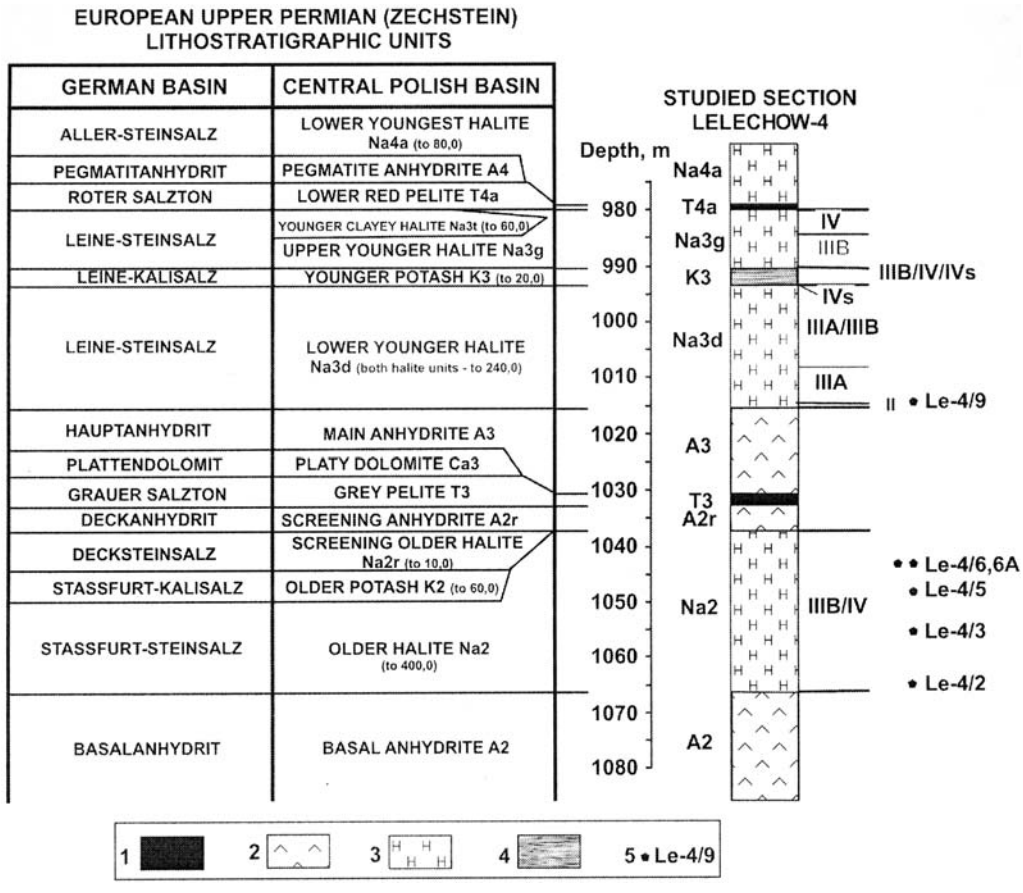

Fig. 2. Simplified profile of studied evaporite units in the Lelechow-4 borehole, shown together with the corresponding part of general stratigraphic succession of the German and the Central Polish Zechstein basins (stratigraphic units after Wagner 1987, 1994). 1, Claystone; 2, anhydrite; 3, rock salt (halite); 4, K–Mg salt (potash); 5, samples in which primary fluid inclusions with daughter crystals of sylvite have been revealed; salt facies: II, open shallow basin; IIIA, deep lagoon; IIIB, shallow lagoon; IV, salt pan; IVs, salina; Na2, A2, lithostratigraphic units (see text); (22,5), unit thickness (in metres).

(cubic) shape and contain daughter crystals of sylvite (Fig. 3) which make up 2–2.5% of inclusion volume.

Sedimentary structures (chevrons) are present in samples Le-4/2, 3, 5, 6, 6A outlined by fluid inclusions with size from a few micrometres to 80 μm (in Le-4/2 sample to 150 μm). In the Le-4/2 sample were also revealed rare cubic hopper crystals and solid inclusions of sylvite in halite. Chevron structures in halite from sample Le-4/9 are formed by rather small (up to 20 μm) two-phase fluid inclusions.

Methods

The chemical composition of brines from individual fluid inclusions was determined by means of an ultramicrochemical (UMCA) method (Petrychenko 1973). This method allows determination of the content of K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} ions in brines. The analytical error is 15–23% for K and Mg and 37–43% for Ca and SO_4. In order to improve quality of our results we ran a few analyses of each ion. The minimal inclusion size necessary for analyses is 40 μm. Na and Cl ion content within the limits of the method precision could be worked out from the tables (McCaffrey *et al.* 1987).

The data for potassium content obtained by the UMCA method do not include the amount of this ion in daughter crystals, which were precipitated from the inclusion brine and thus should be included in the total. The quantity of potassium in daughter crystal of sylvite was estimated by comparison of optically determined volumes of

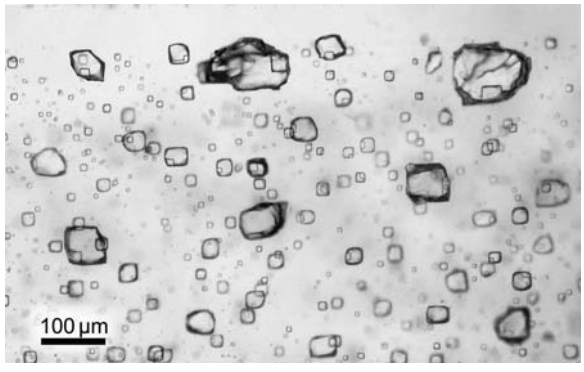

Fig. 3. Fragment of chevron structure in halite, outlined by fluid inclusions with daughter crystals of sylvite. Sample Le-4/2.

inclusion and crystal. This was possible because both negative crystal-shaped inclusions in halite and sylvite daughter crystals are close to cubic shape (Fig. 3). Under the microscope we measured two out of three edges of the cube; the third was taken as an average between the measured ones. Total potassium content was calculated by summing up amounts of K from inclusion brine and sylvite daughter crystals.

The homogenization temperatures (the end of sylvite daughter crystal dissolution in a heated halite plate) were measured under the microscope in cleavage fragments of chevron halite. A modified heat-chamber designed by Kalyuzhny has been used in this study (Kalyuzhny 1982). This camera allows measurement of the temperature with an accuracy of ± 1 °C. The heating velocity utilized in this study was 0.2 °C/min. In each sample seven to 20 inclusions were investigated.

Br content was determined by means of X-ray fluorescent spectrometry. Halite samples were pretreated in order to eliminate Br-enriched fluid inclusion brines. Artificial standards were made by adding solid NaBr to halite samples in which Br content was below the sensitivity of measurement using this method. Measurements were made using a Phillips PW2400 spectrometer. Analytical error was 3%.

The isotopic composition of sulphate sulphur and oxygen was studied in the laboratory of Barcelona University. The samples were dissolved in boiling water and then filtered to remove insoluble residue (mainly silicates and carbonates). Dissolved SO_4^{2-} was precipitated with excess $BaCl_2$ at pH values 1–2, which prevented simultaneous $BaCO_3$ precipitation. $BaSO_4$ was then filtered and dried at 120 °C. $\delta^{18}O$ values were determined from CO, which was obtained by heating the admixture of $BaSO_4$ and graphite. $\delta^{34}S$ values were determined from SO_2, which was obtained by heating the admixture of $BaSO_4$ and V_2O_5. The analytical error was 0.3% for $\delta^{34}S$ and 0.4% for $\delta^{18}O$.

Results

The major ion content is given in Table 2. The potassium content determined with UMCA method varies from 36 to 44 g l^{-1} but it was worked out that the total content of this ion (at an increased homogenization temperature) in the included brine was 20–25 g l^{-1} higher and thus reached 56–70 g l^{-1}.

Homogenization temperatures of the studied fluid inclusions are between 50 and 135 °C (Table 3). Most of the data fall within the range 53–60 °C; in individual plates temperatures higher than 80 °C were also registered. Br content values fell within range 49–77 ppm (Table 4).

Table 2. *Chemical composition of inclusion brines and Janecke units*

Sample	Chemical composition, g l^{-1} (average of 2–4 analyses)			Janecke units		
	K^+	Mg^{2+}	SO_4^{2-}	2K	Mg	SO_4
Le-4/2	44	72	55	14	72	14
Le-4/5	45.2	42.5	12.4	24	71	5
Le-4/6A	35.7	47.15	3	19	80	1
mSW	3.9	12.6	17.6			
mSW*	27.1	85.9	115			

mSW, modern seawater concentrated to the beginning of halite precipitation (McCaffrey *et al.* 1987); mSW*, modern seawater concentrated to the beginning of sylvite precipitation (McCaffrey *et al.* 1987).

Table 3. *Homogenization temperatures of inclusions in chevron halite*

Sample	*T* (°C)
Le-4/2	59; 59; 59; 59; 60; 60; 60; 60; 60; 60; 61; 61; 61; 61 (60)
Le-4/3	plate 1: 57; 58; 60; 60; 60; 60; 61 (59) 82; 84; 85; 85; 85; 90; 92; 104; 106; 135 plate 2: 51; 52; 52; 53; 53; 54; 55; 56; 57; 57; 57; (54) 89; 96; 98; 105
Le-4/5	50; 53; 54; 54; 55; (53) 82; 94; 109
Le-4/6	51; 52; 52; 52; 52; 53; 54; 54; 54; 54 (53)
Le-4/9	56; 56: 57; 57; 58; 58; 58; 58; 59; 59 (58)

In brackets is shown the average of results considered as corresponding to basin brine temperatures (see text).

The results of a study of oxygen isotopic composition were between 9.44 and 10.41‰ SMOW; that of sulphate sulphur was between 9.42 and 13.30‰ CDT (Table 5).

Table 4. *Bromine content in halite*

Sample	Br (ppm)
Le-4/2	77
Le-4/10 A	79
Le-4/15	49

Table 5. *Isotopic composition of sulphate sulphur and oxygen in studied salts*

Sample	$\delta^{34}S$ (‰ CDT)	$\delta^{18}O$ (‰ SMOW)
Le-4/2	9.44	9.42
Le-4/10a	10.41	13.30
Le-4/15	9.52	12.70

Interpretation and discussion

Zechstein salts are undoubtedly of marine origin (Braitsch 1971). This notion is confirmed by numerous fluid inclusion studies (Kovalevych *et al.* 2000; Vovnyuk *et al.* 2004). The results of our study of chemical composition of brines from individual primary inclusions in halite from borehole Lelechow-4 (Table 2) also confirm the marine origin of studied salts and are in good agreement with the existing notion about the Na–K–Mg–Cl–SO_4 (SO_4-rich) brine type of Zechstein evaporite basin (Kovalevych *et al.* 2000; Vovnyuk *et al.* 2004). The SO_4/Mg ratio of the studied inclusion brines is lower than that of concentrated modern seawater (McCaffrey *et al.* 1987) and is typical for Late Permian seawater (Kovalevych *et al.* 1998, 2002). Furthermore, in studied brines an anomalously high potassium content was detected. The potassium content calculated from UMCA analyses is 36–44 g l^{-1}. Taking into account the additional K from daughter crystals we can estimate that real potassium content in inclusion brines before sylvite precipitation was approximately 20–25 g l^{-1} higher and reached 56–70 g l^{-1}. This is more than twice the maximum possible concentration of this ion at saturated modern seawater (McCaffrey *et al.* 1987). Such high K content could be reached due to redeposition of earlier formed sylvinite deposits and increased temperature of basin brines.

Most of the homogenization temperatures (the end of sylvite daughter crystal dissolution in a slowly heated plate of chevron halite) fall within narrow range of 50–62 °C. These data reflect the temperature of salt precipitation (Fig. 4). Such temperatures could be reached due to a basinal greenhouse effect within a density-stratified brine column. Thus, the lower, bottom layer of basin brines was heated to this temperature during crystal growth. The brine stratification is confirmed by the occurrence of cubic hopper crystals. Such crystals precipitate when brines of different saturation are mixed, which apparently happens in stratified basin brines (Raup 1970). The individual inclusions show significantly higher homogenization temperatures (up to 135 °C). These results do not reflect the actual temperature in the sedimentary basin; extremely high temperature values and a wide range of data allow us to interpret them as the result of sporadic trapping of sylvite crystals by growing halite.

Salts in studied area precipitated from brines with potassium concentration about 70 g l^{-1} and with temperature about 50–60 °C. Cooling of these brines made it possible to reach supersaturation with respect to K, which favoured primary sylvite precipitation. The points of brine composition of all three studied samples on a Janecke diagram for a six-component system, Na–K–Mg–Ca–SO_4–Cl–H_2O at 25 °C (Eugster *et al.* 1980), are within the sylvite stability field, which could be considered as reasonable evidence for sylvite precipitation (Fig. 5). This mechanism was described by Lowenstein (Lowenstein & Spencer 1990) as major for primary formation of sylvite in three ancient basins (Oligocene Rhine Graben, Alsace, France; Permian Salado Formation, New

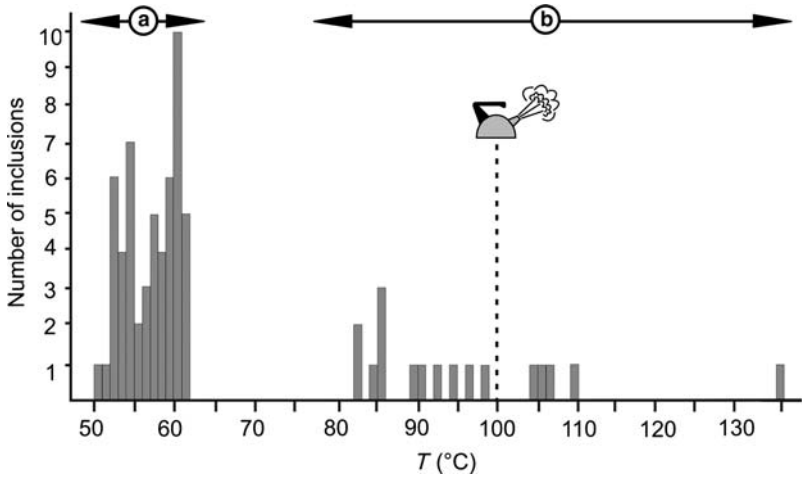

Fig. 4. Histogram of homogenization temperature data (as shown in Table 3). (**a**) Data that reflect the real temperature of basin brines during precipitation of studied halite; (**b**) data considered by us as a result of sporadic trapping of sylvite crystals by growing halite.

Mexico, USA; and the Devonian Prairie Formation, Saskatchewan, Canada). Halite in these deposits crystallized from relatively hot brines (at temperatures 39–71 °C, the cooling of which favoured primary sylvite precipitation. Primary halite from these formations also contains fluid inclusions with daughter crystals of sylvite. The presence of such inclusions in halite are considered as evidence that conditions for sylvite precipitation from basin brines existed in the basin. Such inclusions are also described in halite from other two deposits (German Zechstein and Prypiat Trough; Devonian Starobinsk Deposit, Pripyat, Belarus; Petrychenko 1977). Recently inclusions with daughter crystals of sylvite have also been discovered in primary halite from Lower Permian salts of Uralian Foredeep (Upper Kama Potash Deposit, Russia; unpublished author data). Taking into consideration the data from seven deposits of different ages we can conclude that sylvite crystallization from brines, supersaturated with respect to KCl by cooling, was the general mechanism of sylvite formation in most of ancient potash-bearing deposits. During diagenesis of the deposit formation sylvite underwent significant recrystallization.

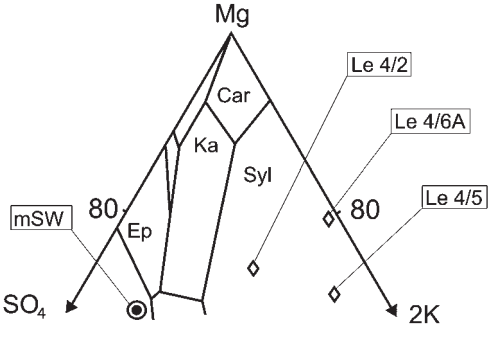

Fig. 5. Chemical composition of individual inclusion brines (as shown in Table 2), plotted on Janecke diagram (Eugster *et al.* 1980) for a six-component (Na–K–Mg–SO_4–Cl–H_2O) system at 25 °C. Stability fields: Car, carnallite; Ka, kainite; Ep, epsomite; Syl, sylvite. mSW, point of composition of modern seawater, concentrated to halite precipitation (McCaffrey *et al.* 1980).

The bromine content in these studied samples (Table 3) is typical for salts of marine origin. However, taking into account the high stage of brine concentration, the Br content could exceed 160 ppm (Bilonizhka 1975) or even reach 270 ppm (Valyashko 1962), so we can consider the values of this component, obtained in this study, as quite low. To our opinion this evidences dissolution and redeposition of earlier formed salts. The dissolution had taken place after inflows of fresh portions of less concentrated seawater into this sedimentary basin. The role of non-marine waters in this process was apparently insignificant, which is confirmed not only by Br content but also by sulphate sulphur and oxygen isotopic composition (Table 5), which is typical for Permian marine sulphate (Claypool *et al.* 1980; Strauss 1997).

Conclusions

The chemical composition of primary inclusions in sedimentary halite from the Polish Zechstein belongs to the Na–K–Mg–Cl–SO_4 (SO_4-rich)

type and differs from the composition typical for other Zechstein salts by an elevated potassium content. The high K content in basin brines was caused by redeposition of potassium salts during inflow of fresh seawater into the sedimentary basin. The homogenization temperature of primary inclusions in halite with sylvite daughter crystals reflects the increased temperature (53–60 °C) of basin brines, caused by a greenhouse effect due to density stratification of the brines. After study of sulphur isotopic composition of the anhydrite as well as the bromine content in halite, the conclusion has been drawn that these salts had a marine origin and that there was an insignificant role of non-marine waters.

Finally we conclude that the Zechstein salts studied here were deposited with major contributions due to intrabasinal redeposition, at an elevated temperature, from concentrated seawater with a high potassium content. These conditions favoured precipitation of primary sylvite.

Together with the consideration of data from several other deposits, we can assume that primary sylvite precipitation from brines supersaturated by cooling was the typical mechanism of sylvite formation in many ancient potash-bearing basins.

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