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FLUID INCLUSIONS IN SALT - AN ANNOTATED BIBLIOGRAPHY

Dana J. Isherwood

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FLUID INCLUSIONS IN SALT - AN ANNOTATED BIBLIOGRAPHY

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ABSTRACT

This annotated bibliography was compiled while searching the literature for information on fluid inclusions in salt for the Nuclear Regulatory Commission's study on the deep-geologic disposal of nuclear waste. The migration of fluid inclusions in a thermal gradient is a potential hazard to the safe disposal of nuclear waste in a salt repository. At the present time, we cannot predict whether this hazard precludes the use of salt for waste disposal. Limited data from the "Salt-Vault" in situ heater experiments in the early 1960's (Bradshaw and McClain, 1971) give little doubt that fluid inclusions can migrate towards a heat source. In addition to the bibliography, there is a brief summary of the physical and chemical characteristics that together with the temperature of the waste will determine the chemical composition of the brine in contact with the waste canister, the rate of fluid migration, and the brine-canister-waste interactions.

SUMMARY

PHYSICAL CHARACTERISTICS

Size. The size of an inclusion varies greatly within any one sample. Sizes from 2 or 3 microns to 250 microns are common, however, inclusions of several millimeters can easily be found in many deposits.

Shape. There is a wide variety of forms in the larger inclusions--tubular, crab-like, bent channels, etc. It is characteristic that the smaller the inclusion, the more its shape approaches a cubic or rectangular configuration.

Distribution. The distribution of inclusions is usually irregular and depends on the crystallization history of the salt. The volume of liquid inclusions can be surprisingly high--as much as 10-28% of the overall volume of a sample (Petrichenko, 1973).

Bedded salt vs. dome salt. There are differences in the amount and type of fluid inclusions present in layered salt and dome salt. These differences could favor salt domes for nuclear waste disposal.

1. In the formation of salt domes, sedimentary halite undergoes plastic deformation at elevated temperatures. Recrystallization of the salt under these conditions favors the formation of gaseous inclusions (Petrichenko, 1973). Anthony and Cline (1974) have shown that inclusions with a high gas to liquid ratio will migrate away from a heat source.
2. Since salt domes generally contain less water than bedded salt, they have greater thermal stability. Bradshaw et al (1968) found dome salt resisted fracturing up to 400°C, while bedded salt fractured at between 260 and 380°C in 43 out of 45 samples.

CHEMICAL CHARACTERISTICS

Currently, little is known about the chemistry of fluid inclusions in salt. The Russian literature is the only major source of information on chemical

composition. The Russians have devised a number of creative techniques for analyzing micro-inclusions (Petrichenko, 1973). Unfortunately, these techniques have not been tested by American researchers; hence, Russian data, especially analyses of trace constituents, Eh and pH, should be viewed with caution.

Composition. Fluid inclusions start out as samples of fluids that are present when the salt crystallizes. These inclusions undergo changes upon cooling, often resulting in the formation of gas and/or solid phases. All three phases may be present in a single inclusion. Some researchers believe single phase liquid inclusions are meta-stable (E. Roedder, personal communication).

Fluid inclusions in salt are generally composed of Ca-Mg brines with varying amounts of Na^+ , K^+ , Cl^- , SO_4^{2-} and trace constituents. Solid phases reportedly found in fluid inclusions in salt are sylvite (KCl), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). Gas phases may be composed of but are not limited to water vapor, CO_2 , CH_4 , H_2 and H_2S .

As stated above, the composition of an inclusion is initially linked to the composition of the fluid when the surrounding crystal forms. For this reason, inclusions that are formed at different periods of crystal growth can and do have dissimilar chemical compositions. Post-depositional processes (e.g., multiple sequences of re-crystallization) will subsequently alter the original composition. A combination of depositional and post-depositional conditions can create a wide variation of composition in a single deposit (Figure 1). Even adjacent inclusions may have compositional differences of one or two orders of magnitude.

Eh/pH. Measurements of Eh and pH are limited to a few Russian studies. The Russian samples showed pH values that are generally acidic (3.5 to 6.5). Eh for individual inclusions ranged from -260 to +320 mV. Petrichenko (1973) found that fluid inclusions in sedimentary halite tend towards the higher oxidation potentials, while inclusions in salt domes are typically reducing.

FIGURE 1
Russian analyses of brine inclusions in halite

ACKNOWLEDGEMENTS

A special thanks is due Dr. Edwin Roedder (U.S. Geological Survey) for giving so generously of his time and for allowing me a preview of his next volume of Fluid Inclusion Research.

ANNOTATED BIBLIOGRAPHY

Most of the abstracts in this bibliography were taken directly from Fluid Inclusion Research (E. Roedder, Editor), the most comprehensive source of information on fluid inclusions available. A search was also done using the on-line computer information retrieval system: DOE/RECON, SCI (Science Citation Index), and CHEM ABSTRACTS.

ANTHONY, T.R., and CLINE, H.E., 1974, Thermomigration of liquid droplets in salt, in Fourth symposium on salt, v. 1, p. 313-321, A.H. Coogan, ed.: Cleveland, Ohio, Northern Ohio Geological Society.

Although salt burial is generally considered a good method for nuclear waste disposal, the vigorous self-heating of these waste products leads to some potential problems. Natural salt formations regularly contain small brine inclusions which will migrate up the thermal gradients generated by the self-heating of the waste products. The resulting inflow of brine around the waste canister is undesirable because the brine may accelerate the waste canister corrosion and lead to radionuclide contamination of currently unused sections of the repository. In addition, contaminated vapor-liquid biphasic droplets generated on the walls of the canister hole are capable of dispersing fission products throughout the salt formation since these unusual inclusions migrate down thermal gradients, in contrast to the normal thermomigration of simple gas or liquid droplets up thermal gradients in salt. By considering viscous gas flow, vapor diffusion, liquid diffusion, evaporation and condensation, and liquid currents driven by surface tension gradients, the odd thermomigration behavior of the vapor-liquid droplets observed in the present investigation is explained. It is concluded that a modest dispersal of radioactive wastes may occur in the salt formation. However, because of droplet trapping by the grain boundaries in the salt, the escape of radioactivity to the outside environment is unlikely even on a geological time scale. (From the Authors' abstract)

BORISHENKO, A., 1977, Cryometric techniques applied to studies of saline composition of solutions in gaseous-fluid inclusions in minerals: Geol. Geofiz., Issue 8, p. 16-27 (in Russian).

BRADSHAW, R., and MC Clain, W., 1971, Project salt vault: A demonstration of the disposal of high activity waste in underground salt mines: Oak Ridge National Laboratory, ORNL-4555.

This report includes 14 sections on the Project Salt Vault experiment for evaluating the feasibility of storing high-level solid radioactive wastes in salt deposits. To determine the effects of radiation on salt at temperatures between 100 and 200°C, reactor fuel assemblies were placed in holes and carefully monitored. Brine collected in the holes as a function of time gave approximate migration rates for fluid inclusions of 0.43 to 9.75 cm/year.

BRADSHAW, R.L. and SANCHEZ, F., 1969, Migration of brine cavities in rock salt: J. Geophy. Research v. 74, p. 4209-4212.

Small quantities of brine trapped in negative crystals (cavities) exist in most rock salt (halite) and have been found to migrate toward a heat source. The theory of Hoekstra and others on the migration of liquid inclusions in ice crystals was modified for predicting the migration rates of brine cavities in salt. The driving force for the migration is the difference in solubility between the warm and colder sides of the brine cavity. The theoretical model indicates that the migration rate is a function of temperature and is directly proportional to the temperature gradient. Calculated cavity migration rates for a 1°C/cm gradient ranged from about 0 at 20°C to 7.7 cm/yr at 300°C. The theoretical predictions were found to be in reasonable agreement with migration rates measured in the laboratory, although there was considerable spread in the experimental data. Specimens consisted of relatively pure salt crystals from the Hutchinson, Kansas mine, about 2-1/2 cm on a side, containing brine cavities between 2 and 10 mm in maximum dimension. Thirty-one rate measurements (on twelve separate cavities) were obtained, covering the temperature range of 75°-244°C, with gradients ranging from 4 to 34°C/cm. Migration periods varied from about 20 to 358 hours, and the observed distances of migration ranged from 0.8 to 8 mm. The theoretical predictions also tended to confirm the approximate (but difficult to measure) rates of brine migration into a number of heated holes (salt wall temperatures up to 200°C) located in the Kansas mine. (Authors' abstract)

BROWNE, P., ROEDDER, E., and WODZICKI, E., 1976, Comparison of past and present geothermal waters from a study of fluid inclusions: Geological Survey (Prague).

BURRUSS, R., 1978, Thermodynamic framework for analysis of fluid inclusions -- Binary-systems $\text{CO}_2\text{-CH}_4$ and $\text{H}_2\text{O-NaCl}$: Trans. AGU, 59, p. 226.

Assuming a fluid inclusion has a constant composition and constant volume (i.e., no leakage), observation of phase equilibria in that inclusion as a function of temperature on a cooling and heating stage allows description of the thermodynamic properties of the trapped fluid with the Helmholtz free energy (A) for which $dA = -SdT - PdV + \sum \mu_i dn_i$. In a fluid inclusion containing a binary fluid, observation of a univariant phase transition defines a tie-line connecting the molar volume ($\bar{V}$) and composition (X) of the coexisting phases at that temperature. Observation of a second transition at a different temperature defines a second tie-line connecting ($\bar{V}$) and (X) of the coexisting phases at that temperature. The projected intersection of these two tie-lines in $\bar{V}$ -T-X space (Helmholtz free energy space) uniquely defines both $\bar{V}$ and X of the bulk, one-phase fluid. Phase diagrams constructed from literature data for the $\text{CO}_2\text{-CH}_4$ and $\text{H}_2\text{O-NaCl}$ systems quantitatively illustrate the method.

To analyze the immiscible $\text{CO}_2\text{-H}_2\text{O}$ system, it is necessary to assume the mixing properties of $\text{CO}_2\text{-H}_2\text{O}$ fluids and make an estimate of the relative volume % occupied by the coexisting phases at constant temperature (40°C). Given this, it is possible to combine the $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O-NaCl}$ systems and estimate the ($\bar{V}$) and (X) of fluids in the quaternary $\text{CO}_2\text{-CH}_4\text{-H}_2\text{O-NaCl}$ system. (Author's abstract)

DEREVYAGIN, V.S., 1973, Investigations of some microelements in liquid inclusions of rock salt from South of Middle Asia: Abstracts of papers at Fourth Regional Conference on Thermobarogeochemistry of Mineral-Forming Process, 24-30 Sept., 1973: Rostov, Rostov Univ. Press, pp. 167-168 (in Russian; translation provided to Fluid Inclusion Research by A. Kozlowski).

Samples of Upper Jurassic and Lower Cretaceous halite, sylvite and carnallite were extracted for separation of solutions from microinclusions by absolute ethyl alcohol using the routine mode (Slivko and Petrichenko 1967). Three fractions: fresh salt rock, dry residue of alcohol leachates, and salt after extraction were analysed for Li, Rb, Cs, Tl, B and Br.

Following results were received:

1. Li and Cs were found in all analysed dried alcohol leachates in trace amounts (0.0001%). Cs is present in trace amounts in samples of carnallite washed with alcohol. Li and Cs accumulate in solutions during crystallization of salts of various composition, and Cs accumulates in carnallites.
2. The amount of Rb in the dried residue of alcohol leachates regularly increases from halite to carnallite: 0.0022-0.0024-0.0030%, also proving the accumulation of Rb in solution during salt crystallization. The amount of Rb in sylvite and carnallite after washing with alcohol remains relatively high (2-10 times more than in the solutions). For this reason, it seems that Rb accumulates mainly in the solid phase of these K-salts.
3. The lack of Tl (<0.0001%) in all fractions of carnallite rock supports the conclusions (Malikova, 1967) on precipitation of this element in the solid phase before crystallization of Carnallite. In halite the concentration of Tl is equal 0.0002, 0.0015 and 0.0001% respectively, i.e., amount of Tl in liquid inclusions in halite is nearly 10 times higher than in the host mineral.
4. Concentration of B in all types of rocks is lower than the sensitivity of method of determination ($B_2O_3 < 0.01$).
5. On the basis of calculated bromine/chlorine ratios (4.8-8.0) in inclusions of brine in halite of various age saline formations from Middle Asia, similar ratios were calculated for halite crystallized from solutions included in fluid inclusions (0.18-0.30). The last values are lower than normal ones (0.11-0.087), as obtained during evaporation of ocean water. Br/Cl data are given as an index: $Br \times 1000/Cl$.

Sedimentary solutions, developed in the salt rocks, and in underlying and overlying deposits are also characterized by low bromine/chlorine ratios. Probably the brine of the parent salt basins of J₃ and C₁ age was poor in

bromine. On the other hand, the calculated ratios for halite are 2-3 times (for salts of J₃ age) and 15-30 times (for salts of C₁ age) higher than the analytical determinations on samples of fossil salt (halite) from the region discussed.

Results: 1) statement of forms of occurrence of trace elements in salts and ascertaining of the mechanism of accumulation of these elements during crystallization of salt; 2) proposition of existence of additional factors (discussed in another paper), leading to decrease of amount of Br in salt rocks.

Some solutions from this area that have concentrations of Li, B and I that are sometimes higher than in solutions of liquid inclusions, evidently had, in addition to ocean water, additional sources of enrichment of these elements. (Authors' abstract).

GAFFNEY, E., and CHEUNG, H., 1978, Migration of fluid inclusions in salt adjacent to a radioactive waste canister: EOS, Trans. AGU, 59, p. 1065.

Inclusions of bittern brine are common in bedded salt deposits; at the site of the WIPP they account for about 0.5 percent water by weight (about 1 percent brine by volume). These inclusions will migrate under the influence of temperature and pressure gradients. For inclusions larger than 1 mm and temperatures above 100°C the governing equation for migration velocity (v) is

$$v = - \frac{D C_h}{\rho} \left[\left(\frac{\partial \ln C_h}{\partial \phi} + v \right) \frac{d\phi}{dx} \right]$$

where D = diffusion coefficient; C_h = concentration of host in solution; ρ = density of host mineral; φ = temperature (T) or pressure (P); v = Soret coefficient if φ = T or v = $\bar{V}_s/RT$ with $\bar{V}_s$ being the partial molar volume of host and R being the gas constant if φ = P; and X = distance along φ gradient. Smaller inclusions will move slower. Applying this relation to the situation of Project Salt Vault an accumulated brine volume of 13 to 26

liters per canister is calculated. This is 2 to 3 times the amount of steam condensate reported for that test. However, when allowance is made for vapor pressure effects in the brine, the two values are quite consistent. Extrapolation to a 10 year retrieval period in WIPP would indicate 15 to 40 liters of brine accumulation. (Authors' abstract)

GEGUZIN, Ya.E., and DZYUBA, A.S., 1973a, The investigation of liquid inclusions in a rock-salt crystal in the entire temperature interval of their existence: *Kristallografiya*, v. 18, no. 4, p. 813-818 (in Russian).

The behavior of inclusions of saturated aqueous solution in natural single crystals of NaCl was examined from the temperature of crystallization to temperatures exceeding the critical state of the material of the inclusions, when it passed into the gaseous phase. Frames from motion picture sequences are presented, showing the behavior at temperatures up to 410°C, and after subsequent cooling. (Abstract by E. Roedder)

GEGUZIN, Ya.E., and DZYUBA, A.S., 1973b, Study of liquid inclusions in rock salt crystals in the entire range of their existence: *Kristallografiya*, v. 18, no. 7, p. 800-807 (in Russian).

Influence of heating and cooling on liquid inclusions in natural single crystals of NaCl was studied visually. Vapor phase appears at ~370°C and inclusions become homogeneous at ~410°C. Heating leads to plastic deformation of the crystals which results in increasing volume of the inclusion. This deformation can be measured by estimation of the volume of residual gas phase at room temperature after cooling of preheated sample. Freezing of the sample and crystallization of the inclusions causes cracking of the matrix. A simple theory of the observed phenomena is given. Dependence of pressure inside the inclusions on temperature is estimated. Microphotographs of the studied inclusions at different temperatures are presented. (Abstract courtesy of T. Sushchevskaya)

GEGUZIN, Ya.E., and DZYUBA, A.S., 1973c, Elastic diffusion interaction of liquid inclusions in an NaCl single crystal: *Kristallografiya*, v. 18, no. 5, p. 1053-1056 (in Russian).

GEGUZIN, Ya.E., and DZYUBA, A.S., 1974, On the peculiarities of boundary kinetics during the motion of liquid and gas-liquid inclusions in Rochelle salt single crystals in a temperature gradient: *Kristallografiya*, v. 19, no. 5, p. 1030-1033 (in Russian).

An experimental and theoretical discussion of the motion. (Abstract by E. Roedder)

HAAS, J., 1971, Effect of salinity on the maximum thermal gradient of a hydrothermal system at hydrostatic pressure: *Econ. Geol.*, 66, p. 940-946.

The effect of salinity on the temperature-depth relations of a brine of constant composition enclosed in a vein system but freely connected to the surface, and everywhere at the b.p. for the hydrostatic head, was calculated by using a mathematical model. The Na-Ca-K-Cl brines which are found in thermal springs and in fluid inclusions in ore minerals were approximated by the available data for vapor-saturated NaCl-H₂O solutions. As a practical rule, the depth to an isotherm in a 5, 10, 15, 20, and 25 wt. % NaCl brine system is respectively, 92, 84, 77, 70, and 63% (+2%) of the depth to the same isotherm in a H₂O system. The minimum depth to the growth site of crystals containing fluid inclusions which indicate boiling of the brine can be estimated. These results are useful in understanding the behavior of brines in geothermal areas which may or may not contain compositional stratification.

HOLDOWAY, K.A., 1974, Behavior of fluid inclusions in salt during heating and irradiation: in *Fourth Symp. on Salt*, v. 1, A.H. Coogan, ed.: Cleveland Ohio, Northern Ohio Geol. Soc. p. 303-312.

Rock salt was heated and irradiated in situ by implanted radioactive wastes during the Project Salt Vault experiment, which was carried out at Lyons, Kansas, in the abandoned Carey salt mine between 1965 and 1967. Petrographic examination showed that irradiation resulted in coloration of the salt, producing colors ranging from blue-black nearest the radiation source, to pale blue and purple farther from the source. Bleached areas are common in the radiation-colored salt, many representing trails produced by the migration of fluid inclusions towards the heat source. During laboratory radiation studies, it was found that these bleached areas frequently colored much less readily than

ordinary colorless salt which had not been irradiated previously. This observation, and the relationship between primary chevron structures and migrated fluid inclusions, suggests that the bleached trails represent the total amount of migration of the inclusions from the beginning of Project Salt Vault, until the ambient temperature was reached after the conclusion of the experiment. (Authors' abstract)

HOLSER, W.T., 1968, Chemistry of brine inclusions in Permian salt from Hutchinson, Kansas: in Internat. Conf. Saline Deposits, Houston, Tex., 1962, Geol. Soc. Amer. Special Paper 88, 1968, p. 537.

Brine inclusions from halite crystals in the Permian Wellington Formation at Hutchinson, Kansas, have been extracted, analyzed, and compared with inclusions of other localities and ages as well as with formation waters. Those studied were from very coarse (2-20cm) cleavages of halite that occur as irregular white masses crosscutting the bedded halite in the Carey mine and in a drill core from the Naval Air Station.

Bromide, magnesium, and potassium are not precipitated in significant amounts in the halite facies, so their ratios remain constant. Most of the Br/Mg ratios in the brine inclusions from Hutchinson are close to that of sea water and to modern bitterns. This indicated both that the inclusions are virtually unchanged samples of the bitterns left behind in Permian time and that the Br/Mg ratio of the sea has remained constant since the Permian. On the other hand, the ratios of bromides, magnesium, and potassium to chloride each increases steadily as salt is crystallized through the halite facies, so any of these ratios is a measure of the degree of evaporation of the bittern. The ratios in the Hutchinson inclusions indicate a high degree of evaporation, almost equivalent to the potash facies. The composition of these inclusions contrasts strongly with (1) highly saline "connate" waters permeating deep sandstones and limestones in the midcontinent, which are low in Br, Mg, and K; and (2) brines due to re-solution of salt by fresh water, which are even lower in these elements.

Brine inclusions from the Silurian of the Michigan basin have a similar composition, but some from the Permian Salado Formation at Carlsbad, New Mexico, have an anomalously low Br content.

This investigation has shown that at least some of the large inclusions are good samples of Permian bittersalts despite the recrystallization that was evidently necessary to form the large crystals. Bromide in solid solution in the halite itself corresponds to a much lower stage of evaporation, which may indicate that the inclusions have lost some water since crystallization of the main mass of halite. (Author's abstract)

KALJUZHNY, V., 1978, Approximate VTX-diagram of H_2O -NaCl system and its significance for investigation of fluid inclusions in minerals: *Dopovidi Akademii Nauk Ukrainskoi RSR Seriya B*, v. 1978, No. 4, p. 302-305 (in Ukrainian).

KAPCHENKO, L.N., REGOZINA, Ye.A., SOKOLOVA, N. Ya., 1973, Gas micro-inclusions in salts of the Inder salt dome, the Caspian Basin: *Geol. Nefti Gaza*, no. 5, p. 71-75 (in Russian).

KNOD'KOVA, S., 1977, Use of data on the composition and homogenization temperature of microinclusions in salt crystals for solving genetic problems: *Litol. Polezn. Iskop.*, Issue 6, p. 140-143 (in Russian).

KOVALEVICH, V.M., 1975a, Thermometric studies of inclusions in artificial crystals of halite, (abst.), p. 25-26, in *Carbon and its compounds in endogenic processes of mineral formation* (data on studies of fluid inclusions in minerals) - Abstracts of Regional Meeting, L'vov, Sept., 1975: L'vov, Acad. Sci. Ukrainian SSR (in Russian).

Halite crystals were grown from solutions of ocean water composition and from pure NaCl solutions at $T = 20, 58, 75$ and $100^\circ C \pm 0.75^\circ C$. The temperature values were selected in accordance with T_H data on halite from salt deposits from Forecarpathians. In synthetic halite crystals all the types of inclusions known from natural halite were found: one-phase, two-phase and three-phase (solid phase - sylvite). T_H of 2- and 3-phase inclusions agrees with T_F of halite. (Abstract by A. Kozłowski)

KOVALEVICH, V.M., 1975b, Conditions of formation of Verkhnevorotyschen-skiye saline deposits in the region of Stebnik, based on inclusions in halite: *Geology and Geochemistry of Fuels*, v. 44, p. 42-50, Kiev (in Russian).

Primary (sedimentary) halite usually bears inclusions in a skeletal crystal array. Inclusions are commonly 10-15 μm long, but some of diameter 100-150 μm were found. In some large inclusions a sylvite crystal occurs (≤ 1 vol. %).

Individual inclusions have concentrations of ions in g/liter of: K^+ 12.8 - 42.2 (60 determinations); SO_4^{2-} 46.1 - 98.5 (56 determinations); Mg^{2+} 53.3 - 95.2 (42 determinations), general concentration of salts about 430 g/l, with density equal to 1.310 g/cm³; concentration of NaCl ~40 g/l, so halite was salted out from brine. T_H of inclusions with sylvite crystals (two phase) were 38-42°C (10 determinations) and 56-60°C (2 determinations). Primary halite formed in a late stage of development of the sedimentary basin.

Secondary halite (coarse grained, recrystallized) bears two-phase gas (G) plus liquid (L) or crystal (C) + L inclusions, and rarely one-phase liquid inclusions. The crystal (sylvite) usually occupies 3% of the volume. Inclusions with sylvite (C + L) have concentrations of ions such that: K^+ 28.2 - 55.4 (24 determinations), SO_4^{2-} 10.0 - 89.9 (24 determinations), Mg^{2+} 43.0 - 90.3 (18 determinations), Ca^{2+} not found; G + L inclusions and L inclusions bear ions; K^+ 16.6 - 32.1 (24 determinations), SO_4^{2+} 80.4 - 91.1 (5 determinations), Mg^{2+} 9.0 - 68.5 (15 determinations), Ca^{2+} 30.5 - 60.0 (25 determinations). T_H of C + L inclusions are 56-86°C, the average of 80 determinations was 71°C; increased pressure was noted for after opening inclusions boiling occurred or the gas bubbles enlarged 150-250 times. T_H of similar inclusions in halite from sylvite rock was higher (100-120°C, 10 determinations). (Abstract by A. Kozłowski)

KRAMER, J., 1965, History of sea water. Constant temperature-pressure equilibrium models compared to liquid inclusions analyses: *Geochim. Cosmochim. Acta*, 29, p. 921-945.

Liquid inclusion analyses from salt and chert from the Silurian Salina and Niagaran Groups of Michigan, Ontario, Ohio and Wisconsin compare very favorably with modern ocean compositions except that Ca and Mg appear to be reversed.

Liquid inclusion results. Values are molar ratios.

	Ocean	Inclusions				Brine seep
		Salt Ontario	Ohio	Ontario	Chert Wisconsin	
$\text{Ca}^{+2}/\text{Cl}^-$	1.8	11	10	15(?)	12	28×10^{-2}
$\text{Mg}^{+2}/\text{Cl}^-$	9.9	2.2	2.1	4.5	11	11×10^{-2}
$\text{SO}_4^{-2}/\text{Cl}^-$	6.9	15	9.7	13	1.2	7×10^{-3}
$\text{Na}^{+1}/\text{Cl}^-$	0.84	0.97	0.94	0.78	0.86	2.2×10^{-1}
$\text{K}^{+1}/\text{Cl}^-$	1.8	2.7	2.9	3.0	7.8(?)	20×10^{-2}
F^-/Cl^-	1.3	10	8.1	1.0	6.8	1×10^{-4}
Ionic strength/ Cl^-	1.3	1.5	1.4	1.5	1.6	

NESMELOVA, Z.N. AND TRAVNIKOVA, L.G., 1973, Microincluded gases in fossil salts: Abstracts of papers from the Fourth Regional Conference on Thermobarogeochemistry of Mineral-Forming Processes, 24-30 Sept., 1973: Rostov, Rostov Univ. Press, p. 166 (in Russian; translation to Fluid Inclusion Research through the courtesy of A. Kozlowski).

Gases of sylvite, halite and carnallite from the Verkhnekamskoe and Starobinskoe potassium deposits were investigated. Gases were separated by dissolving the salt in water in a special vacuum apparatus. Analysis was made by gas chromatography. Inert gases were separated by melting the samples in vacuum.

The amount of composition of gases are connected with composition of parent minerals. The maximum amount of gases is in sylvite (up to 200 ml per kg); halite from the same salt horizons contains one tenth as much gas.

The gases are mainly CH_4 and N_2 , with minor methane homologs, H_2 , CO_2 , H_2S , rare gases, etc. In individual cases H_2 and CO_2 were the main components.

Investigation of the amounts of inert gases in salts and their isotopic ratios indicates that Ar and He are radiogenic and syngenetic with the salts.

The combination of saturation by gases with microelements (Pb, Cu, Br, etc.), isotopic composition of hydrogen of the water of crystallization of the salts, peculiarities of chemical composition and mode of occurrence of gases in rock salt, as well as many other geochemical regularities, are difficult to explain on the basis of primary-sedimentary theory of salt formation from sea water of shallow basins. (Authors' abstract)

PANOV, V.V., 1975, Paleo-temperature studies on gas-liquid inclusions in halite: Akad. Nauk Belorusskoi SSR, Doklady, v. 19, no. 3, P. 257-260 (in Russian).

Lists in a table 25 samples, their depth in meters (up to 4178), their stratigraphic horizon, the Ts from gas-liquid inclusions (each a range, total range 240-360°C) and the "Paleotemperatures determination by the method of actualism." These latter are also ranges, with total range 225-375°C. (Abstract by E. Roedder)

PETRITCHENKO, O.I., SLIVKO, E.P., 1971, Physico-chemical conditions of formation of halogen deposits of Ukraine according to the studies of inclusions in halite: International Geochemical Congress, Moscow, 1971, Abstracts of Reports, v. 2, p. 847-848 (in English).

According to the investigation of the oil and gas content in salt plugs of some regions of the Ukraine, the physico-chemical conditions of forming of stocks (domes?) of rock salt in Dnieprovsko-Donietsk basin (Devonian-Permian) and in Transcarpathian trough (Neogene) were studied. When solving this problem some results from the study of inclusions in halite (liquid, gas and solid) were used. The chemical composition (K^{+1} , Mg^{+2} , Ca^{+2} , SO_4^{-2} , Cl^{-1} , Fe^{+2} , Fe^{+3}) as well as pH-Eh of solutions of separate inclusions, the content of gases (N_2 , H_2 , CO_2 , CH_4) and their internal pressure, were determined. The nature and the typomorphic peculiarities of solid inclusions (authigenic minerals) in halite were also studied.

It was stated that the solutions of primary inclusions in the sedimentary halite from the Devonian rock salt belong to a chloride type Cl-Na-Ca of the structure having (in g/l): K^{+1} 0.5-2.5, Mg^{+2} 8-32, Ca^{+2} 40-90, pH = 5.4-5.8, Eh = +110-160mV; the temperature of homogenization of monophasic inclusions being 45-80°C. During the formation of stocks the rock salt was undergoing processes of metamorphism at elevated temperature (90-120°C) and pressure (150-300 atm). This was testified by the composition of solution of the individual inclusions in the recrystallized halite (in g/l): K^{+1} 0.5-10, Mg^{+2} 7-17, Ca^{+2} 30-110 and by some other physicochemical parameters: pH 3.7-6.1, Eh = -10-160 mV, P = 60-35 atm. The content of gases in the essential-gas and gas-liquid inclusions is as follows: (in percent) N_2 = 10-50, CO_2 = 26-51, H_2 = 5-15, CH_4 = 10-52.

The solutions of inclusions in the sedimentary halite from the Permian rock salt belong to a sulphate type of the structure having (in g/l): K 10-30, Mg 8-44, Ca 0.5, pH = 4.7-6.3, Eh = +130-260 mV. During the metamorphism of the Permian salts the processes of desulphatization of the solutions took place, as well as lowering of pH (up to 4.3-5.6) and Eh (up to -10-120 mV) of the medium, increasing of temperature up to 80-110°C and pressure up to 15-35 atm. The Permian salt underwent the greatest metamorphism in the contact zone with the Devonian salt stocks.

The presence of only monophasic liquid inclusions in the halite of the Neogene rock salt confirms the fact that the halite was not affected by the high temperatures and pressure during the period of the stock formation. The composition of the solutions of the liquid inclusions in the recrystallized halite is very similar to that of the original brine of the evaporites, (in g/l): K^{+1} 4-42, Mg^{+2} 15-25, SO_4^{+2} 20-43, Ca^{+2} below 0.5. The parameters of pH-Eh of the recrystallization medium corresponded to the subacid (pH = 5.3-5.5) recovery (Eh = 160-260 mV) conditions. By these investigations it was determined that the formation of the salt sediments in the old evaporites in the Ukraine area took place as a result of the evaporation of the chloride (in Devonian) and sulphate (in Permian and Neogene) type solutions. During the formation of the salt stocks the rock salt underwent the influence of dynamic metamorphism processes,

hydrothermal activity, and contact metamorphism, as well as the influence of the mobile phases of the enclosing rock. (Authors' abstract).

PETRICHENKO, O.I., and SLIVKO, E.P., 1973a, On the conditions of formation of Permian salt deposits of Donbass: L'vov. Mineral. Sborn., v. 27, no. 3, p. 201-214 (in Russian; abstract courtesy T.M. Sushchevskaya).

Chemical composition of liquid inclusions in halite was studied. Three stages were found for the process of halite formation: sedimentary, syngenetic and diagenetic. Study of inclusions in sedimentary halite show that brines from which halite crystallized were of sulphate type with high potassium. Average content of Mg^{+2} in the inclusion solution is 43 g/l, of K^{+1} 19.5 g/l and of SO_4^{-2} 28 g/l. Concentration of these varies considerably and increases in inclusions in halite formed during the late stages of precipitation. The SO_4^{-2} in inclusions from the center of the crystals is higher than that from the periphery. Average Br^-/Cl^- ratio is $9.13 \cdot 10^{-3}$, pH = 5.4, Eh = +174 mV. Study of the inclusions showed that K^{+1} content in the brine increased during the formation of one of the deposits (310 years) from 6 g/l: all the salt precipitated at $>40^\circ C$.

Inclusions in crystals that have undergone syngenetic alteration contain less SO_4^{-2} , more Mg^{+2} and practically the same concentration of K^{+1} ; pH of these solutions is almost the same as in primary inclusions and Eh is about 0 mV.; temperature of syngenetic alteration was $\leq 45^\circ C$. Inclusions corresponding to the diagenetic stage are relatively large (up to 2.5 cm^3) and contain: K^{+1} 12 g/l, Mg^{+2} 16 g/l, SO_4^{-2} 1.3 g/l, Ca^{+2} 1.28, HCO_3^- 1.68, Br^- 2.06 g/l, pH = 4.5 - 5.6, Eh = 10 to -210 mV. Temperature of diagenetic alteration was $\sim 60^\circ$, P = 11 - 17 atm. Chemical composition of the inclusions proves that seawater took part in this process. Data on inclusions composition from Devonian rock salt are given for comparison. These inclusions contain very little K^{+1} , less Mg^{+2} , no SO_4^{-2} and a lot of Ca^{+2} .

PETRICHENKO, O.I. and SLIVKO, E.P., 1973b, On the mineral formation conditions during the formation of Permian salt deposits of the Donbas: L'vov Mineral. Sborn., v. 27, no. 3, p. 263-274 (in Russian).

Data on inclusion pH, Eh, and compositions are combined with phase equilibrium data in salt systems to try to estimate the conditions. (Abstract by E. Roedder)

PETRICHENKO, O.I., KOVALEVICH, V.M. and CHALYI, V.M., 1974, Geochemical conditions of salt origin in Tortonian evaporite basin in NW Predkarpat'ye: *Geologiya i geokhimiya goryuchikh iskopaemykh*, v. 41, p. 74-80 (in Russian).

The investigated rocks consist of halite, anhydrite and detrital minerals. On basis of inclusion studies, two varieties of halite were distinguished, sedimentary and recrystallized, illustrated with photos of typical inclusions. Halite bears one- and two-phase inclusions, sometimes with gas bubbles (or with solid phases). Data on inclusions fillings (all in g/l of inclusion solution, made on individual inclusions, unless otherwise noted): a) sedimentary halite: K^+ - average of 66 determinations 12.4 (3-45); Mg^{2+} average of 36 determinations 26.8 (6-45); Ca^{2+} average of 14 determinations 0.5; SO_4^{2-} average of 40 determinations 31.0 (10-55); Br^- 0.3-1 (6 determinations); Cl^- average 170; Fe 5-10 mg/l ($Fe^{2+} + Fe^{3+}$); BO_3^{3-} ≤ 50 mg/l; Cu found; Eh average of 11 determinations + 408 mV (+340 to +515 mV); pH 5.3-6.4 (4 determinations); total concentration 260-280 g/l; $d=1.230$ to 1.260 g/cm³; gases not found, no phase changes on cooling to -20°C; P in inclusions ~1 atm. b) recrystallized halite: K^+ average of 25 determinations 13.9; Mg^{2+} average of 21 determinations 26.9; Ca^{2+} average of 10 determinations, 1.9 (0.5-13); SO_4^{2-} average of 28 determinations 27.0; Br and Cl as in the sedimentary halite; Eh average + 308 mV; pH 5.3 to 6.0; general concentration 260 to 280; $d=1.250$ to 1.280 g/cm³; gases rarely occur under a pressure of 1 to 15 atm; frequency of inclusions bearing gases is 90 to 99%, proving the external origin of the gases. (Abstract courtesy of A. Kozlowski)

PETRICHENKO, O.I., 1973, Methods of study of inclusions in minerals of saline deposits: Kiev, "Naukova Dumka" Pub. House, 92 pp., plus 58 photographs (in Ukrainian).

This little book, with a total printing of only 350 copies, at 66 kopecks, brings together much of Dr. Petrichenko's careful work on the origin, chemistry, and significance of fluid inclusions in saline minerals, including what are

probably the only experimentally determined values for Eh in inclusions.
(Abstract by E. Roedder)

PETRICHENKO, O.T., DOLISHNIY, B.V., and SVOREN', I.M., 1975, Compounds of carbon in inclusions in halite, (abst.), p. 10-12, in Carbon and its compounds in endogenic processes of mineral information (data on studies of fluid inclusions in minerals)-Abstracts of Regional Meeting, L'vov, Sept., 1975: L'vov, Acad. Sci. Ukrainian SSR (in Russian).

Saline rocks of Devonian age from the 500-950m in Dniepr-Donets rift zone were hydrothermally altered. Temperature in the ores decreased from 400-350°C to 50°C, P from 600-500 to 10-30 atm. Gas composition changed from complex (CO_2 , CH_4 , heavy HCs, M_2S , N_2 , H_2) to simple CH_4 and CO_2). Low-temperature minerals (calcite, quartz) bear oil inclusions.

Inclusions in halite adjacent to ores are gaseous (CO_2 80-95%, CH_4 0.1-0.5%); in more distant zones gas ratios change (CO_2 40-55%, CH_4 35-45%). Central parts of salt bodies bear inclusions with gases consisting of 50-60% CH_4 and 10-20% CO_2 and with the rare liquid, HC_5 . Each salt body has its own typical gas ratios; sometimes N_2 is the main component. P of gas (from 350-180 to 100-60 atm) does not correspond to lithostatic P of overlying rocks. Authors suppose that carbon-bearing gases formed from organic matter from evaporites. (Abstract by A. Kozlowski)

POTTER, R., 1977, Pressure corrections for fluid-inclusions homogenization temperatures based on the volumetric properties of the system $\text{NaCl-H}_2\text{O}$: J. Res. U.S. Geol. Surv., 5, p. 603-607.

A series of pressure correction diagrams for 1, 5, 10, 20, and 25% NaCl solutions was generated from the volumetric data for NaCl. The diagrams cover the temperature range from 20° to 400°C at pressures up to 200 megapascals (2000 bars). These data can be used to correct fluid-inclusion homogenization temperatures for pressures greater than the liquid-vapor pressure-temperature curve.

ROEDDER, EDWIN, 1972, The Composition of Fluid Inclusions: Chapter JJ in Data of Geochemistry, Sixth Edition, M. Fleischer, Ed., U.S. Geol.

Survey Professional Paper, 440 JJ, 164 pp., 12 plates, color frontispiece.

This extensive review of the world literature (1600 references) places particular emphasis on the methodology and significance of studies on inclusion composition. Inclusions in salt are discussed briefly.

ROEDDER, E., and H. BELKIN, 1978a, Application of studies of fluid inclusions in Permian Salad Salt, New Mexico, to problems of siting a nuclear waste repository: in Proceedings Symposium Science Underlying Radioactive Waste Management, Materials Research Society Annual Meeting, Boston (in press).

Fluid inclusions are a ubiquitous component of the salt at several potential United States repositories in salt medium. Results of studies of the behavior of these inclusions have been discrepant, and evaluation by different investigators of their significance to the possible safety of waste repositories ranges from "trivial" to major concern about repository operation.

A continuing study of the ERDA no. 9 core, and comparison with other samples, reveals that much of the apparent discrepancy can be explained by the extreme variability of the amount and nature of the included fluids in the test samples, even in adjacent vertical slabs from the same piece of core. The fluid inclusions commonly show various types of metastability, including both extensive supercooling and stretched liquids under negative pressure (Roedder, 1967¹, 1971²). Additional problems stem from some seemingly minor details of sample preparation and laboratory technique. We made use of the freezing, heating, and crushing stages on the microscope, to understand the origin, mineralogy, and geological history of this basin (Roedder and Belkin, 1978) and to anticipate what problems the inclusions might cause during long-term storage of high-level wastes.

The inclusions consist mainly of two types: A - primary: sheets and zones of very minute (mostly $<5\mu\text{m}$) but dense populations ($\leq 10^{10} \text{ cc}^{-1}$) outlining original cubic hopper growth stages, and B - recrystallized: randomly

¹E. Roedder, 1967, Science, v. 155, p. 1413-1417.

²E. Roedder, 1971, Soc. Mining Geol. Japan, Spec. Issue 3, p. 327-334.

arrayed, large inclusions (many in range $100\mu\text{m}$ - 2mm). About 99% of the total salt examined has recrystallized and forms a matrix for small patches of unrecrystallized hopper salt. Inclusion water in the prepared slabs (by optical measurement of inclusion volumes) ranges from <0.1 to 1.7 wt. % (avg. 0.36), $>90\%$ of which is found as $>1\text{mm}$ type B inclusions. The in situ water content must be higher and may well be twice as large, as estimated from coarse intergranular porosity seen in the cores. The larger inclusions ($>100\mu\text{m}$) have a small vapor bubble (~ 0.1 to 0.3 vol. %) and most have a homogenization temperature (T_H) of 20 - 40°C . Some type B inclusions have one or more birefringent crystal phases, believed, on the basis of highly irregular distribution, to be accidentally trapped solids rather than daughter crystals. Both A and B inclusions show first melting temperatures of -32 to -51°C . These require the presence of major amounts of Ca or Mg chlorides, and sulfates may also be present; none show the -21°C characteristic of simple NaCl solutions. Attempts at actual chemical analysis are in progress. Noncondensable gas content was widely variable, even in seemingly coeval inclusions: some bubbles contain $<10^{-14}\text{g}$ (i.e., $<$ a billion molecules); others (only in B-type) contain unidentified gases under pressures ≤ 100 atm at 20°C .

Several types of irreversible and hence irreproducible behavior were noted on heating. These phenomena are strongly sample dependent, as well as very dependent on both heating rates and temperatures. Most inclusions $>100\mu\text{m}$, and hence the great bulk of the fluids present, are released by decrepitation at atmospheric pressure in several days at 250°C . Larger inclusions ($\sim 1\text{mm}$) may decrepitate even at 60°C . This also causes extensive fracturing and crumbling of the 100-g pieces of core used. The H_2O loss averaged 0.73 wt. %; in the experiments, the released fluids could only lose enough water to lower vapor pressure to ~ 1 atm. Many inclusions $<100\mu\text{m}$ do not decrepitate, even at 250°C . They become more rounded (in part by dissolution) and expand ≤ 5 vol. % by permanently deforming the host salt due to the internal pressure, particularly at $> T_H$. The expansion (and the resulting higher T_H) increases with the maximum temperature attained. It is also a function of the original gas pressure, and confining pressure, and probably of several other variables as well. This "stretching" of the walls can occur even at low temperatures. For example, slowly overheating an inclusion 20°C above its T_H of 20°C caused enough stretching to yield a new T_H of 39°C .

Even under isothermal 20°C conditions, visible changes in inclusion volume and shape occurred within minutes when the host salt was subjected to uniaxial stress below that necessary to cause a fracture. Thermal gradients (~ 0.4 to $2^\circ\text{C}.\text{mm}^{-1}$), maintained for periods of hours at ~ 250 - 350°C , caused the liquid-filled inclusions to move up the gradient at rates of 7mm to 1m/year, mainly as a direct function of inclusion size, with an apparent threshold at $\sim 10\mu\text{m}$, below which no movement was detected. Too many factors influence this rate to permit useful theoretical modeling at this time. Tight grain boundaries between crystals cause small moving inclusions to hang up; larger inclusions cross these boundaries. If the boundary contains foreign material or is open, the moving inclusions do not cross.

From these data we conclude the following: (1) The highly saline bitterns trapped in the original hopper salt have been in part freed and reentrapped during recrystallization of the bulk of these beds at temperatures $< 100^\circ\text{C}$. (2) The fluid composition present at different stages of this diagenesis varied, particularly in gas content. (3) The distribution of the primary inclusions shows that they have not moved measurably since deposition 225 m.y. ago, even though subjected to the small but finite geothermal gradient during that time. (4) Although highly irregular in distribution, the amount of included water is not trivial. (5) The high concentration of salts (and even higher when heated) will greatly reduce the vapor pressure and increase the corrosiveness of the released fluids. (6) Decrepitation is estimated to be much more important in releasing fluids than migration to grain boundaries but how this decrepitation (and physical disaggregation), and the physical expansion of salt around undecrepitated inclusions will be influenced by the actual confining pressures in a repository are unknown. (7) The fate of the fluid from a decrepitating or moving inclusion at a slightly open grain boundary in a field of thermal and pressure gradients is also unknown. (8) Fluid inclusions, even in single crystals, react quickly to uniaxial stress, and $\sim 1\%$ liquid in apparently "bone-dry" salt of structural members of a repository could have important effects. This is particularly true if slight deformation causes cracks through inclusions; this would release fluids where they would have the greatest effect on the physical strength. (Authors' abstract)

ROEDDER, E. and H. BELKIN, 1978b, Fluids present during the diagenetic history of the Salado Formation, Delaware Basin, Southeastern New Mexico, as recorded by fluid inclusions: Transactions AGU, 59, p. 226.

Inclusions were examined in cores from the site of a proposed underground nuclear waste repository in the Permian Salado salt beds. Petrography, and freezing, heating, and crushing stages were used. The aim was to help understand the origin and geological history of the basin and the diagenetic mineral assemblages, and to anticipate what problems the inclusions might cause during long-term waste storage. The available data indicate the following diagenetic stages:

The original fine-grained, dark-gray salt contains vast numbers of $\sim 1\text{-}2\mu\text{m}$, mostly one-phase primary liquid inclusions ($\leq 10^{10}\text{cm}^{-3}$) in arrays outlining cubic hopper growth. Low first-melting temperatures show the trapped fluid to be a strong bittern, not simply saturated NaCl. Subsequent recrystallization and grain growth caused inclusion coalescence, yielding a few larger inclusions in coarse clear salt. Only $\sim 1\%$ of the salt remained unrecrystallized. The new inclusions also contain strong bitterns, variable in composition, possibly derived in part from those in the original hopper crystals. Some contain unidentified birefringent daughter crystals. Large inclusions ($\sim 1\text{mm}$) have small shrinkage (vapor) bubbles, containing no detectable noncondensable gas (10^{-14}g ; crushing stage data), homogenizing at $20^{\circ}\text{-}46^{\circ}\text{C}$. Later, fracturing in the presence of a pore fluid containing bubbles of gas (methane?) under pressure (crushing stage data) caused trapping of this mixture in some opened inclusions, yielding variable G/L ratios.

These inclusions make up $<1\text{ vol.}\%$, an additional possibly even greater volume % fluid is present in situ, filling intergranular pores. The evidence for extensive recrystallization is important, but available data do not permit more than qualitative evaluations of the deleterious effects of such fluids on atomic waste storage. (Authors' abstract)

SEOLETSKII, V.I., TRUFANOV, V.N., and MAISKII, YU.G., 1973, Mechanism of mobilization and the nature of highly-mineralized brines in halogenide

formations: Abstracts of papers at Fourth Regional Conference on Thermo-barogeochemistry of Mineral-Forming Processes, 24-30 Sept., 1973: Rostov, Rostov Univ. Press, pp. 42-44 (in Russian; translation provided to Fluid Inclusions Research through the courtesy of A. Kozlowski).

Halogenide formations of various regions of the world contain highly concentrated brines (320-500 g of salts/l). In composition, chlorides of Ca, Na, and Mg prevail, plus relatively high concentrations of B, Li, Rb, Sr and other minor elements in amounts that cannot be explained by condensation processes in the primitive brine. A number of components were found which are not characteristic of the parent salt basins, such as I, NH_3 , naphthenes and humic acids, combustible gases, and bitumens. Often in salt deposits there occur relatively large voids filled by CO_2 , CH_4 , N_2 and other gases.

Investigations of the parent fluid inclusions dispersed in saline rocks prove that they have the composition as the above brines, and permits an inference of genetic connections.

To explain the kinetics of solution mobilization and migration in salt formations and for recognition of the scale of these processes, experiments on thermodynamic activation of fluid inclusions were made in halite and sylvite. The inclusions ranged from 1500 to 2500 per mm^3 (1.5-2.0 liter of brine per cubic meter of rock).

Experiments were made as follows: specimens were placed in an autoclave, the working volume of which was filled with thermo-resistant silicone oil and runs made at 100, 200 and 300°C. At 100-150°C the coalescence of inclusion vacuoles became the major process, and at 150-200°C the phase relations between gas and solution in inclusions of various primary filling ratios are equalized. At 200-300°C necking of inclusions becomes the dominant process, resulting in divided inclusions of fluid and gas. The next process is their migration, with speeds of 0.1 - 0.3 micrometer/hr., toward higher temperatures and lower pressures.

On the basis of these experimental data, the origin of the highly concentrated brine lenses in salt formations and their specific composition may be explained by the evolution of the fluids migrating in the salt formation and their localization in structurally weakened zones. In this case, the salt formations are the "geological membrane" with a selective permeability for individual chemical compounds, and, on the other hand, they determine the main form of material transport as discrete microportions of highly-mobile fluid.

Such a mechanism of fluid transport may explain the significant hydrocarbon enrichment of gas accumulations above salt formations, in comparison with those lying below the salts, as a result of influx of certain components from the underlying oil-bearing layers. Also this may explain the accumulations of borates in certain parts of salt domes. (Authors' abstract)

SHAYDETSKAYA, V.S., 1975, Inclusions of liquid CO_2 in halite from Devonian salts of Dniepr-Donets rift (abst.), p. 65-66, in Carbon and its compounds in endogenic processes of mineral formation (data on studies of fluid inclusions in minerals) - Abstracts of Regional Meeting, L'vov, Sept., 1975: L'vov, Acad. Sci. Ukrainian SSR (in Russian).

Inclusions in halite from salt dome at Novo-Senzharskaya area yielded $P = 100-125$ atm, $T \sim 50^\circ\text{C}$, and a Cl-Ca-Na fluid. Ca^{+2} conc. 75-150 g/l, Mg^{+2} 5-20 g/l, K^{+1} 8-15 g/l, Fe^{2+} 0.0005-0.1%, Fe^{3+} 0.0005%, BO_3^{3-} 0.001%, pH 5.65-6.15 (± 0.2). Inclusions with liquid CO_2 were found only in coarse-grained transparent halite in fracture ("halite veins") cutting salt wall rock. Inclusions are of two types: liquid + CO_2 and liquid + CO_2 + solids; shape cubic; dim. 0.1 - 1 mm; $F = 38-67\%$, most common 50%. Triple point (solid + L + G) -56°C , T_H (partial) in $L_{\text{CO}_2} = 10-14^\circ\text{C}$. Solid phases are accidental solid inclusions (not dms). L is solution of Cl-Ca-Na type (Ca^{+2} 21-50 g/l, Mg^{+2} 2-4 g/l, K^{+1} 32.5-44.5 g/l, Fe^{3+} present; pH 4.5-4.9, ± 0.2 ; Eh 120 to 180 mV). Halite crystallized from heterogeneous solutions of $\text{H}_2\text{O} + \text{CO}_2$. CO_2 -bearing inclusions were found also in halite from Bogdany and E. Slavyanskaya. (Abstract by A. Kozlowski)

SLIVKO, E., and PETRICHENKO, O., 1977, Petrochemical conditions of the formation of salt-containing deposits in the Ukraine: Probl. Soisnakopleniya, (Sb. Mater. Vses. Soveshch), 1, p. 155-158 (conf. proc. in Russian).

THIEDE, David S., and CAMERON, Eugene, N., 1975, Concentration of heavy metals in the Elk Point evaporite sequence, Saskatchewan: Geol.Soc. Amer., Abstracts with Programs, v. 7, p. 1297.

Cores representing a complete section of the Elk Point evaporite sequence in the Saskatchewan Sub-basin have been analyzed for copper, lead, and zinc. Relative to sea water, all members of the sequence are enriched in all three metals, by factors ranging from 14 to 392 for copper, from 10^4 to 9×10^5 for lead, and from 97 to 1745 for zinc. Enrichment is highest in basal shales, dolomite, and anhydrite, lowest in halite, carnallitic halite, and sylvinite. The enrichment of shales, dolomite, and anhydrite in lead is extraordinary; amounts of lead present are far too great to be furnished by evaporation of water in the Saskatchewan Sub-basin.

The data bear on the general problem of the relation of evaporite sequences to stratabound deposits of copper and deposits of the Mississippi Valley type. It appears that an evaporite basin can be both a source of large amounts of metals and a source of chloride-rich brines capable of transporting metals. Any of three types of metal-bearing brines might be generated during the history of such a basin: (1) brines residual from evaporation, (2) diagenetic urines released by dehydration of gypsum to anhydrite, and (3) postdepositional brines generated when evaporites are dissolved and leached by circulating groundwater. Calculations from analytical data for the Elk Point Group suggest that copper-bearing residual brines were possible, but that lead or zinc-bearing brines could have been generated only during diagenesis or during postdepositional groundwater circulation. (Authors' abstract.)

TOURAY, J.C., 1970a, Thermal and optical analysis of families of inclusions in salt deposits (mainly halite): Schweiz. Mineralog. Petrog. Mitt., v. 50, pt. 1, p. 67-79 (in French).

The reasons of inconsistent thermometric behavior of fluid inclusions seemingly belonging to the same (primary) family are investigated. Homogenization is defined in two ways: Ts, disappearance of the solid phase, and Tb, disappearance of the vapor phase. When Ts is lower than Tb, we are dealing with

undersaturated brines and thus need freezing data for the equivalent NaCl content. When T_s is higher than T_b we are dealing with saturated solutions and can use the temperature difference for pressure estimations. Once inconsistencies in single groups of inclusions due to secondary phenomena (leakage and necking down) are ruled out, primary differences should be due to pressure and temperature gradients. An example of constant pressure and decreasing temperature is provided by fluorite from a salt deposit near El Hamman (Morocco). Salinity remained constant: 30% NaCl: T dropped from 180-190°C to 110-120°C, and P remained at 300-400 bars. An example of increasing T and constant P is provided by inclusions in halite (containing sylvite and carnallite) from a geothermal area near Dallol (Ethiopia). Saturated solutions + crystals at 45°C were heated ($T_s=T_b$) to 100°C and became unsaturated between 100 and 150°C. Inclusions in albites from Rock Tourné (France) indicate high initial pressures: 2.2 - 3.0 Kb at 360°C, dropping to 1.5 - 1.7 Kb at 300°C, the T_s-T_b values vary from 200° to 140°C. (Abstract by P.J.M. Ypma).