OIL WATERS OF SE SLOPES
OF THE BOHEMIAN MASSIF

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In the framework of oil prospecting in SE slopes of the Bohemian Massif the chemical and isotopic composition of gas and oil field waters was investigated. The study should have clarified the relations between the chemical and isotopic composition of waters reflecting the physico-chemical development in the system water-oil or gas source rock, of the paleoclimate and of paleohydrological conditions.

Experimental procedures

Prevailing part of water samples was taken from pilot boreholes during the pumping tests. An exception were the oil producing wells and iodine-bromine thermal waters with overflow. Chemical composition of the waters was analysed in laboratories of Moravské naftové doly, k.p. Hodonín, gas analyses were carried out in labs of the Geological Survey, Brno branch, and isotopic analyses in the isotopic laboratories of the Geological Survey and Bundesversuchs- und Forschungsanstalt Arsenal, Vienna.

Geology of the sites

The location of wells (Fig.1) of deep oil waters analysed reflects at once also their regional geological pertinence. Water samples Nos. 2,24,25,31,42 derive from the Miocene aquifers of the Vienna Basin, from the Miocene of the Carpathian Foredeep section North are waters Nos. 3,4,5,18,19,20,21,33,34,37, from the underlying Paleozoic — Culm (Lower Carboniferous) the water No.1, from the crystalline complex of the section North the water No.43. In the southern and middle part of SE slopes of the Bohemian Massif the geological pertinence of the waters is wider — to the Miocene of the Carpathian Foredeep refer the waters Nos. 12,13,35,36,39 and 23, to the autochthonous Lower Oligocene the waters Nos. 14,22,27,45,46, to the autochthonous Mesozoic of the Bohemian Massif — the Jurassic — the waters Nos. 9,10,28,29,30,44, to the autochthonous Paleozoic of the Devonian and the Carboniferous the waters Nos. 7,26,40. The allochthonous Paleogene of the Carpathian Flysch Belt is in our set represented only by waters Nos. 41,15,16 and 17. From the basement of the crystalline rocks of the section South and Centre are the waters Nos. 8,11,38, whereas the waters Nos. 47—60 are Miocene. The oil iodine-bromine water from the southern Slovak Oligocene No.32 and the mineral water from the central Carpathian Mesozoic No.6 were involved for comparison.

The deposition of lithographical horizons during the Miocene, Paleogene, Mesozoic and Paleozoic in SE slopes of the Bohemian Massif was mainly marine. The deposition of the Middle Badenian and Sarmatian of the Vienna Basin corresponded to the salinity of 18—30 g/l. Fresh water development was proved in the Lower Carpathian overlying the nappes of the Middle Carpathian Mesozoic of the Slovak part of the Vienna Basin.

Discussion

In accordance with Janák's theory (Janák 1955) proved by Michalíček (Michalíček 1965), the oil field waters studied are regarded as synsedimentary marine-brackish, sodium-chloride waters metamorphosed in the water-rock system with dispersed organic substances which transform to gaseous and liquid hydrocarbons. The alteration processes of marine to brackish oceanic waters are always accompanied by a change in water chemistry. It is mainly a very low concentration of sulphates, a difference in the ratio of Na/Ca, Mg/Ca, HCO_3^-/Cl^-, Cl^-/Br^- and the Cl^-/I^-. A high concentration of iodides of biogenic origin is typical. In the waters investigated Cl^-/I^- ratio varies from 100 to 400 whereas in the case of marine water the value of the Cl^-/I^- ratio is about 380 000. The Cl^-/Br^- ratio is being considered as the genetical coefficient (Valjaško 1956, Rittenhouse 1967). Numerous authors have proved the coefficient to deal with the presence of the organic substances. In Bars'opinion (Bars 1957) the Cl^-/Br^- ratio oscillating around 180 indicates the contact with some oil deposit, someone (Kölbl 1967) suggests that the brine bromides of the Middle Mesozoic basement of the Vienna Basin have an organogenic origin. These presumptions were verified by Michalíček (Michalíček 1978, 1986).

Along with the chemical composition also the isotopic composition of the studied waters was analyzed. Simultaneous knowledge of δD and $\delta^{18}O$ distribution enables us to determine the origin and mixing of the waters. Fig.2a shows the interdependence of D and ^{18}O contents in a common sedimentary basin. It illustrates the dependence of δD on $\delta^{18}O$ for meteoric water — meteoric water line, the Standard Mean Ocean Water, changes in isotopic composition resulting from fractionation processes during the interaction with rocks, evaporation, hyperfiltration and resulting mixtures of formation brines with meteoric waters. Fig.2b gives the dependence of δD on $\delta^{18}O$ for the water samples studied.

On this dependence, several typical water groups may be distinguished: at first, the low-mineralized waters Nos. 1,6,7,8,9 and 10. These are infiltrated meteoric waters the deuterium excess of which $d = \delta D - 8\delta^{18}O$, is lower than 10. (The value of 10 is typical of recent meteoric waters but of 30—50 thousand years old waters as well (Rozanski 1985)). Higher value of d indicates a drier continental climate than the today's. The value of the He/Ar coefficient speaks of the pertinence of these waters to exposed (or opened) hydrogeological zones with a direct water exchange (Michalíček 1987).

The straight line connecting water samples Nos.35,42,36 crosses the meteoric water line at the present value of δD, $\delta^{18}O$ ($\delta D = -70$ ‰, $\delta^{18}O = -10$ ‰). The next group of water samples linearly dependent in δD vs $\delta^{18}O$ plot are samples Nos. 12,16,24,25,23,37,14,29 and 2. The line connecting these points crosses the meteoric water line at values corresponding to a warmer climate ($\delta D = -54$ ‰, $\delta^{18}O = -8$ ‰). Such linearly depending groups of samples are usually interpreted as mixtures of the original brines with infiltrated meteoric water (Clayton et al. 1966). The marginal points — samples 29 and 2 — can be taken as the "original" primary brines in the first approximation — at least as to the value of δD and their mineralization. Based on these values primary brines may be considered as marine-brackish water with a 60—70 per cent marine water content.

Above the linearly depending "mixed" waters there is a large group of oil and gas accompanying waters with narrow-ranged δD values and markedly variable $\delta^{18}O$. In their values these waters resemble oil field waters from other areas (Kharaka, Carothers 1986). Considerably wide-ranged $\delta^{18}O$ values result from equilibrium isotopic exchange of water with the surrounding carbonate rocks. Their typical $\delta^{18}O$ values vary from -4 to -7 ‰ on PDB scale (i.e. approx. 26.5-24 ‰ on SMOW scale).If one considers the geothermal gradient as one degree centigrade per a 30—33 m depth, then the temperature of waters at a 1 000 m depth is about 45 °C, at 2 000 m about 80 °C, at 3 000 m about 110 °C. The $\delta^{18}O$ values of water in isotopic equilibrium

Fig. 1: Location of mineral, oil and gas-accompanying waters sampled. ČM Bohemian Massif, PČM Paleozoic of the Bohemian Massif, NVP Neogene of the Vienna Basin, NPK the Carpathian foredeep, P-K (FPK) Cretaceous-Paleogene flysch of the Carpathian, A Neogene, B autochthonous Paleogene, C Mesozoic, D Paleozoic, E crystalline complex, 1 water flow, 2 water overflow, 3 water flow with gas, 4 water overflow with gas, 5 water flow with spontaneous gas, 6 water overflow with spontaneous gas, 7 water with oil, 8 water overflow with oil, 9 water flow with traces of oil, 10 water overflow with traces of oil and gas, 11 water flow with oil and gas.
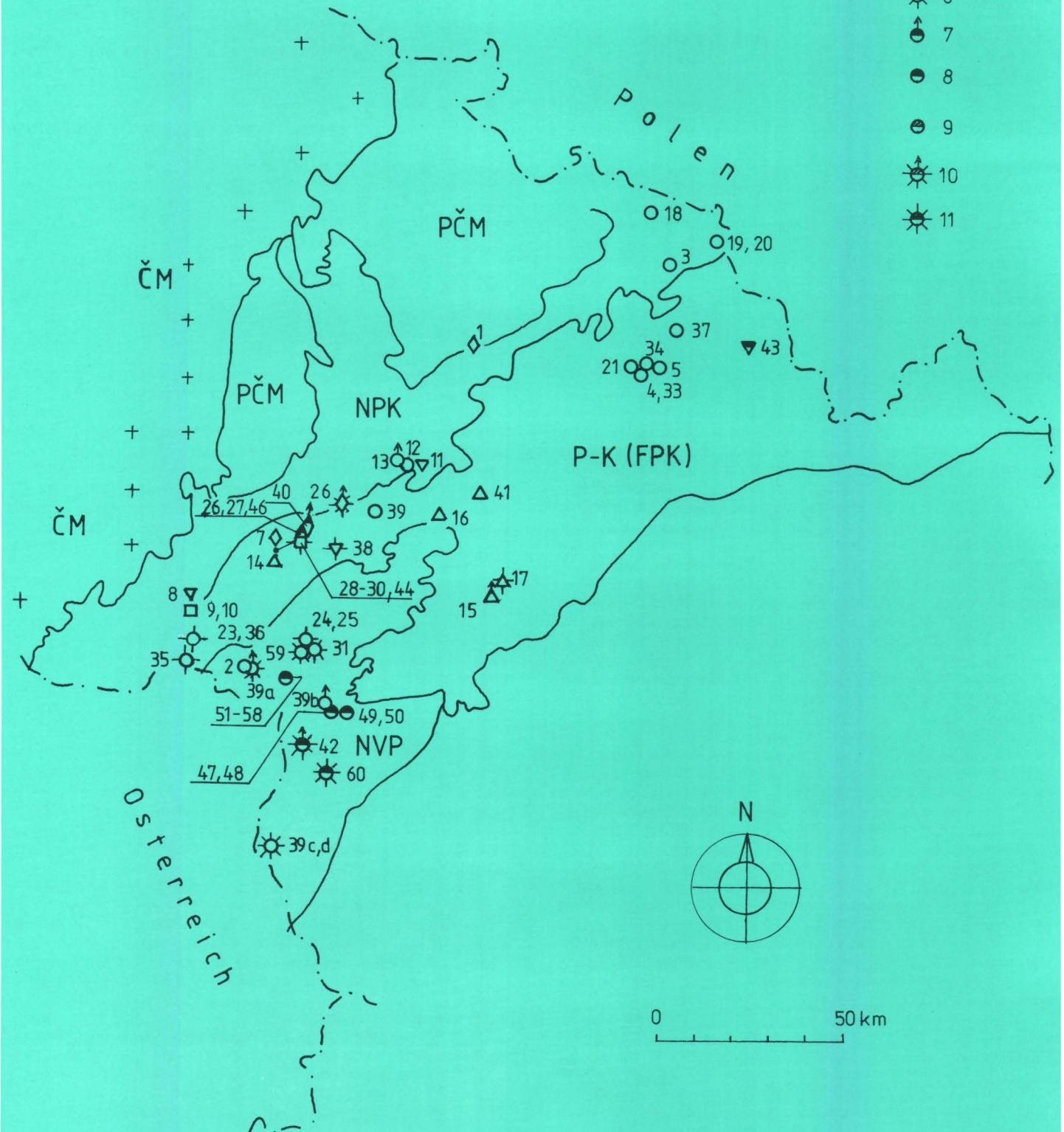
Fig. 2a: Schematic dependence of δD upon δ¹⁸O illustrating fractionation processes and mixing of different water types in sedimentary basin.
A — local meteoric waters; B — primary formation solution; C — local meteoric waters in the past (warmer) climate; D — solution before hyperfiltration; E — solution after hyperfiltration; OW — recent ocean water; MWL — recent meteoric water line (Craig 1961).
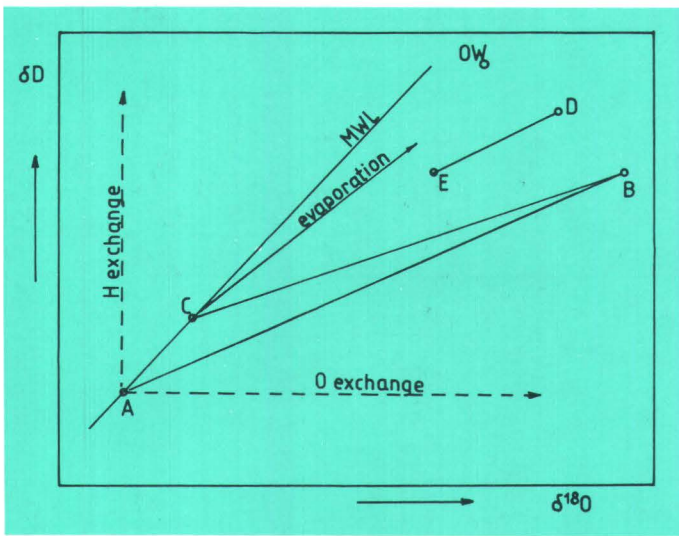
with the carbonates fluctuate at these temperatures from 0 to 6 ‰ on SMOW scale (Clayton et al. 1966).

For the further discussion relations between the isotopic composition (particularly δD which is not so much influenced by the interaction with rocks and keeps the original value) and water mineralization should be taken into consideration. For Na-Cl water type the chloride contents is important. Fig.3 shows chloride concentrations in dependence upon the bromide contents.

The sampled brines were originally considered as secondary, that means of an infiltration origin (Michalíček 1971) resulting from infiltration of the metamorphosed Tertiary brackish to fresh waters into the Mesozoic evaporites. The Cl/Br ratio of the primary brines is similar as in the marine water and makes about 300. The concentration of Br in the solution rises at the beginning of halite crystallization. Dissolving the evaporites, the solutions get richer in chlorides and the Cl/Br ratio increases. In Fig.3 virtually all samples (except for No.42) do not exceed the line of evaporite dissolving. It means the waters are the secondary saline waters in which salt precipitation did not take place, only concentration and dilution of the primary solution. The sample No.42 was mineralized evidently due to evaporites dissolving. Although the hypersaline development with evaporite formation has been proved in the area under study, the searched samples display primary salinity. All of them are

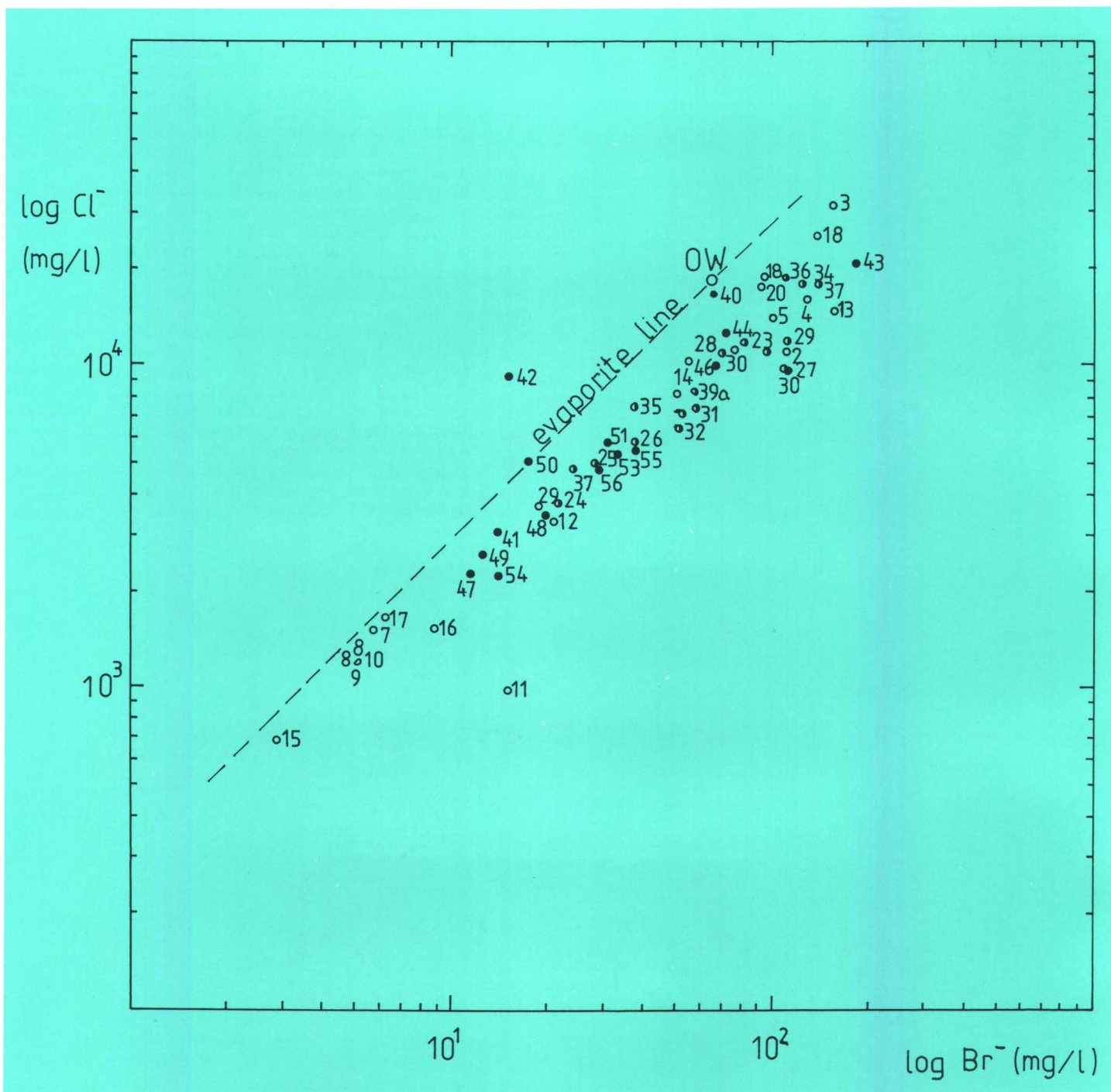Fig. 2b: Dependence of δD upon δ¹⁸O for the deep waters studied.
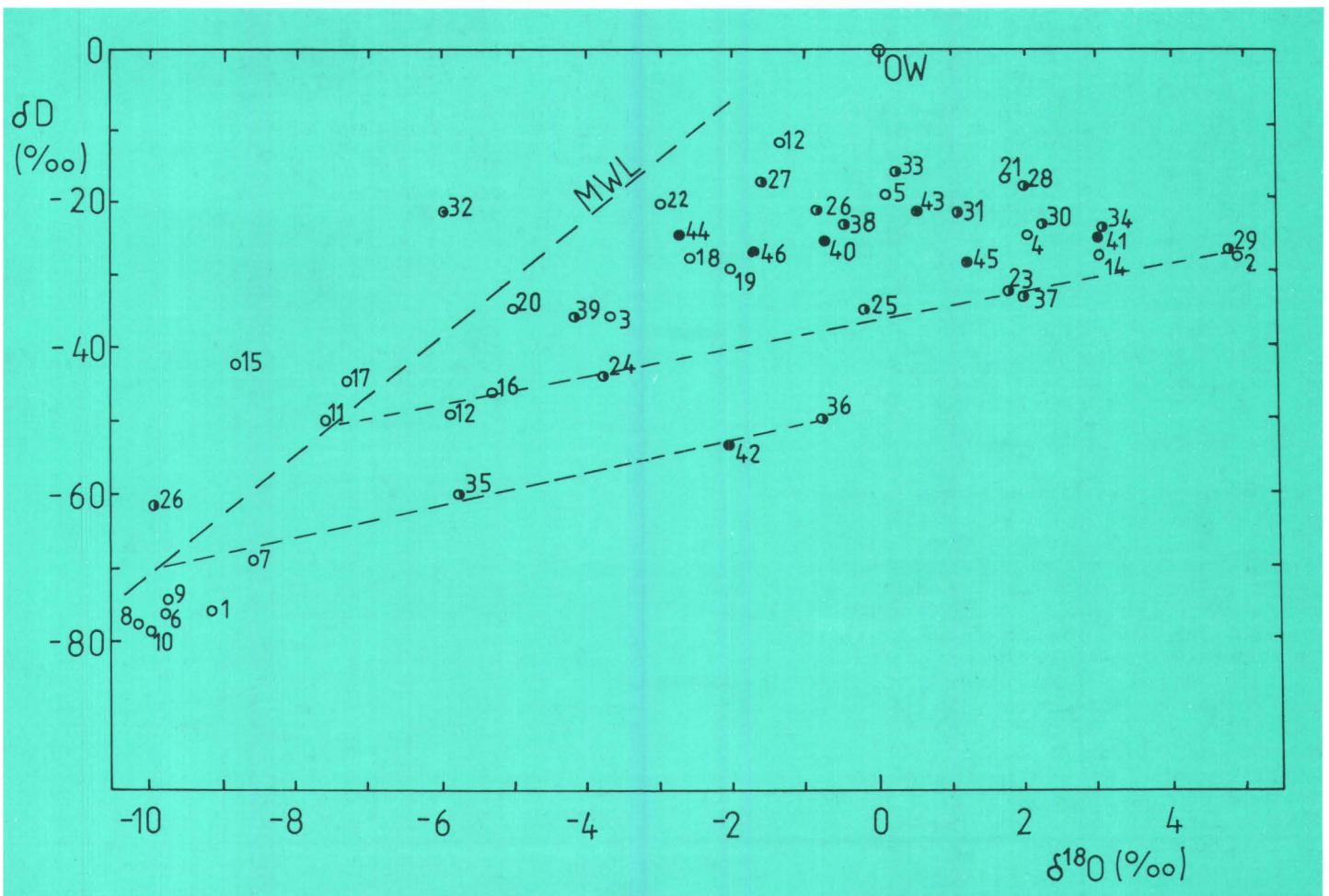
Fig. 3: Dependence of log Cl⁻ upon log Br⁻ for the studied waters.

in good linear dependence being under the level of the evaporites. In the periods of non-deposition they might have been altered by infiltration into marine-brackish waters — the secondary saline waters. These are, however, only hardly distinguishable by chemism.

For the discussion on the relationships between the isotopic composition of waters and the chloride contents the dependence of %Cl on %D was inferred. It should better characterize the problems of mixed waters than the simple dependence of Cl⁻ upon δD. %Cl and %D speak of the marine water contents in the given sample calculated from the balance of hypothetic mixture of marine and meteoric water. The equations 1—3 give balance relations for %D.

$$x_D \cdot \delta D_{OW} + (1 - x_D) \cdot \delta D_{MW} = \delta D_{SAMPLE} \qquad (1)$$

$$x_D = \frac{\delta D_{SAMPLE} - \delta D_{MW}}{\delta D_{OW} - \delta D_{MW}} \qquad (2)$$

$$\%D = x_D \cdot 100 \% \qquad (3)$$

x_D is the marine water content in a theoretic mixture, δD_{OW}, δD_{MW} and δD_{SAMPLE} are the isotopic composition of marine water, meteoric water, and of the given sample, respectively. A similar balance relation holds also for %Cl. For simplicity, the recent value of δD_{MW} was taken as -70 ‰, being later recalculated with more accuracy e.g. from the value of the intersection on the meteoric water line in Fig.2b. The %Cl dependence upon %D is illustrated in Fig.4. The diagram is centred by the proportionality line with
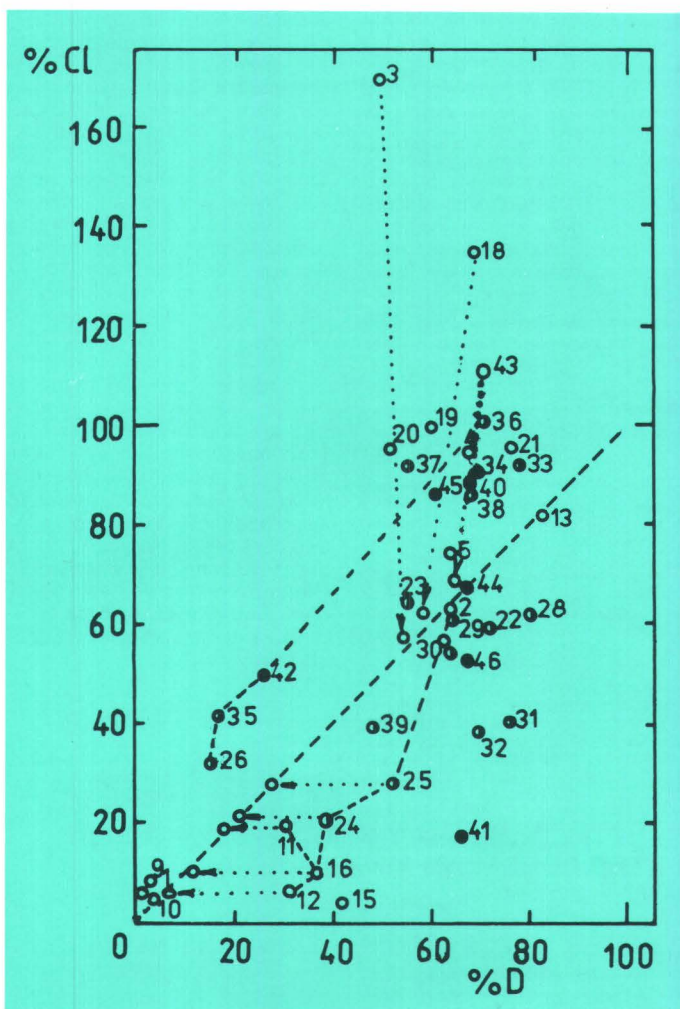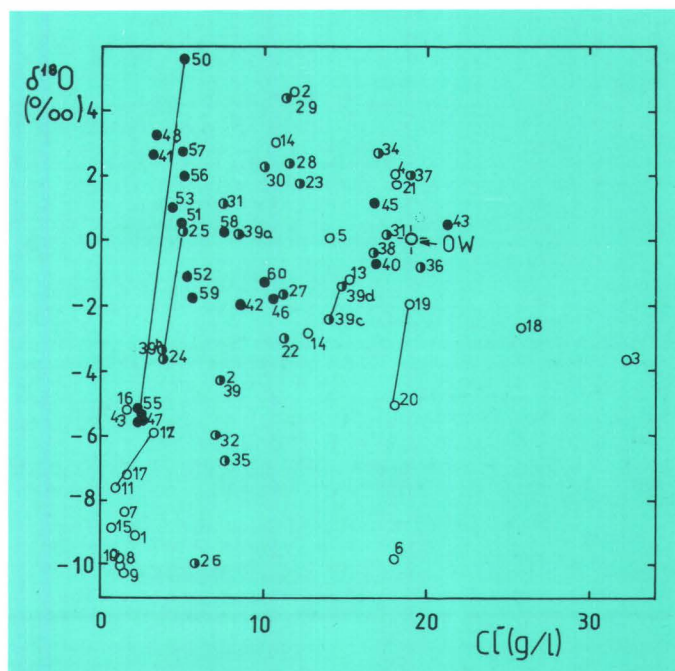
Fig. 4: Percentage of Cl⁻ and δD of studied waters calculated for theoretic mixtures of meteoric and marine waters.

The high variability of chloride contents in samples with %D values attaining to 60—80 % of marine water is hardly explainable.Samples with mineralization higher than corresponds to the marine water contents — above the proportionality line — can be interpreted by dilution of originally hypersaline solutions by meteoric water. For instance, evaporation of the NaCl solution to 0.4 of the initial water phase volume, leads to a shift of δD by 30—40 ‰ to more positive values according to the humidity of the surrounding atmosphere (Sofer, Gat 1975). Dilution of such solutions by meteoric waters to about 30 % causes shifting of brines Nos. 3 and 18 roughly parallel to the %Cl axis. The Cl contents changes and %D gets closer to the proportionality line. Also $\delta^{18}O$ values of the saline waters correspond to possible shifts of original values due to evaporation. Significant changes in $\delta^{18}O$ should be considered as resulting mainly from equilibrium isotope exchange with carbonates. These changes are obvious from the $\delta^{18}O$ vs Cl⁻ plot — see Fig.5. The lines connect the samples deriving from the same location, which differ in sampling depth only. Changes of mineralization do not take place virtually, however, there are remarkable shifts toward positive values of $\delta^{18}O$ according to the higher temperature of the exchange reaction with carbonate. Samples under the proportionality line in Fig.4 exhibit lower chloride contents than would correspond to their δD values. Some of them can approach the proportionality line by choosing more suitable meteoric water composition — as was done in the case of samples Nos. 11,12?16,24,23,25,29,2. However, this is not valid for samples with strikingly lower salinity as e.g. No. 41. Moreover, this sample it is not even in the range of linear dependence in δD, $\delta^{18}O$ diagram. Low mineralized oil field waters with rather positive values of δD are usually interpreted as condensation waters accompanying gas deposits (Kharaka, Carothers 1986, Kato, Kijiwara 1986). Otherwise they can be interpreted as "hyperfiltrated" waters squeezed from sediments under strong geopressures. In the case of the deposit No.41 the capacity is not large enough to allow the formation of sufficient amount of the condensate. The sample, however, was taken at a 3 000 m depth, where the pressures are even twice higher than the hydrostatic one. Hyperfiltration is reliable.

Fig. 5: δ¹⁸O dependence upon Cl⁻ contents for the water studied.

points having identical %Cl and %D values and corresponding to an ideal mixture of ocean and meteoric water. A surprisingly large number of samples in this dependence has the %D values in the range of 60—80 %D. As during the alteration processes δD of the formation water does not change considerably, the original composition of brackish solutions may be supposed. For example, the samples Nos. 2,29 of mixed waters discussed before, are on the proportionality line in the proximity of these values.

How do the fore-discussed mixed waters in this dependence look like? The straight line connecting the samples Nos. 26,35,42,36 parallels the proportionality line in the area of higher Cl contents. It proves that the original solution (sample No.36 ?) was more mineralized than the marine water — e.g. due to evaporation before the secondary dilution. Sample 42 might be assigned to this line accidentally due to the possible present meteoric water contents. Next group of mixed waters (samples Nos. 11, 12, 16, 24, 25, 23, 37, 29, 2) in the dependence illustrated on Fig.4 cannot be unequivocally interpreted. But as %Cl vs %D plot was calculated for the present meteoric water (δD = -70 ‰) all we have to do is to apply the value δD_{MW} = -54 ‰ from Fig.2b. After that a majority of the points will approach the proportionality line, too. Sample No.37 is the only exception. It has higher chloride contents and its involvement was improper (it differs in chemical composition having high HCO_3^- contents — 2 646 mg/l and SO_4^{2-} — 394 mg/l). The recalculation shifts of points are indicated by lines paralleling %D axis.

The occurrence of clays in sedimentary complexes is significant namely in the Miocene, Paleogene, Carpathian flysch, autochthonous Oligocene, Jurassic, and Lower Carboniferous. Exceptionally high tectonic pressures were proved in Miocene trenches of the Vienna Basin, and are supposed also in allochthonous Paleogene complexes of the Flysch Carpathians and the Lower Carboniferous — the Culm. In the whole area of SE slopes of the Bohemian Massif hydrostatic pressures can be observed throughout the sedimentary complexes. It indirectly points to vertical — capillary connection of fluids closed in sediments. The theory of ions balance and chemical alteration of deep waters was based on Janák (1955). Diffusion processes give rise both to low- and higher-mineralized solutions, which differ in shift of δD values from the evaporated ones.

Conclusions

From the discussion several types of water can be presumed. The low-mineralized brines were primarily brackish waters with approx. 60—70 % marine water contents. The brines with mineralization of 35—50 g/l were originally marine waters concentrated by evaporation without any salt precipitation. Later these primary brines were diluted by infiltration of meteoric waters at different climatic stages. The low-mineralized brines with more positive δD values may in fact be hyperfiltrated primary brines. Only one of the waters studied was mineralized by evaporite dissolution.
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Abstrakt

V rámci prospekce ropoplynonosnosti JV svahů Českého masívu byly vzorkovány vody doprovázející ropu a plyn. Vody byly analyzovány chemicky a izotopicky (D,^{18}O). Podle mineralizace jde o formační vody naředěné srážkovými vodami. Rozsah zředění primárních solanek byl určen ze závislosti δD na δ ^{18}O. Porovnáním obsahů chloridů a izotopického složení deuteria bylo určeno složení primárních formačních roztoků. Jde o brakické solanky s obsahem cca 70 % mořské vody. Více mineralizované roztoky byly nakoncentrovány pouze odparem, ne rozpouštěním evaporitů. Zřeďování primárních solanek probíhalo v různých klimatických obdobích.

Zusammenfassung

Im Rahmen der Erdöl- und Erdgaserkundung an der SO-Abdachung der Böhmischen Masse wurden Proben von Erdöl- und Erdgasbegleitwässern entnommen. Es wurden ihre chemische Zusammensetzung und ihre Isotopenverhältnisse untersucht. Aufgrund des Mineralgehaltes handelt es sich um durch Niederschlagswasser verdünnte Formationswässer. Das Ausmaß der Verdünnung ursprünglicher Salzwässer wurde aus der Beziehung δD — δ^{18}O bestimmt. Aus dem Vergleich von Chloridgehalt und Wasserstoffisotopenverhältnis wurde die Zusammensetzung der ursprünglichen Formationswässer ermittelt. Es handelt sich um Brackwasser mit einem Meerwasseranteil von etwa 70 %. Für die Entstehung stärker mineralisierter Wässer sind ausschließlich Verdampfungsprozesse verantwortlich, nicht die Auflösung von Evaporiten. Die Verdünnung der ursprünglichen Salzwässer erfolgte während unterschiedlicher Klimastadien.

GENETIC TYPES OF THE KAOLIN DEPOSITS IN THE BOHEMIAN MASSIF

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Introduction

The deposits of kaolins of the Bohemian Massif (B. M.) belong (with exception of some non-economic occurrences of kaolins of hydrothermal or chemogenic origin) to the weathering type and, apart from the kaolins in the Inner Phyllites of Moravikum, have originated by kaolinization of the rocks rich in feldspars. The majority of these deposits are primary, however a very important volume of kaolins are redeposited. These secondary kaolins, represented by only two deposits (Kaznějov and Horní Bříza) probably experienced a short transport. Parent rocks of the primary kaolins of the B. M. are granitoids, metamorphites (orthogneisses to granulitic gneisses, paragneisses, phyllites), sediments (arkosic sandstones to arkoses, feldspar sands) and occasionally volcanites (Permo-Carboniferous). Kaolinization has occurred in two periods: 1, Carboniferous (Westphalian C — Stephanian) and 2, (Jurassic-) Cretaceous — Paleogene (-Middle Miocene). KÖSTER (1980) also mentioned kaolinization of Triassic age from the w. border of the B. M.

Geological summaries of the kaolin deposits of the ČSSR, were presented by KUŽVART (1969) and KUŽVART et al. (1983). Characteristics of the particular types of the deposits summarized in our paper come from the publications cited below. Newly, mineralogical studies (XRD, EDX, SEM) of 16 samples of kaolins taken from exploited or opened deposits of ČSSR were performed in the laboratories of the Institut für Baugeologie, Vienna. The results were studied from the point of view of the genesis of the deposits (Plates 1—4). Comparative material was taken