

## Uplift-related hydrocarbon accumulations: the release of natural gas from groundwater

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**Abstract:** Vertical tectonic movements often change the structural style and physico-chemical habitat of sedimentary basins. Changes in pressure, temperature and salinity of the groundwater caused by tectonic uplift may result in the release of previously dissolved gas. This process of gas exsolution from groundwater is shown to be an important mechanism in the formation of gas accumulations in uplifted basins. Two principal types of gas release are discussed. A hydrodynamic type is active when groundwater flows into areas of lower pressure or mixes with water of different temperature or salinity. It is anticipated that this effect is more of local importance, but over long periods of groundwater flow large volumes of gas may be exsolved. The hydrostatic type of gas release can occur in any sequence of sedimentary rocks where uplift causes a drop in pressure and temperature. This phenomenon may act basin-wide. Mass balance calculations show that the largest gas accumulations on Earth, such as the Urengoy field in West Siberia, could have been formed by this process.

During uplift of sedimentary rocks, maturation of sedimentary organic matter and associated hydrocarbon generation cease as a result of the drop in temperature. In addition, various uplift-related processes are known to be responsible for the destruction of petroleum reservoirs. The understanding of these mechanisms led to the evaluation of many inverted sedimentary basins as non-prospective for commercial hydrocarbon accumulations. The influence of uplift on hydrocarbon systems of sedimentary basins is much more complex and may either cause destruction of hydrocarbon accumulations or induce redistribution of hydrocarbons into new, uplift-related types of accumulations (Doré & Jensen 1996). Processes that influence the distribution of hydrocarbons in exhumed basin settings include: (1) the dismigration of hydrocarbons as a result of structural tilting and fracturing of cap rocks; (2) the diffusional losses of light hydrocarbons from the reservoir, which are not replenished as hydrocarbon generation ceases during uplift; (3) anomalous rock properties such as mature or cemented rocks at shallow depth; (4) the presence of fluids in disequilibrium

leading to gas exsolution from pore water or liquid hydrocarbons, expansion of fluids, especially gas, and retrograde condensation. Of these phenomena we address here the exsolution of gas from formation water as an uplift-related process resulting in new accumulations of natural gas. After a short review of the solubility and occurrence of gas in the deep hydrosphere, the mechanisms of uplift-related gas release from groundwater are discussed.

### Solubility of gas in water

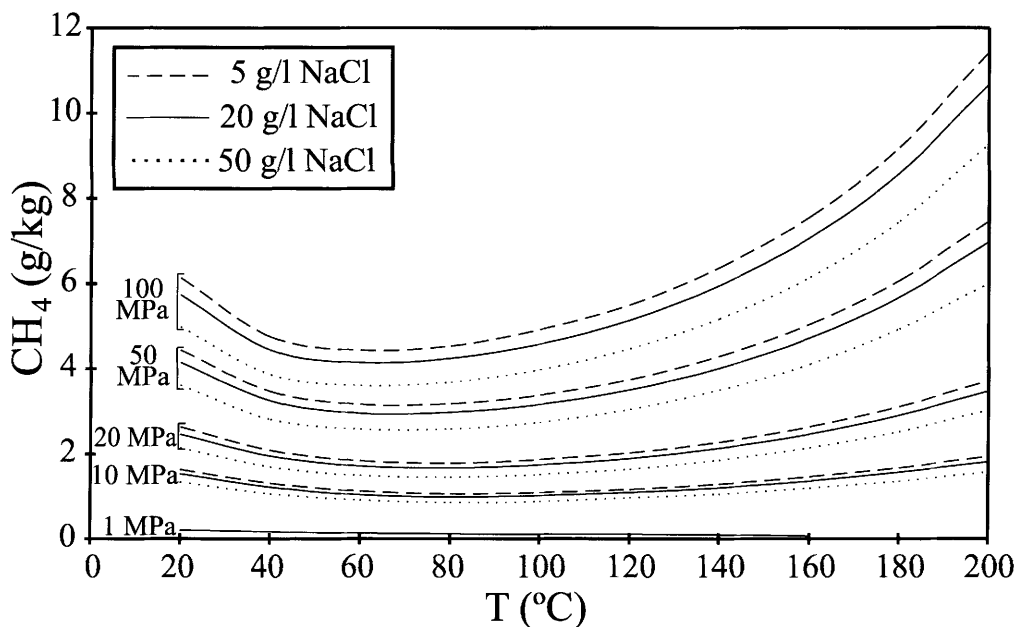
The solubility of gas components in water depends on a variety of factors. Pressure ( $P$ ), temperature ( $T$ ), concentration and composition of inorganic components in the water, as well as the contribution of other gas components in solution are the most important known factors. A large number of measurements of gas solubility in water over wide ranges of pressure, temperature and salinity are available, with most published experimental data focused on the solubility of methane in pure water or water with a single electrolyte such as sodium chloride or

calcium chloride (Culberson & McKetta 1951; O'Sullivan & Smith 1970; Sultanov *et al.* 1972; Bonham 1978; Price 1979; Cramer 1980; Price *et al.* 1981; Rettich *et al.* 1981). Some experimental data are available also for ethane (Culberson & McKetta 1950; Rettich *et al.* 1981; Crovetto *et al.* 1984). Investigations of the solubility of binary or ternary hydrocarbon gas mixtures in water are limited to moderate  $P$ - $T$  conditions (Amirijafari & Campbell 1972). Only one series of measurements has been published on the solubility of a real natural gas in oilfield brines under a limited range of pressure and temperature conditions (Dodson & Standing 1945).

Calculated with a model based on experimental data (Haas 1978), Fig. 1 summarizes the solubility of methane for temperatures between 20 and 200 °C and pressures ranging from 1 to 100 MPa in brines with three NaCl concentrations. Some general conclusions can be drawn regarding the solubility of methane under pressure, temperature and salinity conditions typical for groundwater within the uppermost 6–8 km of the Earth's crust: (1) At constant temperature, the solubility of methane increases with increasing pressure. (2) Between about 60 and 90 °C the solubility of methane in water has a minimum for a constant pressure. At temperatures above this minimum, the solubility

increases with rise in temperature. The influence of temperature exceeds the effect of pressure on methane solubility. (3) Increasing salinity of the brine suppresses the solubility of methane (salting out). Differences between electrolytes in the salting-out effect appear to be small compared with the overall effect. (4) Solubilities of hydrocarbon mixtures are greater than the solubilities of the pure components at the same pressure and temperature. (5) For the normal covariant rise in pressure and temperature with depth, methane solubility increases steadily, although not at constant rates.

To predict methane solubility under geologically relevant conditions a variety of mathematical models is available from the literature. The concepts for these models vary from semi-empirical equations mainly based on curve-fitting procedures (Haas 1978; Coco & Johnson 1981; Price *et al.* 1981; Battino 1984) to more theoretically based models applying the Pitzer phenomenology for the liquid phase (Barta & Bradley 1985) and an equation of state for the vapour phase (Duan *et al.* 1992). Although differences are obvious in the precision of these models and in the physicochemical conditions they cover, it is believed that they all are suited to predict methane solubility in water under  $P$ - $T$  conditions relevant to sedimentary basins.



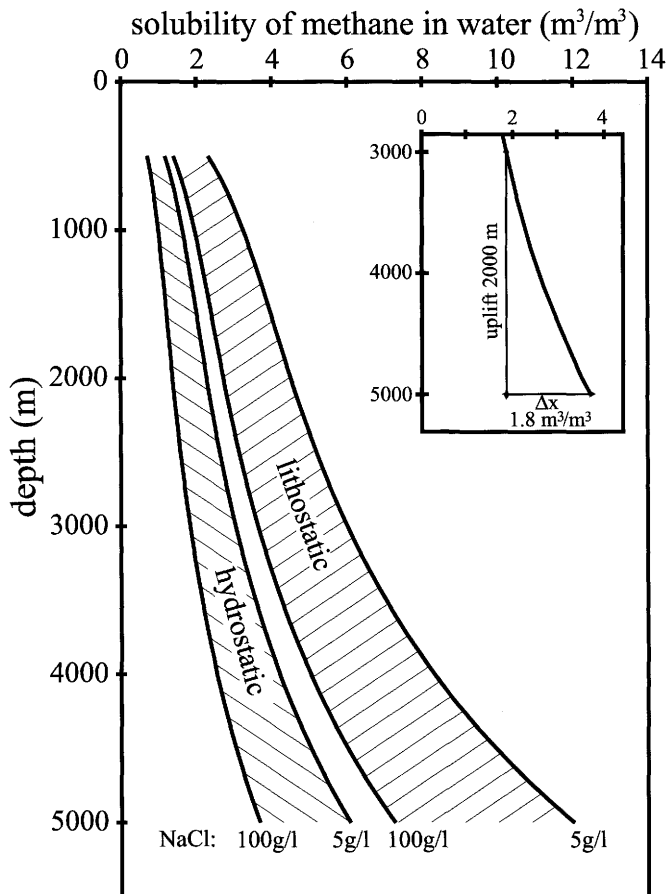
**Fig. 1.** Solubility of methane in water as a function of pressure, temperature and NaCl concentration, calculated with the model of Haas (1978).

### Dissolved gas in the Earth's crust

The principal gas components dissolved in the crust down to the Mohorovičić discontinuity are methane, carbon dioxide, hydrogen and water vapour (Kortsenshtejn 1979). The composition of gas dissolved in near-surface groundwater is governed by the main atmospheric gas components nitrogen and oxygen. With increasing depth, the influence of the atmosphere decreases and gas from bacterial and thermal degradation of sedimentary organic matter (e.g.  $\text{CH}_4$ ,  $\text{CO}_2$ ), gas from recrystallization processes of minerals (e.g.  $\text{N}_2$ , Ar), as well as gas from mantle degassing (e.g. He, Ar) contribute to the dissolved gas phase of the groundwater. Secondary processes such as the decomposition or generation of individual gas components, as a

result of bacterial activity or the thermal degradation of hydrocarbons, may significantly change the composition of the gas dissolved in deep groundwater. At least within the depth range of hydrocarbon generation from sedimentary organic matter, methane is by far the most important gas component dissolved in groundwater (Barkan & Yakutseni 1981).

The role of groundwater as a vast storage medium for gas in the subsurface was emphasized by Kortsenshtejn (1979). He estimated that at least  $1 \times 10^{19} \text{ m}^3$  gas (all volumes of gas are given in  $\text{m}^3$  STP (standard temperature and pressure);  $15.6^\circ\text{C}$ ,  $1.013 \text{ kPa}$ ) are dissolved in water of the subsurface hydrosphere. This equals about twice the volume of the Earth's atmospheric gas. The volume of gas dissolved in free groundwater of the upper 5 km of sedimentary



**Fig. 2.** Solubility regimes of methane in subsurface groundwater for hydrostatic and lithostatic pressure conditions and salinity range of  $5\text{--}100 \text{ g l}^{-1}$  NaCl. A geothermal gradient of  $30^\circ\text{C km}^{-1}$  was assumed. In the example, 2 km uplift results in a drop in solubility of methane from  $3.7$  to  $1.9 \text{ m}^3 \text{ m}^{-3}$ , with  $1.8 \text{ m}^3 \text{ m}^{-3}$  released from the groundwater.

rocks is estimated to be at least  $1.5 \times 10^{15} \text{ m}^3$ , with methane as the main constituent (Kortsenshtejn 1979). This is 10 times the estimated volume of the global conventional gas reserves (c.  $0.15 \times 10^{15} \text{ m}^3$ ; Barthel *et al.* 1999).

In the geological environment the factors influencing gas solubility in water described above lead to a general increase of gas solubility with increasing depth (Fig. 2). The temperature minimum below  $90^\circ\text{C}$  shown in Fig. 1 is compensated in the subsurface by the effect of increasing pressure. Nevertheless, because of the temperature minimum in solubility, the temperature range up to  $90^\circ\text{C}$ , corresponding to a depth down to 2500–3500 m, is characterized by a lower rate of increase in methane solubility than at greater depth (Fig. 2). Under hydrostatic pressure within the uppermost 5 km of the Earth's crust, the solubility of methane can exceed  $5 \text{ m}^3 \text{ m}^{-3}$  (Fig. 2). Under lithostatic pressure  $> 10 \text{ m}^3 \text{ m}^{-3}$  of methane can be dissolved in the pore water at about 5 km depth.

In the past, the interest in dissolved gas in the subsurface was mainly focused on the economic potential of gas dissolved in brines (Kuuskraa & Meyers 1983; Marsden 1993) as well as on the role of dissolved gas for the deep gas potential of sedimentary basins. Because water is able to store gas effectively over a long time, dissolved gas in pore water is believed to support hydrocarbon potential even below the depth of main hydrocarbon generation (Barkan *et al.* 1984; Price 1997).

### Uplift-related gas release from groundwater

Until recently, the processes responsible for gas release from groundwater in the deep hydrosphere have not been investigated in much detail. However, it is clear now that the principal reasons for gas exsolution are changes in the physicochemical habitat of the groundwater; uplift-related changes in pore pressure, temperature and salinity may cause the release of previously dissolved gas. Processes of gas release from groundwater can be classified as: (1) hydrostatic effect, not related to hydrodynamic activity; (2) hydrodynamic effect, related to the flow of groundwater. Hydrostatic gas release may occur in all sedimentary sequences where regional uplift causes a drop in subsurface pressure and temperature. Depending on the initial gas content of the pore water and on the amount of uplift, a critical point will be reached at which gas solubility drops

sufficiently to initiate gas release from the water. In contrast, gas release related to hydrodynamic activity may occur if a change in pressure, temperature or salinity of the water is induced by groundwater flow, either by water flowing to a region of lower pressure or by mixing with cooler or more saline groundwater. During the exhumation of a sedimentary basin with an active hydrodynamic system, both effects, hydrostatic as well as hydrodynamic, will simultaneously contribute to the release of gas.

#### *Hydrostatic effect*

To illustrate the potential of this process to release gas, methane-saturated groundwater is assumed to have a salinity equivalent to  $100 \text{ g l}^{-1}$  NaCl in a sedimentary formation at 5 km depth with a geothermal gradient of  $30^\circ\text{C km}^{-1}$  and hydrostatic pressure (Fig. 2). The basin is lifted 2000 m and the solubility of methane drops from c.  $3.7$  to  $1.9 \text{ m}^3 \text{ m}^{-3}$ . About  $1.8 \text{ m}^3 \text{ m}^{-3}$  of methane could potentially be released from the water. In a water-saturated sedimentary layer of 10 m thickness with an average porosity of 8% and a lateral extent of  $1 \text{ km}^2$  this uplift would release about  $1.4 \times 10^6 \text{ m}^3$  of methane from the water. The duration of the uplift and the rate of upward movement are not considered in this calculation, because it is not believed that time plays a significant role in this type of gas exsolution. However, time becomes crucial when looking at the processes of gas migration to a trap and diffusional losses from an accumulation.

Hydrostatic gas release often occurs at a regional to basin-wide scale. The amount of gas released can be enormous. To evaluate the economic potential of this process, it is important to consider the geological factors promoting effective gas release from groundwater and accumulation of the gas in accessible hydrocarbon traps. Favourable conditions are: (1) thick aquifer systems with high porosity; (2) high contents of methane dissolved in the water (fully saturated) at maximum burial depth; (3) effective buoyancy-driven migration of the released gas into (4) hydrocarbon traps with effective cap rocks under prevailing conditions.

Factors (1) and (2), which determine the volumetrics of the gas release, seem to be mutually exclusive. In general, good aquifers are found at comparatively shallow depth, where the solubility of methane in water is still low. In contrast, high gas contents in the pore water are expected to be found at greater depth (Fig. 2), where the porosity of sediments is reduced. Exsolution of large volumes of gas requires that

**Table 1.** Published mass balance calculations on the hydrostatic gas release during uplift

Region	Gas field	Initial depth of aquifer (m)	Assumed amount of uplift (m)	Salinity of groundwater (g l <sup>-1</sup> )	Change in solubility (m <sup>3</sup> m <sup>-3</sup> )	Methane release below drainage area (m <sup>3</sup> )
General model (1)	–	6000	3000	350	4.1	–
General model (2)	–	6000	3000	100	8.3	–
Barents Sea (3)	Snøhvit	3400	1500	100–165	2.0	(50–200) × 10 <sup>9</sup>
West Siberia (4)	Urengoy	1800–4500	600–1000	10–25	≤ 1.7	≤ 9 × 10 <sup>12</sup>

1, Barkan & Yakutseni (1981); 2, Maximov *et al.* (1984); 3, Oygard and Eliassen, cited by Doré & Jensen (1996); 4, Cramer *et al.* (1999).

at least one of the two factors is favourable. Therefore, effective gas release from pore water can be expected at all depth ranges, but in the case of shallow aquifers down to *c.* 2500 m depth, sediments with high porosity are a prerequisite.

Although the formation of very large gas and gas-condensate accumulations as a result of gas release from groundwater is believed to be of global importance (Maximov *et al.* 1984), reports on actual cases are sparse. Table 1 summarizes published mass balance calculations of the effect of uplift-related gas exsolution. Whereas the first two estimates are more general in nature (Table 1), the calculations for the Snøhvit field in the Barents Sea and the Urengoy field in West Siberia are actual case studies. Doré & Jensen (1996) postulated that over the entire Barents Sea area vast amounts of gas may have been released during Plio-Pleistocene uplift and that the formation of major gas accumulations such as the Shtokmanovskoe field can be attributed to this process. From the overall model of the West Siberian Basin as a system of huge aquifers discharging to the north, Cramer *et al.* (1999) deduced that all dry gas fields in the north of West Siberia were sourced by this process, and that the region of a gas release from water extends into the Kara Sea. In summary, the entire region from the Middle Ob in West Siberia over the Kara Sea into the Barents Sea experienced uplift during Cenozoic time and was potentially subjected to release of gas from groundwater and charging of the giant gas accumulations identified in this area.

Basin-centred gas fields (such as the Alberta Deep Basin or the San Juan Basin) are also likely to have been sourced by an exsolution mechanism (Doré & Jensen 1996). These gas

accumulations lie in deep parts of inverted basins, downdip from water with no apparent intervening permeability barrier. According to Price (cited by Doré & Jensen 1996) the underlying mechanism is, most probably, that gas is exsolved from water and forms static gas bubbles that block the pore throats and prevent further migration. The blocking of pore space by gas exsolved from groundwater has also been emphasized by Kuo (1997).

#### Hydrodynamic effect

In all cases where Darcy flow of water through a permeable rock as a result of lateral differences in pressure is active, the water may pass a point where the drop in hydrostatic pressure is sufficient to initiate a release of dissolved gas. From this point, the water will continuously release gas during its passage through the rock. This hydrodynamic gas release is not restricted to uplifted basin settings. However, the tectonic tilting of a sedimentary basin can activate hydrodynamic systems, because of an increase in pressure in the continuously subsiding region and a drop in pressure in the uplifted parts. This mechanism was shown to be active in the West Siberian Basin (Cramer *et al.* 1999), where a recent hydraulic gradient of  $6 \times 10^{-5} \text{ m m}^{-1}$  within the artesian Cretaceous aquifer causes a groundwater flow with an average linear velocity of about  $20 \text{ km Ma}^{-1}$ . The difference in pressure between the southern and the northern edge of the Urengoy anticline, which is in the flow direction of the groundwater, causes a drop in the solubility of methane of up to  $0.017 \text{ m}^3 \text{ m}^{-3}$  over this distance. This amount of gas was potentially released by each cubic metre of groundwater passing the Urengoy recharge area, probably



over a long time span. Cramer *et al.* (1999) calculated that up to  $1 \times 10^{12} \text{ m}^3$  of methane were released during Cenozoic uplift, as a result of the hydrodynamic effect within the recharge area of the Urengoy field. Therefore, this mechanism accounts for a considerable portion, up to 12%, of the gas in place within the Urengoy field.

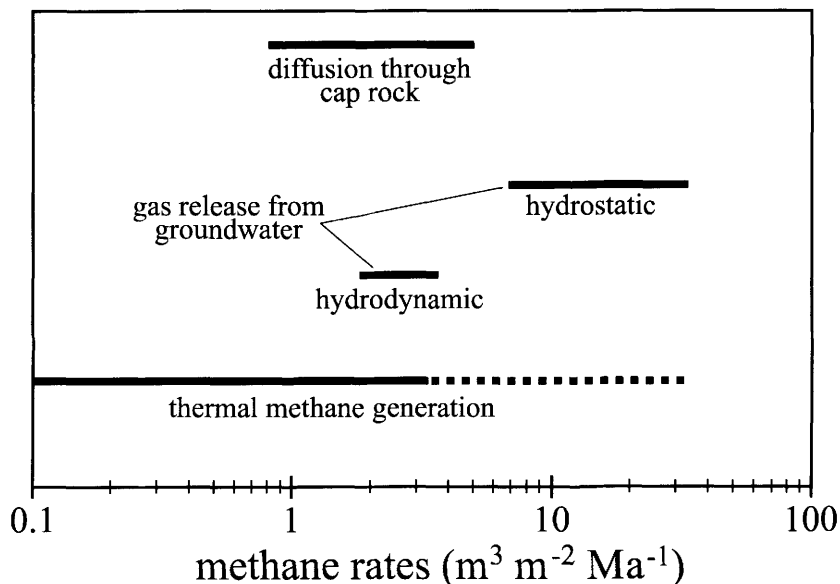
Other possible mechanisms for activating groundwater flow are upward-directed water flow along faults that were opened as a result of the uplift, or an uplift-related depressurization of a sealed compartment, caused by cap rock or fault seal failure, in which large volumes of gas were dissolved in the pore water. In both cases, the subsequent mixing of groundwaters with different salinities may accelerate gas release. Methane exsolution from water may also be enhanced when water flows past salt domes and become more saline during migration (Kuo 1997).

Hydrodynamic gas release can be a regional or local phenomenon. In comparison with hydrostatic gas release, this process has a much smaller potential to generate economic gas accumulations. However, the time factor plays an important role; gas exsolution related to a long-lasting hydrodynamic system can potentially release large volumes of gas.

### Efficiency of gas release from groundwater

Accumulations of natural gas are dynamic systems with continuous diffusional losses of gas through the cap rock. A process such as the release of gas from groundwater can generate significant accumulations only if the rate of charging exceeds the rate of loss. To illustrate the efficiency of gas release from groundwater, Fig. 3 displays a comparison of rates of thermal methane generation, gas release from groundwater and diffusional losses, calculated for the Urengoy gas field of West Siberia. For the calculations, the underlying model of the Urengoy field (including the thickness of the Pokur Formation and pressure and temperature data) was taken from Cramer *et al.* (1999).

It was assumed that methane thermally generated from the terrestrial organic matter of the Pokur Formation contributed to the West Siberian gas fields (Galimov 1988). To compare this gas generation with gas release from groundwater, the rate of thermal methane generation (Fig. 3) was calculated applying a specific set of reaction kinetic data for the Pokur Formation (Cramer *et al.* 1998). The continuous line in Fig. 3 indicates the generation rates (up to  $3.4 \text{ m}^3 \text{ m}^{-2} \text{ Ma}^{-1}$ ) for the thermal history of the Pokur Formation beneath the Urengoy field given



**Fig. 3.** Rates of thermal methane generation, gas release from groundwater and diffusional losses for the Urengoy gas field, West Siberia. Methane rates are normalised to cubic metre of methane (STP) per square metre and million years. (For further explanation see text.)

by Littke *et al.* (1999). The dotted line displays the maximum generation rates (up to  $33.5 \text{ m}^3 \text{ m}^{-2} \text{ Ma}^{-1}$ ) for a  $2 \text{ K Ma}^{-1}$  heating rate. The rates for gas release from groundwater are taken from the detailed calculations of Cramer *et al.* (1999), with up to  $3.6 \text{ m}^3 \text{ m}^{-2} \text{ Ma}^{-1}$  methane released as a result of the hydrodynamic effect and up to  $33.3 \text{ m}^3 \text{ m}^{-2} \text{ Ma}^{-1}$  as a result of the hydrostatic effect.

Diffusional losses of gas from the Urengoy field (Fig. 3) were calculated based on experimental measurements of methane diffusion under *in situ* conditions through a sample of the cap rock, the Kuznetsov Formation. The methane diffusion through a water-saturated rock plug of about 1 cm thickness and about 2.8 cm diameter was measured in a triaxial flow cell at  $35^\circ \text{C}$  and 10 MPa pore fluid pressure. Experimental details have been given by Schlömer (1998). The effective diffusion coefficient for the sample under investigation was determined to be  $2.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . The cumulative amount of methane loss from the reservoir and the steady-state diffusion rates were calculated according to the relationship for diffusive transport through a plane sheet (Krooss *et al.* 1992a, 1992b). Considering the effective diffusion coefficient and the bulk-rock methane concentration under the relevant subsurface conditions ( $0.036 \text{ kg CH}_4 \text{ m}^{-3} \text{ rock}$ ) the highest steady-state diffusive loss rate through the 80 m rock sequence amounts to  $c. 5.0 \text{ m}^3 \text{ m}^{-2} \text{ Ma}^{-1}$ . Taking into account a larger thickness of the overlying cap rock (including the overlying 400 m thick, fine-grained rocks of the Berezov Formation) the computed rates of diffusive losses from the gas reservoir decrease to  $0.8 \text{ m}^3 \text{ m}^{-2} \text{ Ma}^{-1}$ .

It should be mentioned that all methane rates presented in Fig. 3 are related to  $1 \text{ m}^2$  of the reservoir area. Although diffusional losses from the accumulation are restricted to the reservoir area, the processes of charging, i.e. gas release and thermal generation, have to be related to the effective recharge area. In the case of the Urengoy anticline, this recharge area is up to 4.5 times larger than the recent area of the gas reservoir (Cramer *et al.* 1999). This enlarges the effective rates of the charging processes also by a factor of 4.5.

From the comparison of calculated methane rates it is obvious that gas release from groundwater was rapid enough to charge the Urengoy field. The rate of diffusional losses is at least one order of magnitude smaller than the gas release caused by the hydrostatic effect of uplift. In contrast, the hydrodynamic effect of gas release at the Urengoy field alone has similar rates to the diffusion loss. Also, methane

generation rates from the Pokur Formation (Fig. 3, continuous line) in this case were not sufficient to keep up with diffusion loss and to charge the Urengoy field. Even if diffusional losses are neglected, the effective methane generation rate related to the recharge area cannot account for the huge gas accumulations (Schaefer *et al.* 1999). These findings also argue for gas release as the effective process of gas accumulation in the Urengoy field.

## Conclusions

During subsidence of sedimentary basins gas solubility in water increases with increasing burial and thermally generated methane is continuously dissolved in the pore water. The estimated amount of methane dissolved in the Earth's groundwater by far exceeds the amount of conventional gas reserves. Subsurface water is a vast trap for long-term storage of gas in solution, because dissolved gas is excluded from rapid, buoyancy-driven migration processes. Uplift movements of basin settings can initiate the release of dissolved gas as a result of the associated drop in pressure and temperature (hydrostatic effect) and changes in groundwater flow (hydrodynamic effect). Both processes are shown to be appropriate to release sufficient gas to charge gas fields. For the huge Urengoy field of West Siberia, it is shown that hydrostatic gas release is the dominant gas charging process, overwhelming diffusional loss through the cap rock by at least one order of magnitude.

In general, the process of gas release from groundwater in exhumed basins is believed to be of global importance. Gas fields in basins that experienced uplift in the recent geological past should be re-evaluated with regard to the effect of gas release from groundwater.

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