

Gas migration: evaporites

Description: The knowledge of gas migration in a host rock for radioactive waste disposal in a salt formation is of great importance for the assessment of the repository safety, since a high amount of gases will be generated mainly due to container corrosion and in case of low level waste additionally due to degradation of organic material. The investigation of naturally occurring gas inclusions in a rock salt formation can give important information about the long-term behaviour of gases in this host rock.

Two project phases have been performed. The first project runs from 1995 to 1998, the second project is performed since 2001 and will end in 2005.

Within the first project 428 gas-bearing fluid inclusions of the Gorleben salt dome in Northern Germany have been analysed by Laser Raman spectroscopy in order to understand the origin of the gas inclusions and to see, whether gas migration processes have occurred in the rock salt formation. The Laser Raman spectroscopy allows analysis to be carried out without destruction of the inclusions in the host rock. The investigation can be divided in two parts: in the first part only gas-rich inclusions in samples from different stratigraphic layers from the Zechstein series 2 (Staßfurth) and 3 (Leine) were investigated. In the second part gaseous components in brine-rich inclusions of Zechstein series 2 were investigated. Typical shapes of inclusions are shown in Figure 1.

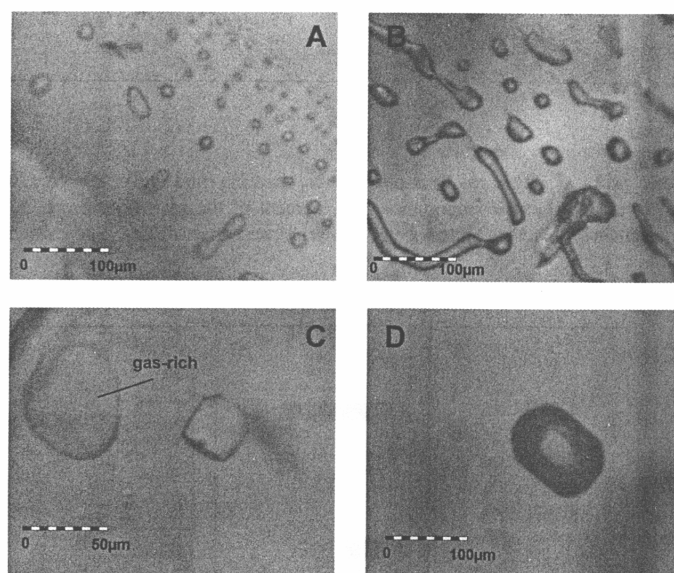


Figure 1. Typical gas-rich inclusions from the samples investigated (Siemann et al. 2001)

In general the gases N_2 , O_2 , CH_4 , C_2H_6 , H_2 and H_2S were detected, no CO_2 was observed. The most abundant gas was $H_2O(g)$, but due to its low importance it was not considered. The observed gas mixtures can be divided into two main groups: the first group containing N_2 or N_2/O_2 mixtures; the second group containing N_2 , CH_4 , and in some cases H_2 and/or H_2S .

The first group containing pure N_2 , or N_2 and O_2 mixtures is the most common group. The frequent occurrence of $N_2:O_2$ -ratios near the modern atmosphere indicate entrapment and storage of paleoatmosphere in the inclusions. The existence of $N_2:O_2$ -ratios $> 80\%$ in a number of samples is probably due to O_2 -consumption by oxidation processes, i.e. oxidation of Fe^{2+} to Fe^{3+} or sulphide to sulphate. An indicator for the oxidation of iron is the orange colour of some Zechstein layers, clearly caused by ferric iron. An enrichment of N_2 by decomposition of organic material is unlikely, since in this case also H_2 and H_2S would be expected, which are rare in abundance.

The second group represents mixtures of N_2 , CH_4 , H_2 and H_2S . All components of this group can be explained by biogenic processes in an anoxic environment, which is typical for marine

sediments. Methane is either built by fermentation of acetate or reduction of CO_2 . In the presence of higher amounts of sulphate, which can be assumed for the corresponding seawater at the time of gas generation, oxidation of acetate to CO_2 and a subsequent reduction of CO_2 to methane probably had played a role. H_2S can be produced by sulphate reducing sulfidogene bacteria under anaerobic conditions. The production of H_2 is typical for fermentation under anoxic conditions. N_2 can be produced by denitrification under anaerobic conditions by reducing NO_3^- from the seawater. Due to the low content of NO_3^- in seawater it is more likely that N_2 stems from degassing processes of early Permian or Carboniferous sediments and was trapped in an early stage of the halokinesis.

A correlation of the different gas mixture groups to stratigraphic layers of the salt formation is observed. The main rock salt of the Zechstein 2 (Staßfurt series) consists of younger (z2HS3) and older (z2HS2) layers. In the older layer z2HS2 all inclusions are from the group containing N_2 or N_2 and O_2 . In the younger layer z2HS3 the gas-rich inclusions are also of this group but the fluid-rich inclusions are containing mainly mixtures of N_2 and CH_4 . These gases are typical for anhydrite rich layers, but the amount of anhydrite in the main rock salt is very low. Therefore as a result from the first project phase it was proposed, that the occurrence of mixtures of N_2 and CH_4 in the main rock salt was an indicator of migration most likely during halokinesis or in an early diagenetic state.

The main objective of the second project was to collect evidence of the existence of migration processes. Therefore a new continuous flow technique for analysis of the $\delta^{13}\text{C}$ and δD values in methane samples was developed and applied to identify the origin of CH_4 . Samples from a whole Zechstein sequence with a thickness of 60 m from the Zielitz mine in northeast Germany have been analysed.

Firstly, it was found that the vertical profile of the Br concentration is typical for a primary evaporate sequence and shows no evidence for complex deposition history. Gases from grain boundaries and fluid inclusions were detected. They consist of CH_4 , H_2 , N_2 and H_2S . The gas mixture as well as $\delta\text{D}_{\text{CH}_4}$ values between -370 ‰ and -240 ‰ (VSMOW) indicate that bacterial fermentation was the main formation pathway for CH_4 and other gases in the middle and upper halite.

The profile of the $\delta^{13}\text{C}_{\text{CH}_4}$ is characterised by values from -45 ‰ to -50 ‰ (VPDB) in the lower halite increasing to ^{13}C -enriched values of +21 ‰ in the potash series at the top of the salt dome. To produce such ^{13}C -enriched CH_4 a further fractionation process must have played a role. The profile can be explained by a model which assumes an evaporation basin, which is a closed water body and in which CO_2 degassed and was removed from the system. Assuming that the dissolved inorganic carbon was then converted to CH_4 in the sediments and applying fractionation factors for fermentation the modelled curve follows the trend of the measured CH_4 values in the evaporite sequence with values around -45 ‰ in the beginning of the evaporation process and $>+20$ ‰ at 95% evaporation (Figure 2).

These results strongly indicate that the gases are of primary origin, having formed during diagenesis of the salt layer. This again gives strong evidence that the gases are fixed in the salt formation and no migration has occurred since the Permian. Therefore, the assumption from the first project that CH_4 migration could have occurred was disproved by these new results.

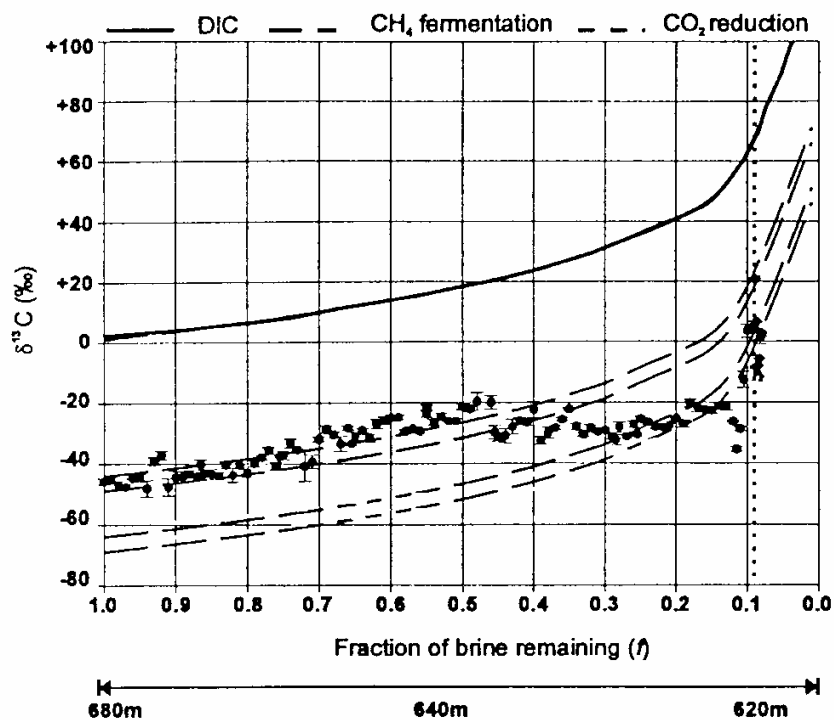


Figure 2 Model showing calculated $\delta^{13}\text{C}$ values for DIC and CH_4 in progressively evaporating basin (Siemann et al. 2004)

Relevance: The knowledge about the behaviour of gases in the salt formation is of great importance, since a high amount of gas will be generated by corrosion of container material and microbial degradation of organics (for LLW and ILW) in the case of water intrusion into the disposal area. The results of the study indicate that no migration of gases has occurred over geological time frames. Therefore, in a repository in a salt formation, when the salt has reached the properties of its initial state due to convergence, it is very likely that no gas migration will occur. Unfortunately, the gas pressure in the inclusions is not precisely known. By Raman Spectroscopy it is evident, that the pressure is higher than atmosphere, but up to now there is no reliable method for quantification of the gas pressure in inclusions available.

Position(s) in the matrix tables: The study illustrates the process of physical integrity of the near-field rock and gas migration in the near-field of a rock salt formation.

Limitations: The study is limited to gas migration in salt formation. The study gives evidence that gases which are trapped in salt formations during diagenesis do not migrate. However, the gas pressure in the inclusions is higher than atmosphere but could not be quantified. Therefore no statement is possible, if gas migration do no occur up to a specific pressure. This information would be desirable for performance assessment. Furthermore the study is limited to formations which have not been influenced by tectonic events. During the last phase of the project another salt formation is investigated, which was affected by tectonic events. Preliminary results indicate that tectonic events had caused some gas migration.

Quantitative information: Mol fractions of naturally occurring gases in a large number of gas-rich and fluid-rich inclusions as well as carbon and hydrogen isotope values of CH_4 in different layers of rock salt formations are available. The results indicate that no gas migration occurred for more than 250 Million years.

Uncertainties: In general experimental data are of good quality. The fractionation model is based on a number of assumptions. There is some uncertainty on the contribution of the two CH_4 formation reactions (bacterial fermentation and CO_2 reduction), which will cause slightly different isotopic signatures.

Time-scale: The time-scale addressed by the study is geological (>> 2 Ma). The gas inclusions are more than 250 Million years old.

PA/safety case applications: The work is still going on and results have not been used up to now in performance assessment.

Communication applications: No application for communication aspects is known so far.

References:

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Final project report will be available in 2005.

Added value comments: If the results clearly show that the gases from inclusions but also from grain boundaries of minerals in the formation origin from the Permian and did not migrate since then, this is a strong argument for the stability and integrity of the salt formation over this long time frame. This information is rather illustrative and should be used in future communication with the public.

Potential follow-up work: The project is still going on. Results will be expected for another salt formation in the area Braunschweig-Lüneburg which was influenced by tectonic events.

In order to receive more quantitative information it would be large step forward to find a method for pressure determination of the gas inclusions. Furthermore, it would be worth to study gas phases in large volume (some m^3) brine-gas pockets to get additional information on gas content, gas pressure (which will probably be easier to determine) and gas migration.

Keywords: marine evaporites, rock salt, gas inclusions, gas migration, methane, isotopes

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