A STABLE ISOTOPE AND INCLUSION STUDY OF GASES IN ZECHSTEIN EVAPORITE DEPOSITS, N. E. GERMANY: IMPLICATIONS FOR UNDERSTANDING THE BEHAVIOUR AND ORIGIN OF GASES IN EVAPORITES

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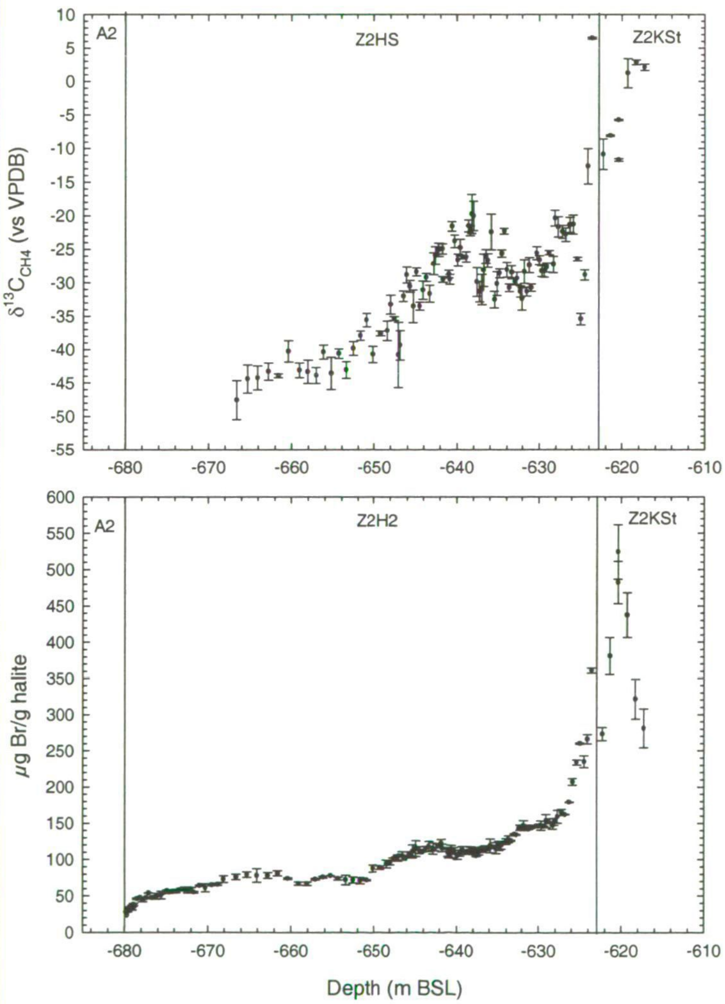
A 200m drill-core through a Permian evaporite sequence was collected from Zielitz mine, near Magdeburg, northeast Germany. The evaporite sequence was taken from the Zechstein Stassfurt Series (Z2) in the "Scholle von Calvörde" area, part of the larger Permian Zechstein basin (ca. 255-256 Ma). The salts in this area are noted for having little or no tectonic or diagenetic alteration. From the basal anhydrite (A2), the main salt series (Z2HS) is homogeneous with no distinguishable sub-series as can be observed in other Stassfurt halite deposits. The main salt is approximately 60m thick and is capped by the Stassfurt potash seam (Z2KSt) consisting of a primary potash assemblage of mainly carnallite, kierserite and halite. The drill core was collected as part of a study to characterise and determine the behaviour of gases (inter- and intra-granular) in salt deposits, with implications for hazardous waste disposal in these salt repositories. The first part of this study is to ascertain the nature of the gases in an undisturbed salt sequence and then compare this with drill core from a tectonised salt sequence. Identification and characterisation of the gases is done using a combination of laser-Raman microprobe analysis on the included gases and stable isotope analysis using a GC-IRMS on the grain boundary and included gases. This is done in conjunction with petrologic and geochemical analysis of the samples. Here, preliminary findings on the nature of the gases in this evaporite sequence are reported and some preliminary interpretations and implications discussed.

FIGURE 1: $\delta^{13}C_{CH4}$ results profile for grain boundary gases in comparison with the Br profile for this evaporite sequence with 1σ error bars



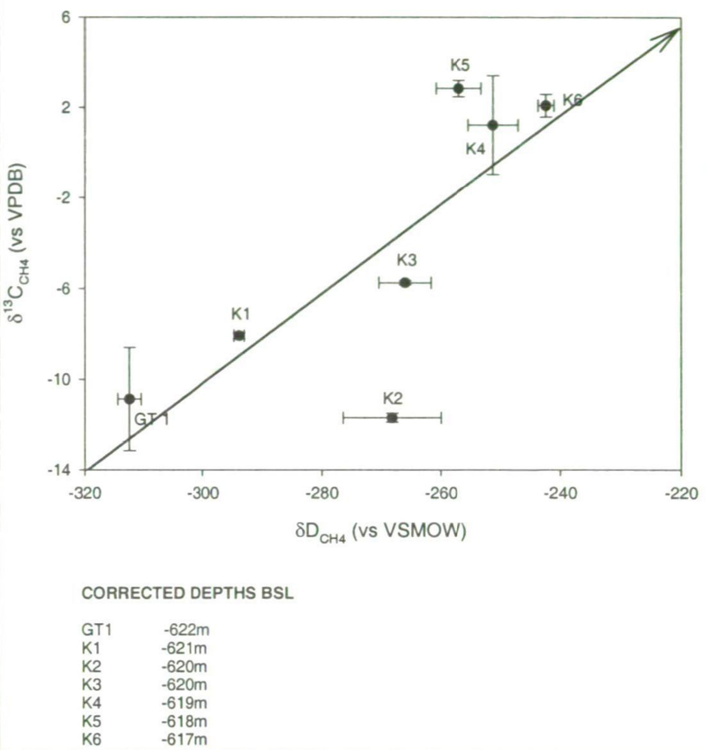
NOTE: Zechstein 2 series: A2 - basal anhydrite, Z2HS - "hauptsalz" series (main salt), Z2KSt - Stassfurt potash seam

During the drilling, 15cm cores were taken every 2m and sealed in gas-tight bags, evacuated by septum on site. The samples, in the laboratory, were gently crushed in an aluminium vice to release any gases trapped on the grain boundaries. The gases were then subsequently identified and analysed by GC-IRMS. After isotopic analysis, the bags were opened and halite crystals collected for Br analysis by ion chromatography. The remaining cores were used for fluid inclusion studies.

Unfortunately, distinguishing and obtaining isotopic results for any N_2 released from the grain boundaries was not possible with this sampling procedure as atmospheric contamination was too great. In the main salt series, only low concentrations of CH_4 were detected (absolute concentrations could not be determined). Toward the top of the main salt, CH_4 concentrations increased radically, (by a factor of 10), and within the potash salts, H_2 was also detected. CH_4 concentrations in the main salt were not high enough to obtain δD_{CH4} values but this was possible in the potash seam. Figure 1 shows the $\delta^{13}C_{CH4}$ and Br profiles throughout the sequence and figure 2, the $\delta^{13}C_{CH4}$ and δD_{CH4} results in the potash seam.

It is apparent from figure 1 that the Br and $\delta^{13}C_{CH4}$ profiles are uncannily similar. The $\delta^{13}C$ values for CH_4 towards the base of the main salt have a typical biogenic signature (-45 to -50 ‰ vs VPDB). However, up sequence, the values progressively become more enriched until by the time the potash seam is reached the $\delta^{13}C_{CH4}$ values range as high as -12 to +6 ‰ vs VPDB. These very unusual values are similar to those reported in other Zechstein potash seams (Gerling et al., 1987) but no satisfactory explanation, for these highly enriched values, has been suggested. The associated Br profile displays a typical, undisturbed, evaporation profile with a steady enrichment of Br from lower than 50 ppm at the base of the main salt, to 250 ppm at the top and concentrations greater than 300 ppm in the potash seams. The low Br concentrations at the basal salt (down to 20 ppm) can been interpreted to have been caused either by Br removal through early infiltration of H_2O from the basal gypsum during recrystallisation to anhydrite (Kühn, 1968) or by a strong reduction of Br partitioning due to a massive change of seawater composition (Siemann, 2000).

FIGURE 2: $\delta^{13}C_{CH4}$ and δD_{CH4} results in the potash seam (Z2KSt)



Of interesting note, both the $\delta^{13}C_{CH4}$ and Br profile show dips in values between -660 and -650m and again between -640 and -630m. The $\delta^{13}C$ and δD values for CH_4 in the potash seams presented in figure 2 show a positive correlation, with δD_{CH4} values showing a similar enrichment up sequence, from -310 to -240 ‰ vs VSMOW, as do the $\delta^{13}C_{CH4}$ values (-13 to +4 ‰). δD values recorded for the associated H_2 are between -670 and -720 ‰ vs VSMOW.

The Br profile shows that this evaporite assemblage has not been tectonised or diagenetically altered, retaining a primary evaporite assemblage. The notable dip in values at -660 to -650m and -640 to -630m (coinciding with a drop in $\delta^{13}C_{CH4}$ values) implies that occasional incursions of freshwater entered the evaporating basin. The similar distribution of values between the $\delta^{13}C_{CH4}$ and Br profiles would suggest that these results had a similar controlling factor (i.e. the evaporative process). The progressive enrichment of ^{13}C in the CH_4 to produce such anomalous $\delta^{13}C$ results outside of accepted source fields (Schoell, 1988), is hard to explain in terms of migration effects or mixing of two sources. However, a model of progressive ^{13}C enrichment in dissolved CH_4 in an evaporating solution, through preferential loss of ^{12}C to the atmosphere, with associated exsolution and entrapment of the dissolved CH_4 upon halite and potash crystallisation, would seem to be a plausible suggestion to explain the range of observed values. At the time of writing this, an ongoing experiment analysing the $\delta^{13}C$ values for dissolved CH_4 during evaporation of synthetic seawater indicates that this does seem to occur, with a positive correlation between $\delta^{13}C_{CH4}$ and density of solution (-41.8 ‰ at $\rho = 1.20$ gcm^{-3} to -21.8 ‰ at $\rho = 1.232$ gcm^{-3}).

Preliminary fluid inclusion studies on these cores have identified two types of fluid inclusions in the main salts: i) < 10 µm, monophase and biphase inclusions restricted to early, 100 µm, euhedral-subhedral crystals of polyhalite, kainite and anhydrite within the halite matrix. Laser-Raman analyses have identified CH_4, N_2, H_2S and H_2, as well as brine in these inclusions and ii) trails of thin, irregular, secondary biphase and monophase fluid inclusions containing brine + N_2. Gas inclusions observed in the potash seams occur as disseminated, irregular, small (< 10 µm) monophase inclusions. These consist of CH_4, N_2 and H_2 and may be interpreted to be primary, exsolving from solution and trapped within the carnallite crystal structure upon crystallisation. These early gas assemblages of CH_4-N_2-H_2S-H_2 in halite and carnallite would indicate that these gases have an initial biogenic origin, involving bacterial organic degradation processes.

Therefore, in summary, the preliminary results here would indicate that gases in these undisturbed evaporite deposits retain primary characteristics, with the evaporative process being the controlling factor on the isotopic values for the trapped CH_4. No evidence of secondary migration of CH_4 (and more significantly H_2) seems to have occurred, which may have important implications when considering these deposits as suitable hazardous waste repositories.

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