Origin of hydrocarbon trace gases in brine-filled Red Sea deeps

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Composition of gases from seawater in hydrothermal active areas, especially hydrocarbon trace gases, give information about fluid sources (e.g. mantle emanation, Welhan and Craig, 1988) and genetic processes (e.g. methanogenesis and bacterial oxidation, Whiticar, Schoell and Faber, 1986; Whiticar and Faber, 1986). During Meteor cruise 31/2 (1995) high concentrations of methane and higher hydrocarbons were found in Red Sea brines. Their thermogenic origin and bacterial methane oxidation in brine/ seawater interfaces was indicated by isotopic data (Faber et al., submitted). High resolution sampling of brine/seawater interfaces during Sonne cruise 121 (1997) provide a better understanding of brine gas characteristics, gas exchange with overlying sea water and bacterial degradation processes.

Sampling and methods

Water samples were taken along depth profiles in Red Sea Atlantis II-SW, Atlantis II-N, Discovery and Kebrit deeps using Hydrobios-Water-Sampler. Insitusampling was performed using both 51 Niskin (PE) bottles and the stainless steel gas tight "Schmitt-Schöpfer". Temperature, sound velocity, light transmission and pressure were recorded by a CTD (Fa. ME). Seawater-/brine samples were degassed onboard applying ultrasonic-/vacuum extraction techniques (Schmitt *et al.*, 1991). Gas samples were stored in glass vacuum containers for stable isotope ratio (¹³C/¹²C, D/H) measurements (Finnigan MAT 252 IRMS). Gas concentrations for methane and higher hydrocarbons up to butane were determined



FIG. 1. Methane concentration profiles and C₁/C₂₊-ratios in Red Sea deeps.



FIG. 2. High resolution profiles in brine/seawater interface of Atlantis-II deep.

by GC-analyses (DANI Gaschromatograph, $Al_2O_3/$ KCl-column, FID-Detector, N_2/H_2 -carrier gas) on board.

Results and discussion

High resolution sampling in 5m depths intervals show significant increases of methane concentrations from normal Red Sea Deep Water to hypersaline brine in the four Deeps. Concentrations vary from 10 nl/l in surface waters to 10³nl/l in the transition zones and to 10^7 nl/l in the brine layers. Highest methane concentration of about 14ml/l corresponding to some 8% of the total gas content were found in Kebrit Deep brine at a depth of 1500 mbs. Methane concentration profiles are strongly related to Red Sea brine interfaces with methane concentrations starting to increase some 10 meters above the brine layers which are indicated by temperature increases (Fig. 1). This may reflect brine-seawater exchange which usually is controlled by diffusion from upper current brine layer to deep sea water (Anschutz and Blanc, 1996).

Ethane and higher hydrocarbons were detected only in brine samples and the calculated ratios of methane to higher HC's ($C_1/C_{2+}<200$) indicate a thermogenic origin of the gases.

A more detailed look at the brine-seawater interface of the Atlantis-II deep, however, shows a more complex situation (Fig.2). Methane concentration maxima superimposed on the diffusion profile were found at 2000 and 2010m depth. Bacterial methane production could be responsible for these high methane concentrations. However, the C_1/C_{2+} ratios are low (<50), and thus, bacterial methane production appears not to be likely. Another explanation for these sharp methane maxima is hydrothermal input of hydrocarbons into distinct brine or seawater layers. This is supported by the sampling position close to the edge of the basin where hydrothermal input may occur (Hartmann *et al.*, 1998).

Microbial methane production is related to strongly anoxic conditions and thus, bacterial methanogenesis could explain the high methane values relative to the higher hydrocarbons (C_1/C_{2+} >2200) in the Atlantis-II deep at 2025 mbs (Fig. 2). However, genetic interpretations of gas geochemical data (concentrations, gas composition) are complicated by secondary aerobe and anaerobe oxidation of hydrocarbons (Whiticar and Faber, 1986). First evidence for these processes occurring within brine/ seawater interfaces are given by Faber *et al.* (submitted) mainly based on stable carbon isotope data.

Ongoing stable isotope analyses will give enlarged information on the complex situation of hydrocarbon formation and oxidation processes within the brines and the brine/seawater interface which may be related to both, biogeochemical processes and inorganic hydrocarbon oxidation at elevated temperatures (Kiyosu and Krouse, 1989).

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