

# Hydrocarbon and noble gases in fluid inclusions of alpine calcite veins : implications for hydrocarbon exploration

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## Hydrocarbon and Noble Gases in Fluid Inclusions of Alpine Calcite Veins- Implications for Hydrocarbon Exploration

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### *Abstract*

The Swiss programme for the disposal of low and intermediate-level radioactive waste has recently included preliminary investigations on highly tectonized Valanginian marl in the Helvetic nappes of the northern Central Swiss Alps (Oberbauenstock and Wellenberg sites). The presence of natural hydrocarbon gases, mainly methane, was observed in boreholes at the Oberbauenstock site, in the Seelisberg motorway tunnel and in soil gas samples taken at both sites.

Gas chromatography and isotope analyses were carried out on gases collected at the well-head of a borehole, on gases released on pulverizing rock samples (marl and calcite fractures) and on vacuum core degassing.

Calcite fractures (veins) are very abundant in the Valanginian marl. The fracture-fill calcite contains up to 3 litres of hydrocarbon gas (STP) per litre of calcite, while, in the marl matrix, only minor amounts of gas are found. Most of the gas is trapped in fluid inclusions at high pressures. The total amount of trapped methane gas in 1 km<sup>3</sup> of Valanginian marl (marl including the calcite fractures) is estimated at 100 to 300 million m<sup>3</sup> of gas (STP). Carbon and hydrogen isotopes, vitrinite reflectance measurements as well as microthermometric investigations of the fluid inclusions indicate a thermogenic origin of the hydrocarbon gas from a highly mature marine source rock (1.7 % < Rr < 3 %). The fluid inclusions were formed during the Alpine orogeny at temperatures of 160-200°C and pressures of 1200 to 1500 bars.

The rare gas system is dominated by atmosphere derived and radiogenic noble gases, with no resolvable mantle component. The ratios of the radiogenic noble gases may be accounted for by radiogenic production in the host Valanginian marl (consistency with marl U/Th/K ratios), but do not rule out noble gas input from outside the Valanginian marl.

Due to their similar isotopic composition, it is assumed that the free hydrocarbon gas from open fractures and probably also the hydrocarbons in the soil gas of the investigated sites derive from leaking calcite fluid inclusions of Valanginian marl bedrock.

Gas seepage from this type of near-surface gas reservoir could cause a significant overprint on gas indicators or anomalies from deep reservoirs and therefore have an impact on exploration strategies. Future work will focus on the investigation of rocks and calcite veins from other stratigraphic units and tectonic settings.

### *Zusammenfassung*

Zur Abklärung der Machbarkeit und Sicherheit eines Endlagers für schwach- und mittelaktive Abfälle hat die Nagra (Nationale Genossenschaft für die Lagerung radioaktiver Abfälle) vor kurzem erste Felduntersuchungen in stark tektonisierten Valanginien-Mergeln des Helvetikums der nördlichen Zentralalpen an den potentiellen Standorten Oberbauenstock und Wellenberg durchgeführt. Vorkommen von natürlichen Kohlenwasserstoffgasen, hauptsächlich Methan, wurden in Bohrungen am Standort Oberbauenstock, im Seelisbergtunnel und in Bodengasproben an beiden Standorten beobachtet.

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Gaschromatographische Analysen und Isotopenuntersuchungen wurden an folgenden Gasproben durchgeführt: Freie Gase, welche am Bohrlochkopf einer Bohrung entnommen wurden; Gase, welche durch Zermahlen von Gesteinsproben (Mergel und Calcit-Klüfte) freigesetzt wurden und Gase, welche mit einer Vakuum-Bohrkernentgasungsanlage gewonnen wurden.

Calcit-Klüfte (-Adern) sind im Valanginien-Mergel sehr verbreitet. Die Calcit-Kluftfüllungen enthalten bis zu 3 Liter Kohlenwasserstoffgas (STP) pro Liter Calcit. Dagegen wurden in der Mergelmatrix nur kleine Gas-mengen gefunden. Der grösste Teil des Gases ist in Fluideinschlüssen unter hohen Drücken gefangen. Die Gesamtmenge von Methangas, welches auf diese Weise in 1 km<sup>3</sup> Valanginien-Mergel (Mergel inklusive Calcit-Klüfte) eingeschlossen ist, wird auf 100-300 Mio. m<sup>3</sup> Gas (STP) geschätzt. Kohlenstoff- und Wasserstoffisotope, Vitritreflexionsmessungen sowie mikrothermometrische Untersuchungen von Fluideinschlüssen weisen auf einen thermogenetischen Ursprung der Kohlenwasserstoffgase aus einem hochreifen (1.7 % < Rr < 3 %) marinen Muttergestein hin. Die Fluideinschlüsse wurden während der alpinen Orogenese bei Temperaturen im Bereich von 160-200°C und Drücken zwischen 1200 und 1500 bar gebildet.

Atmosphärische und radiogene Edelgase dominieren das Edelgas-System; eine Mantelkomponente ist nicht erkennbar. Die Verhältnisse der radiogenen Edelgase können mit einer Produktion im Valanginien-Mergel erklärt werden (Konsistenz mit U/Th/K-Verhältnissen), schliessen aber eine Edelgaszufuhr aus einer anderen Formation nicht aus.

Aufgrund ihrer ähnlichen Isotopenzusammensetzung wird angenommen, dass die freien Kohlenwasserstoffgase aus den offenen Klüften, und wahrscheinlich auch die Bodengase der untersuchten Standorte, aus undicht gewordenen Fluideinschlüssen der Calcite im unterliegenden Valanginien-Mergel stammen.

Eine Gasmigration aus diesem Typus eines oberflächennahen Gasreservoirs kann eine signifikante Ueberprägung von Gasindikationen oder -anomalien, welche von einem tiefliegenden Reservoir erzeugt werden, verursachen und hat deshalb eine wichtige Bedeutung für die Kohlenwasserstoff-Explorationsstrategie.

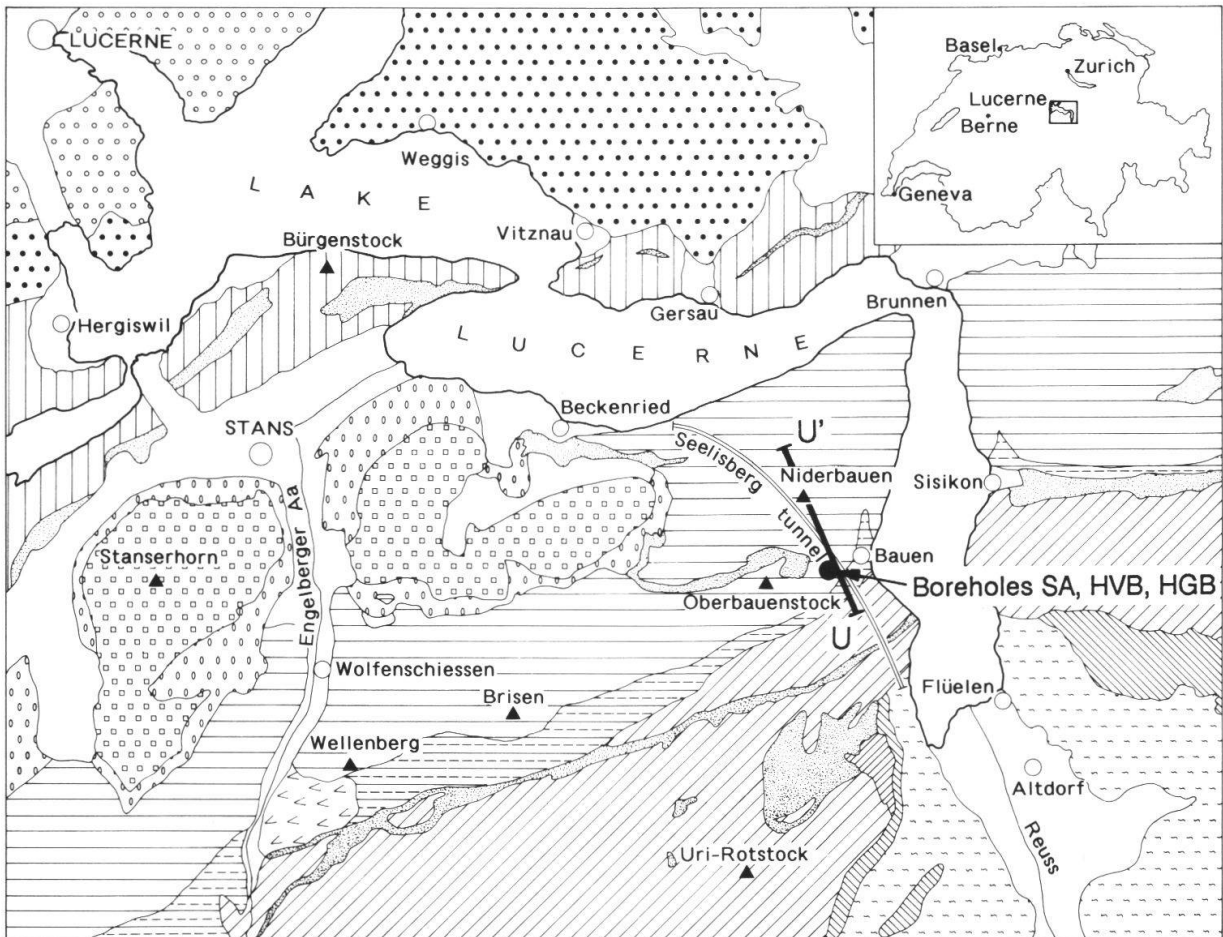
Als Fortsetzung dieser Studie sollen auch Gesteine und Calcitadern von anderen stratigraphischen und tektonischen Einheiten untersucht werden.

## 1. INTRODUCTION

The Swiss programme for the disposal of low and intermediate-level radioactive waste has recently included preliminary site investigations in highly tectonized Valanginian marls in the northern Central Swiss Alps. In the course of these investigations some interesting aspects of hydrocarbon gas occurrences arose. This data is presented in this paper.

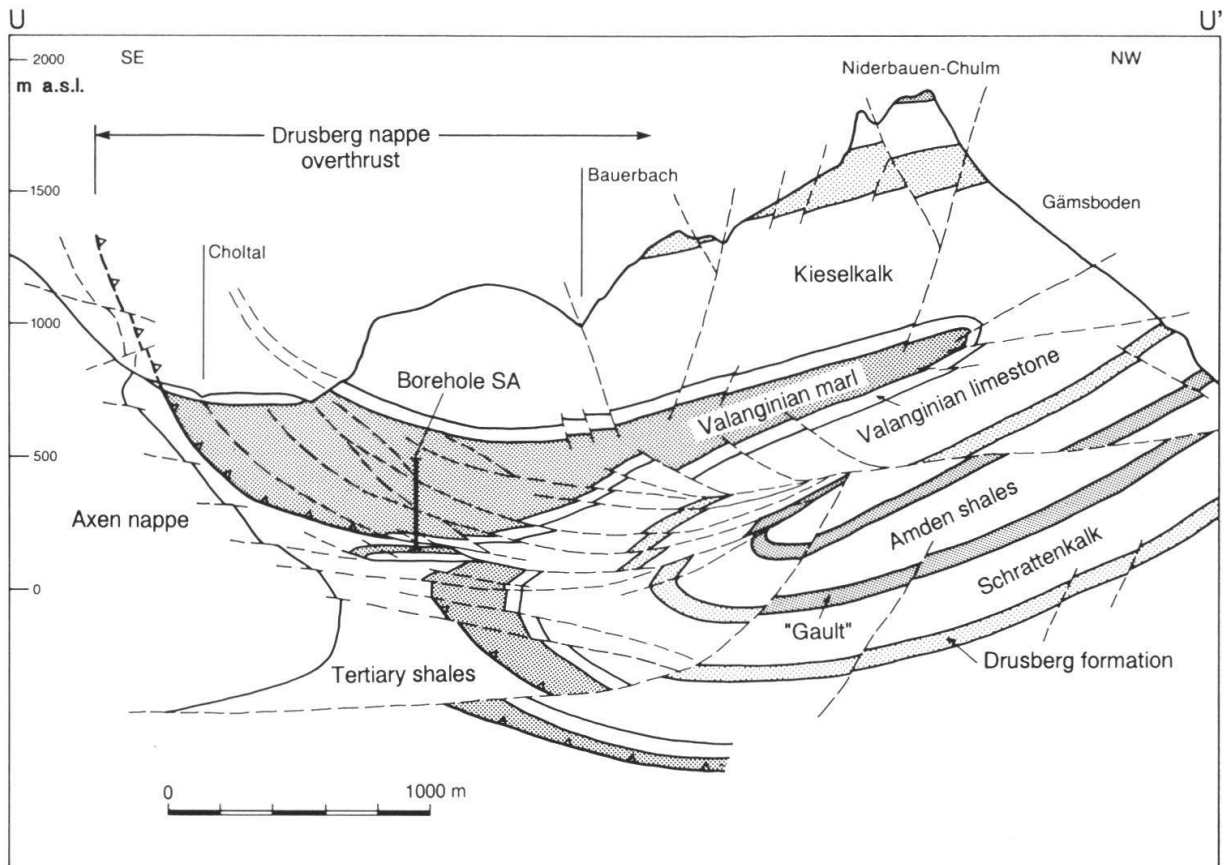
The first phase of investigations has been completed at the Oberbauenstock site near Lake Lucerne (NAGRA, 1988) in the Seelisberg motorway tunnel (Fig. 1). An extensive drilling programme has just been initiated at the Wellenberg site in the Valley of the Engelberger Aa (Fig. 1). The data presented in this paper is therefore mainly from the Oberbauenstock site.

The investigations at the Oberbauenstock site comprised core-drilling, geophysical logging, hydraulic testing and hydrochemical investigations in three boreholes drilled from an adit to the Seelisberg motorway tunnel (Fig. 1 and 2). The three boreholes were designated as HVB - a vertical borehole drilled to a depth of 100.2 m, HGB - an inclined borehole (42°) drilled to 100.6 m (along the hole), and SA - a vertical borehole drilled to a depth of 348.5 m.



**Fig. 1:** Tectonic sketch map of the Lake Lucerne area (simplified after TRUEMPY, 1980). Arrow: Boreholes HVB, HGB and SA, U - U' = cross-section Fig.2.





**Fig. 2:** Geological cross-section of the Oberbauenstock site (from NAGRA, 1988). Boreholes HVB and HGB (not shown) were drilled from the same location as borehole SA.

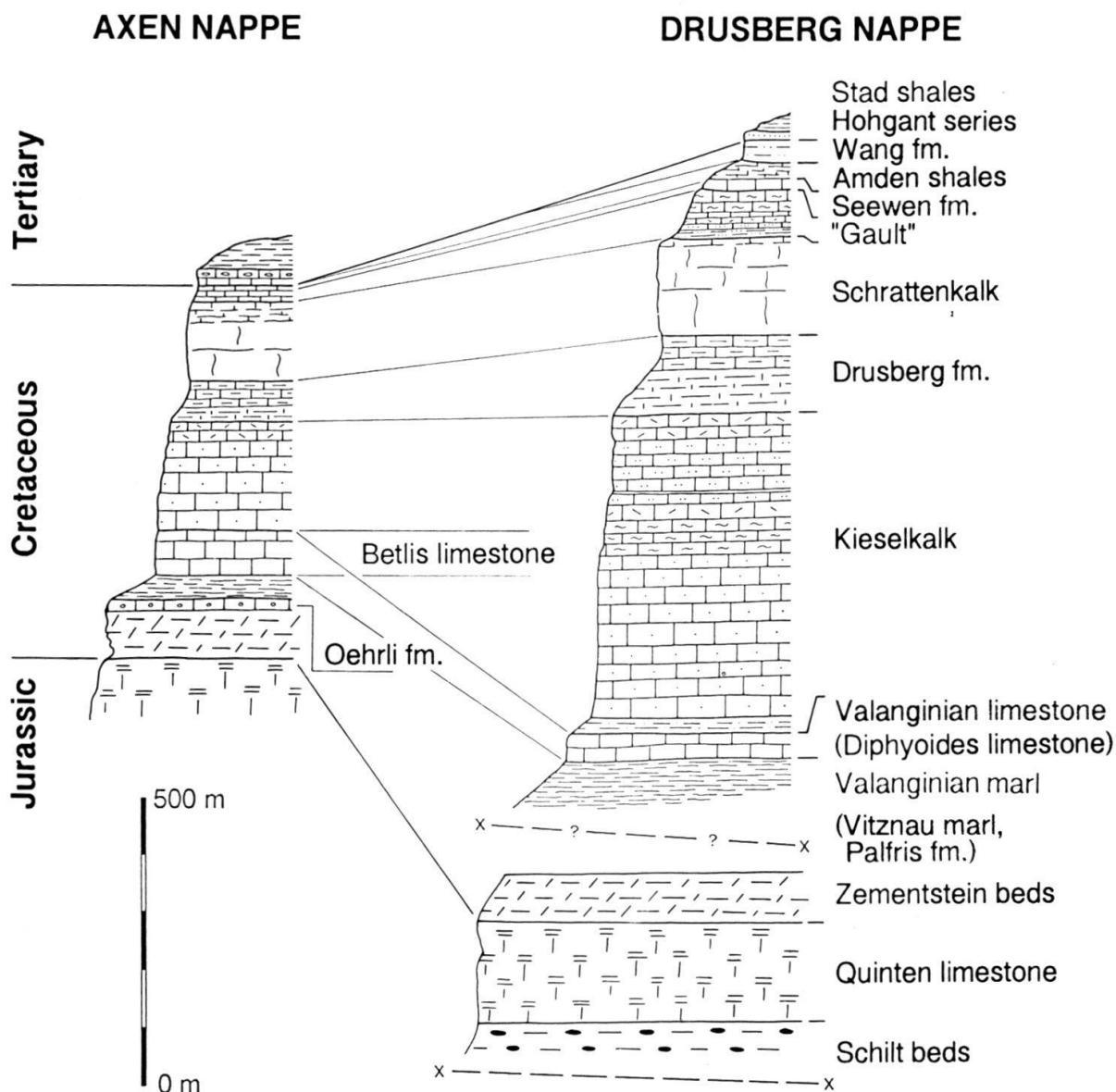
## 2. GEOLOGY AND TECTONICS OF THE OBERBAUENSTOCK SITE

The Oberbauenstock site is located within the Helvetic Drusberg nappe (Fig.1 and 2). The Helvetic nappe emplacement, folding, thrusting and faulting occurred in several, probably continuous phases during the Oligocene and Miocene (e.g. TRUEMPY, 1980) and deep diagenetic / very low-grade metamorphic conditions (terminology after FREY & KISCH, 1987) were reached.

The topographic relief of the Oberbauenstock site ranges from 433 m above sea-level at the nearby Lake Lucerne to approximately 2000 m. The repository host rock consists of highly tectonized Valanginian marl\* accumulated between formations of lower Cretaceous limestone and Tertiary shales (Fig. 2). At the bottom of borehole SA, slices of Tertiary shales, sandstones and Valanginian marl were encountered. A schematic, restored stratigraphic profile of the Axen- and Drusberg nappes around Lake Lucerne is presented in Figure 3.

The Valanginian marl consists mainly of dark gray marly shales with, locally, biotrital lamellae, sandy, carbonate-rich laminae and intercalations of sandy or biotrital limestone layers. The carbonate content in the sequence varies between 32 and 78 vol%

\* According to general use in all publications concerning the Seelisberg tunnel, the informal incorrect term 'Valanginian marl' is used instead of Vitznau marl (upper part of 'Valanginian marl', of Valanginian age) and Palfris formation (lower part of 'Valanginian marl', of Berriasian age) (BURGER & STRASSER, 1981) or Berriasian-Valanginian marl (ISCHI, 1978). In highly tectonized sections, a discrimination between Vitznau marl and Palfris formation is generally not possible.

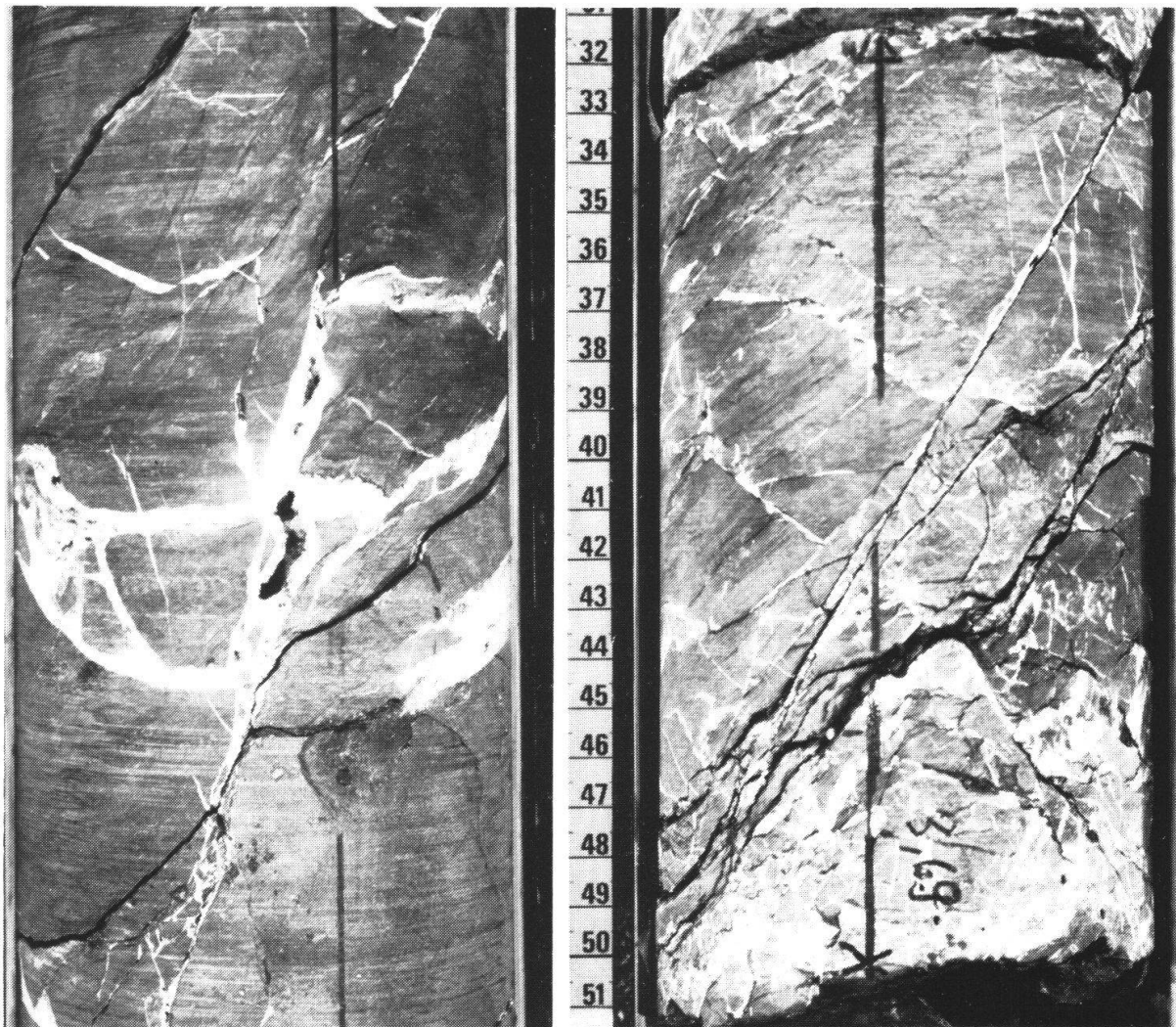


**Fig. 3:** Schematic stratigraphic profiles of Upper Jurassic, Cretaceous and Tertiary formations of the Axen- and Drusberg nappes around Lake Lucerne (slightly modified after SCHNEIDER & KAPPELER, 1984)

(including 1 - 9 % ankerite). Quartz (8 - 22 %) is partly detrital, partly diagenetic. The clay minerals are mainly illite, chlorite, kaolinite and mixed layer minerals. Pyrite is present in all samples but generally < 1 %. The organic carbon content varies from 0.2 to 1.7 %.

The Tertiary sandstone and shale slices encountered in borehole SA contain microfossils and therefore allow an attribution to the 'Stad shales' and 'Hohgant-Series' (Eocene of the Helvetic realm).

The Valanginian marl and the Tertiary rocks contain an extensive and complex multiphase network of syn- to posttectonic fractures (different generations of shear zones, tension joints, 'veins') (Fig. 4). They were formed probably during and subsequent to the deepest burial of the Helvetic nappes from Lower Oligocene to Miocene.



a) Fracture with drusy vugs

b) Shear-fracture cross-cutting older fractures

**Fig. 4:** Valanginian marl with calcite fractures

The fractures vary in thickness ranging from millimetres to several centimetres and are filled with the following minerals: Calcite (generally the main constituent), dolomite, ankerite, celestite, anhydrite/gypsum, quartz, fluorite, sulphides and clay minerals (NAGRA, 1988). These minerals completely fill the fractures or form open druses and vugs with idiomorphic crystals (Fig. 4 a). Hydraulic investigations in the Oberbauenstock boreholes indicate, that some of the druses are isolated and some are part of an extensive fracture or channel system and form active preferential pathways for fluid migration.

### 3. GAS OCCURRENCES IN THE STUDY AREA

The existence of natural gas in the Valanginian marl and in other formations of the northern Alps is well documented (PFISTER, 1972; BUECHI & AMBERG, 1983; SCHNEIDER, 1984; SCHNEIDER & KAPPELER, 1984). In the Oberbauenstock area, soil gas surveys above the Seelisberg tunnel indicated methane concentrations up to 6,200 ppm

across known fracture zones, compared to a normal background concentration of 20 to 50 ppm. Preliminary data from a few soil gas pilot profiles at the Wellenberg site (GEMAG/ENMOTEC, 1990) show maximum values up to 25,700 ppm methane above the Valanginian marl. In addition, significant volumes of hydrocarbon gas, primarily methane, were known to have escaped from the Valanginian marl and partly from other formations during and after the construction of the Seelisberg tunnel. Three significant «gas blowers» (Bläser) and bubble spots (Perlstellen) in water standing on the tunnel floor were observed. The most prominent gas seepage was encountered in an exploration borehole in the Valanginian marl. The gas production of 2-3 l/s from this borehole is reported to have lasted for about ten years, resulting in the production of an estimated 800,000 m<sup>3</sup> of gas (ANDREWS et al., 1988). During the investigation of the Oberbauenstock site, the presence of methane gas was observed in cores, while drilling, during long-term monitoring in the HVB borehole and also by anomalous pressure responses in certain hydraulic test intervals (NAGRA, 1988).

#### **4. MATURITY OF THE ORGANIC MATERIAL IN THE VALANGINIAN MARL**

The organic matter of five samples has been investigated by Prof. M. WOLF, Aachen. All samples originate from the Valanginian marl and are characterised by relatively high C<sub>Org</sub> components (0.7-1.7 wt-%). The results of the measurements are presented in Table 1, together with data from FREY et al. (1980a) for comparison.

As was the case in FREY et al. (1980a), the mean reflectance (random reflectance R<sub>r</sub>) was determined for vitrinitic particles. This is justified as the vitrinites are not obviously anisotropic but rather very small homogeneous components. All samples were found to have a wide scatter of reflectance values ranging between 1.7% and 2.9%. They have a bimodal distribution with a peak for values below 2% and, occasionally, an indistinct second peak above 2%. Since such a wide scatter is unlikely for particles of uniform genesis, the population around the first peak below 2% was selected as representative of the in situ reflectance. The existence of a second population with higher values (R<sub>r</sub> values between 2.16-2.38%) can be explained either by the re-sedimentation of organic material or by its partial oxidation prior to embedding. The representative reflectance values determined in this way vary between 1.83% and 1.93%. They are therefore somewhat lower than the values published in FREY et al. (1980a) for the immediate vicinity of the boreholes, which had an average of 2.04%. However these measurements were carried out on Kieselkalk and 'Gault' samples. The authors also mention that they included «earlier bituminous constituents (metabituminite or meta-exsudatinitite)» in their measurements, with the justification that «Such a procedure is possible in the anthracitic stage where meta-bituminite and vitrinite reach very similar reflectivities». It is therefore possible that their data represent a mixture of values from two somewhat different populations. With a relative error in the mean reflectance of around 10% (here around 0.2%), there is some overlap between the ranges considered in this report and those considered in FREY et al. (1980a).

In the borehole SA the mean reflectance of the samples increases slightly with depth.



Table 1: Mean vitrinite reflectance of Valanginian marl samples from the boreholes SA and HVB and rocks of the Drusberg nappe, after FREY et al. (1980a)

| Sample<br>Depth/Koordinates                          | Stratigraphy          | Lithology                    | Number of<br>measurements | Rr<br>(%) |
|--|-----------------------|------------------------------|---------------------------|-----------|
| <b>Oberbauenstock boreholes</b>                      |                       |                              |                           |           |
| HVB 21.90 m  | Valanginian marl      | Marl, calcareous             | 21                        | 1.83      |
| SA 110.29 m  | Valanginian marl      | Marl, calcareous, sandy      | 24                        | 1.83      |
| SA 268.26 m  | Valanginian marl      | Marl, calcareous, sandy      | 27                        | 1.84      |
| SA 316.78 m  | Valanginian limestone | Marl, with calcite fractures | 22                        | 1.88      |
| SA 345.12 m  | Valanginian marl      | Marl, argillaceous, sandy    | 26                        | 1.96      |
| <b>Drusberg nappe in general (FREY et al. 1980a)</b> |                       |                              |                           |           |
| 689.260/203.450/ 480                                 | Kieselkalk            | Limestone, marly             | 22                        | 2.3       |
| 682.470/200.920/ 850                                 | 'Gault'               | Limestone, marly             | 10                        | 1.4       |
| 684.930/199.880/1840                                 | 'Gault'               | Limestone, marly             | 11                        | 1.6       |
| 689.375/202.590/ 440                                 | Kieselkalk            | Limestone, marly             | 15                        | 2.0       |
| 689.650/201.390/ 450                                 | Kieselkalk            | Limestone, marly             | 9                         | 2.05      |
| 689.650/201.390/ 450                                 | Kieselkalk            | Limestone, marly             | 10                        | 2.1       |
| 689.665/201.350/ 450                                 | Kieselkalk            | Shale, calcareous            | 7                         | 2.0       |

## 5. GAS MEASUREMENTS FOR ROCK AND MINERAL SAMPLES AND FOR ACCUMULATED GAS FROM THE BOREHOLE HVB

To investigate the origin and the migration processes of the hydrocarbon gases (HCG) in the Oberbauenstock area, gas chromatography analyses were carried out on cores from the borehole SA for

- 4 whole rock samples (= rock including calcite fractures) on gases released on vacuum core degassing
- 17 whole rock samples, 4 fracture mineral samples and 3 rock matrix samples on gases released on pulverization

Measurements of C and H isotopes and gas concentrations were carried out for two different groups of gas occurrences:

- gases collected at the well-head of the borehole HVB and
- gases released on pulverization of cores (whole rock samples) from the borehole SA.

In addition, measurements of noble gas concentrations and isotope ratios were performed for three fracture calcite samples.

All the analysis results are presented in Tables 2 to 6.

### 5.1 In situ core degassing measurements

In situ core degassing involves introducing the rock sample into a linked cylinder system which is filled with tap-water and then sealed. An aspirator pump is then used to create an underpressure in the system, allowing the samples to degas for several hours. The gases from the core are collected in one cylinder from where they can be drawn off into a sampling vessel («gas mouse»). The gases are separated chromatographically in the laboratory and analysed by flame ionization.

All the samples originate from the Valanginian marl. The results are given in Table 2a. The gas concentrations vary widely and the maximum of 0.5 cm<sup>3</sup> HCG/l<sub>s</sub>\* (STP) represents a relatively low concentration.

\* cm<sup>3</sup> hydrocarbon gas per 1000 cm<sup>3</sup> of sample material (total volume)

## 5.2 Measurements on pulverized whole rock samples

After weighing, the samples were put into a gas-proof grinding cylinder which was flooded with pure nitrogen. The samples were then ground for 3 to 6 minutes. The gas mixture was subsequently drawn off into glass cylinders, separated chromatographically and analysed by flame ionization. Background values (using porcelain instead of rock) are very low, corresponding to max. 2.5 % of low and <0.1% of high gas contents of the samples.

In the first measurement series, five of a total of six samples were packed in air-tight containers around four hours after removal from the borehole and stored under cooled conditions to await further processing. One sample (OBS-SA 332.02 m) was processed directly after sampling without further «treatment».

Five samples originate from the Valanginian marl. The sample OBS-SA 332.02 m can be assigned stratigraphically to the «Stad shales» (Tertiary). The six samples contain on average 377 cm<sup>3</sup> HCG/l<sub>s</sub> (STP) and the gas concentrations vary widely (Table 2b). Sample OBS-SA 94.49 m contains around 1400 cm<sup>3</sup> HCG/l<sub>s</sub>. The HCG contents of the other five samples are significantly lower, sample OBS-SA 332.02 having the lowest gas content. The relatively high gas concentrations are due to the calcite veins, which are rich in fluid inclusions, also being included in the measurements (see below).

For the second measurement series, the rock grinder was modified and equipped with a barometer to allow the gas volumes released on pulverizing the rock to be estimated directly. The HCG contents of the eleven whole rock samples (Table 2c), which were stored without packing for several weeks, vary between 16 and 206 cm<sup>3</sup> HCG/l<sub>s</sub>, the mean value being 86 cm<sup>3</sup> HCG/l<sub>s</sub>.

The main gas release occurs only at the stage of complete mechanical destruction of the rock. If the gas concentrations for the first and second measurement series are compared, it is apparent that the spontaneous degassing which occurs during storage of the cores is not very significant.

If degassing occurs along fine hair-line fissures, fractionation of the smaller molecules of the gas mixture would be observed. During fractionation, the higher hydrocarbon gases would passively enrich in the rock pores. The samples analysed show a propensity for this enrichment. Any definitive interpretation is rendered impossible by the lack of statistically relevant data.

## 5.3 Measurements on pulverized fracture minerals and rock matrices

The analyses of gas contained in fracture minerals were carried out according to the method used for whole rock gas analyses.

Fracture material which appeared suitable on the basis of its macroscopic properties (clear separation from surrounding rock, monomineralic areas of sufficient volume) was selected for the analysis. For comparison, the surrounding homogeneous



marl/limestone matrix was also analysed in addition to the fracture material (Table 3). An attempt to separate different fracture generations or even fluid inclusion populations (Chapter 6) was not made at this stage.

For the four measurements on fracture minerals the mean HCG concentration is 1460 cm<sup>3</sup> HCG/l<sub>s</sub> (the maximum value is 3052 cm<sup>3</sup> HCG/l<sub>s</sub>). This is around 100 times greater than in the three matrix samples with an average of 16 cm<sup>3</sup> HCG/l<sub>s</sub>.

The isomeric forms of butane (i-C<sub>4</sub>) and pentane (i-C<sub>5</sub>) are around twice as frequent in terms of quantity as the linear forms (n-C<sub>4</sub>, n-C<sub>5</sub>) and the corresponding HCG volumes decrease exponentially with increasing hydrocarbon number. For the mineral samples, there is a good positive linear correlation between the volumes of methane + ethane and those of the higher hydrocarbon gases.

The fracture mineral component in the whole rock ranges from 1 to 10 vol-%. If the hydrocarbon gases originate only from inclusions in fracture minerals, then the whole rock gas concentrations would have to be in the order of 10 to 300 cm<sup>3</sup> HCG/l<sub>s</sub>. This is consistent with the mean values for the whole rock gas concentrations of 377 (first series) and 86 cm<sup>3</sup> HCG/l<sub>s</sub> (second series). The extremely low gas contents of 8 - 30 cm<sup>3</sup>/l<sub>s</sub> for the marl matrices could be trapped in the pore space of the marl due to capillary forces or in fluid inclusions of calcite hair-line fractures.

Assuming that the measured samples are representative for the whole formation, the total amount of trapped methane gas in 1 km<sup>3</sup> of Valanginian marl (marl including the calcite fractures) could be estimated at 100 to 300 million m<sup>3</sup> of gas (STP).

Table 2a: Hydrocarbon gas content of whole rock samples (rock matrix + calcite veins):  
Core degassing measurements (Analysis by Gemag)

| Borehole SA<br>Depth | Stratigraphy/<br>Lithology | ΣHC-Gas<br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>1</sub> +C <sub>2</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>3</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>4</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>5</sub><br>cm <sup>3</sup> /l <sub>s</sub> |
|----------------------|----------------------------|--|---|---|---|---|
| 26.78 m              | Vm / Marl, calcareous      | 0.400                                      | 0.400   | 0.000   | 0.000   | 0.000   |
| 66.64 m              | Vm / Marl, silty           | 0.160                                      | 0.160   | 0.000   | 0.000   | 0.000   |
| 94.58 m              | Vm / Marl                  | 0.101                                      | 0.101   | 0.000   | 0.000   | 0.000   |
| 128.55 m             | Vm / Marl                  | 0.530                                      | 0.530   | 0.000   | 0.000   | 0.000   |
|                      | Mean                       | 0.298                                      | 0.298   | 0.000   | 0.000   | 0.000   |

Vm = Valanginian marl

Table 2b: Hydrocarbon gas content of whole rock samples (rock matrix + calcite veins):  
1st series of measurements on gas released on pulverizing samples (Analysis by Gemag)

| Borehole SA<br>Depth | Stratigraphy/<br>Lithology | $\Sigma$ HC-Gas<br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>1</sub> +C <sub>2</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>3</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>4</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>5</sub><br>cm <sup>3</sup> /l <sub>s</sub> |
|----------------------|----------------------------|--|---|---|---|---|
| 49.17 m              | Vm / Marl                  | 297.3  | 279.2   | 0.1   | 0.0   | 0.0   |
| 49.95 m              | Vm / Marl                  | 154.2  | 154.1   | 0.1   | 0.0   | 0.0   |
| 94.49 m              | Vm / Marl                  | 1424.2   | 1419.8  | 3.9   | 0.5   | 0.0   |
| 94.63 m              | Vm / Marl                  | 200.1  | 199.9   | 0.2   | 0.0   | 0.0   |
| 120.61 m             | Vm / Marl, calcareous      | 138.0  | 137.9   | 0.1   | 0.0   | 0.0   |
| 332.02 m             | T / Sandstone, calcareous  | 49.7   | 47.9  | 1.3   | 0.5   | 0.0   |
|                      | Mean                       | 377.3  | 376.1   | 1.0   | 0.2   | 0.0   |

Vm = Valanginian marl, T = Tertiary

Table 2c: Hydrocarbon gas content of whole rock samples (rock matrix + calcite veins):  
2nd series of measurements on gas released on pulverizing samples (Analysis by Gemag)

| Borehole SA<br>Depth | Stratigraphy/<br>Lithology  | $\Sigma$ HC-Gas<br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>1</sub> +C <sub>2</sub><br>cm <sup>3</sup> /l <sub>s</sub> | C <sub>3</sub><br>cm <sup>3</sup> /l <sub>s</sub> | i-C <sub>4</sub><br>cm <sup>3</sup> /l <sub>s</sub> | n-C <sub>4</sub><br>cm <sup>3</sup> /l <sub>s</sub> | i-C <sub>5</sub><br>cm <sup>3</sup> /l <sub>s</sub> | n-C <sub>5</sub><br>cm <sup>3</sup> /l <sub>s</sub> |
|----------------------|-----------------------------|--|---|---|---|---|---|---|
| 104.59 m             | Vm / Marl, sandy            | 61.7   | 59.3  | 2.1   | 0.2   | 0.1   | 0.0   | 0.0   |
| 134.32 m             | Vm / Marl, calcareous       | 136.1  | 130.2   | 4.3   | 1.1   | 0.4   | 0.1   | 0.0   |
| 153.62 m             | Vm / Marl, argill., sandy   | 24.4   | 18.3  | 4.4   | 1.5   | 0.2   | 0.1   | 0.0   |
| 170.59 m             | Vm / Marl, calcareous       | 98.1   | 94.5  | 2.9   | 0.4   | 0.1   | 0.0   | 0.0   |
| 181.12 m             | Vm / Marl, argill., sandy   | 23.6   | 17.2  | 3.8   | 2.2   | 0.3   | 0.1   | 0.0   |
| 197.11 m             | Vm / Marl, calcareous       | 49.2   | 40.6  | 5.8   | 2.4   | 0.3   | 0.1   | 0.0   |
| 231.51 m             | Vm / Marl, argill., sandy   | 61.1   | 38.3  | 14.8  | 5.8   | 1.6   | 0.4   | 0.1   |
| 243.90 m             | Vm / Marl                   | 120.7  | 120.2   | 0.4   | 0.1   | 0.0   | 0.0   | 0.0   |
| 267.64 m             | Vm / Marl, calc., sandy     | 206.0  | 205.7   | 0.3   | 0.1   | 0.0   | 0.0   | 0.0   |
| 278.17 m             | Vm / Marl, argill., sandy   | 144.7  | 143.6   | 0.9   | 0.1   | 0.0   | 0.0   | 0.0   |
| 307.06 m             | Vl / Limestone, arg., sandy | 16.3   | 16.1  | 0.1   | 0.0   | 0.0   | 0.0   | 0.0   |
|                      | Mean                        | 85.6   | 80.4  | 3.6   | 1.3   | 0.3   | 0.1   | 0.0   |

Vm = Valanginian marl, Vl = Valanginian limestone

Table 3: Hydrocarbon gas content of fracture minerals and surrounding rock matrix  
2<sup>nd</sup> series of measurements on gas released on pulverizing samples (Analysis by Gemag)

| Borehole SA<br>Depth | Stratigraphy/<br>Lithology | $\Sigma$ HC-Gas<br>cm <sup>3</sup> /l <sub>S</sub> | C <sub>1</sub> +C <sub>2</sub><br>cm <sup>3</sup> /l <sub>S</sub> | C <sub>3</sub><br>cm <sup>3</sup> /l <sub>S</sub> | i-C <sub>4</sub><br>cm <sup>3</sup> /l <sub>S</sub> | n-C <sub>4</sub><br>cm <sup>3</sup> /l <sub>S</sub> | i-C <sub>5</sub><br>cm <sup>3</sup> /l <sub>S</sub> | n-C <sub>5</sub><br>cm <sup>3</sup> /l <sub>S</sub> |
|----------------------|----------------------------|--|---|---|---|---|---|---|
| 123.03 m             | Vm / Fracture anhydrite    | 1017.2   | 993.6   | 12.2  | 4.7   | 2.5   | 2.8   | 1.4   |
| 123.03 m             | Vm / Rock matrix           | 8.8  | 8.7   | 0.1   | 0.0   | 0.0   | 0.0   | 0.0   |
| 243.90 m             | Vm / Fracture calcite      | 1421.2   | 1406.4  | 9.8   | 2.5   | 1.1   | 1.1   | 0.3   |
| 243.90 m             | Vm / Rock matrix           | 30.1   | 30.0  | 0.1   | 0.0   | 0.0   | 0.0   | 0.0   |
| 310.14 m             | Vl / Frac. calcite, white  | 3051.6   | 2977.4  | 37.7  | 15.3  | 8.7   | 8.7   | 3.8   |
| 310.14 m             | Vl / Frac. calcite, grey   | 351.4  | 343.5   | 3.9   | 1.6   | 0.9   | 1.0   | 0.5   |
| 310.14 m             | Vl / Rock matrix           | 8.0  | 7.9   | 0.1   | 0.0   | 0.0   | 0.0   | 0.0   |
|                      | Mean fracture minerals     | 1460.4   | 1430.2  | 15.9  | 6.0   | 3.3   | 3.4   | 1.5   |
|                      | Mean rock matrix           | 15.6   | 15.5  | 0.1   | 0.0   | 0.0   | 0.0   | 0.0   |

Vm = Valanginian marl, Vl = Valanginian limestone

## 5.4 Stable isotopes of hydrocarbons and CO<sub>2</sub> from well-head gases and gases released on pulverizing rock samples

### 5.4.1 Experimental

Gas composition and stable carbon and hydrogen isotope ratios are determined on light hydrocarbons to characterize the genetic origin of these gases.

Gas composition (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, hydrocarbons: methane through pentane) were determined in a Siemens Sichromat 2 gas chromatograph using thermal conductivity and flame ionization detectors.

The components to be analysed isotopically were separated in a gas chromatograph (packed column 1/4 in. o.d. stainless steel, 2.5 m length, Porapak Q, temperature programme). The carbon dioxide present in the gas is collected at liquid nitrogen temperature. Methane, ethane and propane are oxidized online to H<sub>2</sub>O and CO<sub>2</sub>, the latter is used for stable carbon isotope determination. The water is reduced on zinc to hydrogen H<sub>2</sub>. Finnigan MAT Type 251 and Finnigan MAT Typ DELTA mass spectrometers are used for <sup>13</sup>C/<sup>12</sup>C and D/H isotope ratio determinations on the CO<sub>2</sub>- and the H<sub>2</sub>-gases. Isotope ratios are given as δ-values relative to the PDB- and SMOW-standard materials (CRAIG, 1957; CRAIG, 1961). Standard deviations are < ± 1 o/oo and < ± 7 o/oo for δ<sup>13</sup>C and δD respectively and depend on the gas quantity. Experimental details on the isotope technique are given by DUMKE et al. (1989).

### 5.4.2 Results

The results of the isotope measurements are given in Tables 4 and 5 and presented in Figures 5 to 7. The data represents 'mixed values' from different generations and populations of fluid inclusions (cf. Chapter 6).

The natural carbon dioxide content in the gas from the pulverized rock samples varies between 0.6 % to 1.1 % but is low ( $< 0.1$  %) in the well-head samples. The carbon isotope ratios are around -20 ‰ in the rock but about -16 ‰ in the well samples (Tab. 4). An explanation for the difference of about 4 ‰ is not available. However, the relatively negative  $\delta^{13}\text{CO}_2$ - values are thought to represent the biogenic (thermal or bacterial) origin of the carbon dioxide from an organic source (cf. GERLING, 1986).

Stable carbon and hydrogen isotope data (Tables 4,5) of hydrocarbon gases from the pulverized rocks (rock gases) and the well-head (well gases) are relatively similar and vary in a narrow range only. A small difference between the data of the two groups of gas samples is found in the gas ratio  $C_1/(C_2 + C_3)$ , which is low for the rock gases but higher for the well gases. Desorption of gases from the rock, i.e. the migration along calcite cleavage planes from fluid inclusions into open fractures, is thought to be responsible for this difference, favouring the escape of methane relative to the higher hydrocarbons, decreasing the ratio  $C_1/(C_2 + C_3)$ . This does not affect the methane isotope ratios, or to a minor extent only.

Considering the above mentioned fractionation in the rock gases, the methane carbon and hydrogen isotope data (Fig. 6) indicate a thermal origin of methane in the well- and the rock gases. An organic source of predominantly marine type and overcooked maturity stage is favoured by the position of the data points in Fig. 6.

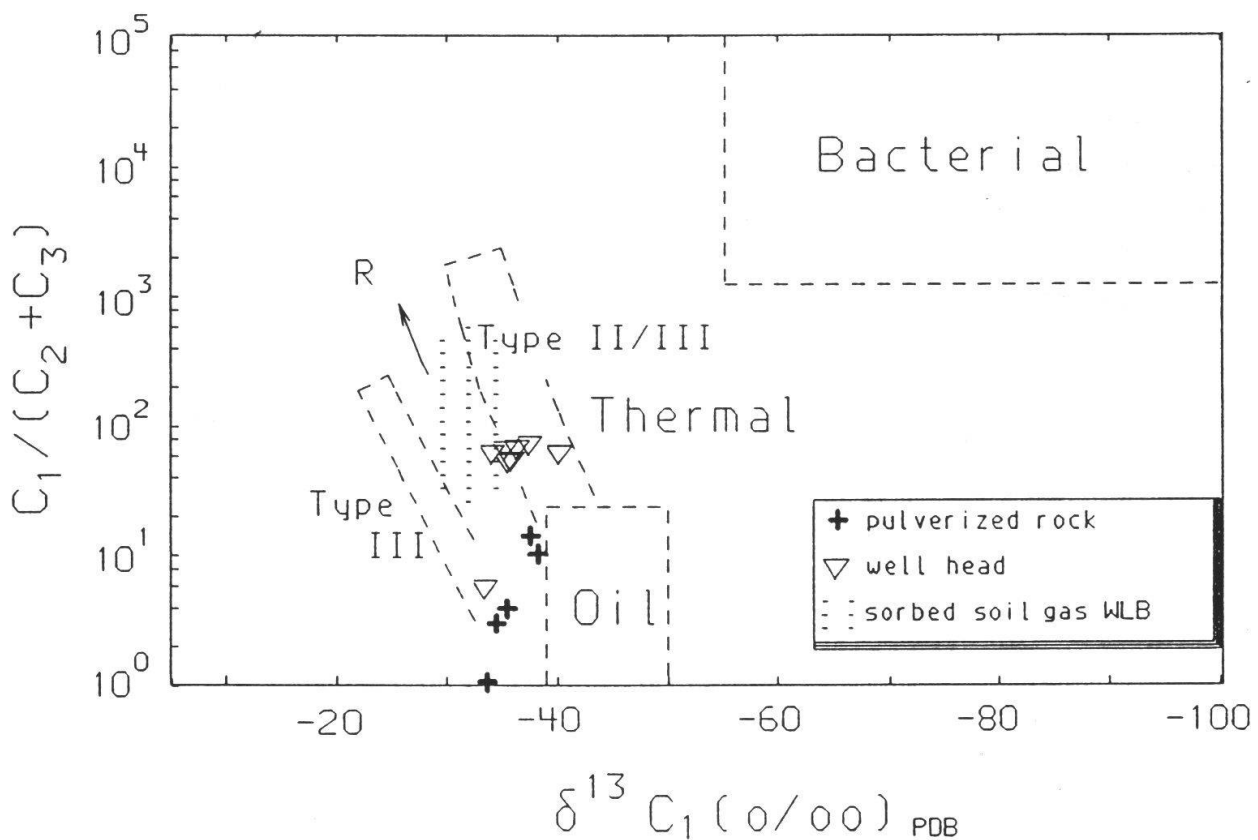


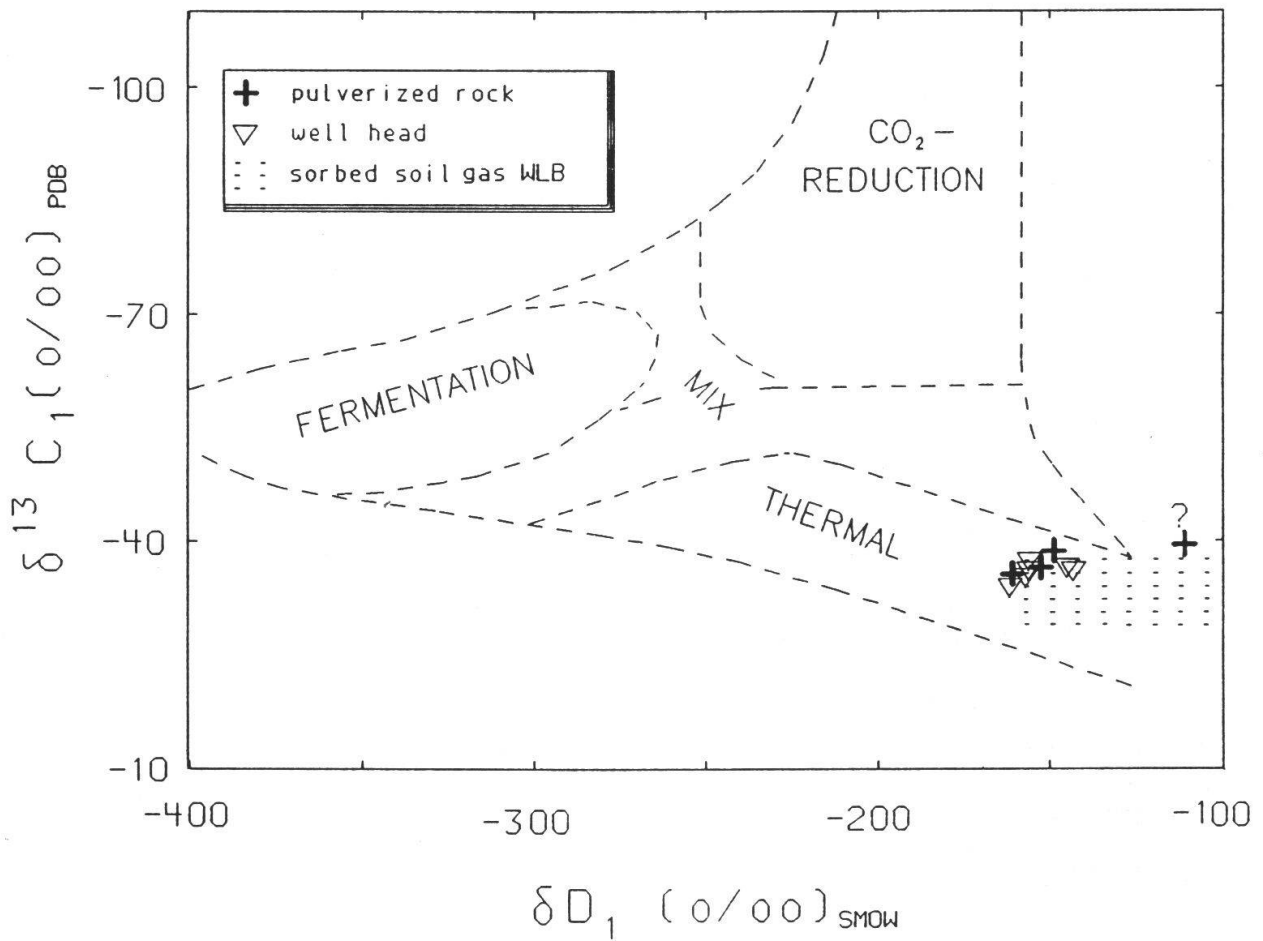
Fig. 5: Gas- and methane carbon isotope ratios of the well-head gases and gases from the pulverized rocks. The range of the data 'sorbed soil gases Wellenberg' is taken from ERNST et al. (1989).

The gas- and methane-isotope ratios (Fig. 5) support the above interpretation, especially for the (un-fractionated) well gases (with one exception). The isotope ratios of the rock gases are more or less identical to the well gases, and the difference in gas ratios is related to the above mentioned desorption fractionation. Therefore it is assumed, that prior to desorption, the gas and isotopic composition of both gas types were similar if not identical, and that the gases from both groups have the same genetic origin.

Carbon isotope ratios of methane and propane are compared to ethane (Fig. 7) and to the correlation lines of cogenetic thermal gases from marine and terrestrial organic sources (FABER, 1987; BERNER, 1989). No significant difference is detectable between the data of the well- and rock gases, confirming the above assumed origin. The methane/ethane data plot very well on the correlation line for marine derived gases, which implies the common origin of ethane and methane from a marine, but not a terrestrial (coal) origin. The maturity of the organic source, estimated from the methane/ethane-correlation line in Fig. 7, ranges from about 1.7 ‰ to < 3 ‰ Rr (vitrinite equivalence). Although the propane concentration in the gases was rather low, and analytical difficulties in the determination of the carbon propane (and ethane) isotope ratios have to be considered, the ethane and propane isotope ratios match well the corresponding correlation line. Ethane and propane are considered to have a common source and confirm the maturity range, given above. This «gas-maturity» matches that measured on the Valanginian marl (Rr 1.83 - 1.96 ‰) or is higher. An origin of the hydrocarbons from the Valanginian marl or formations with higher maturity can be taken into account.

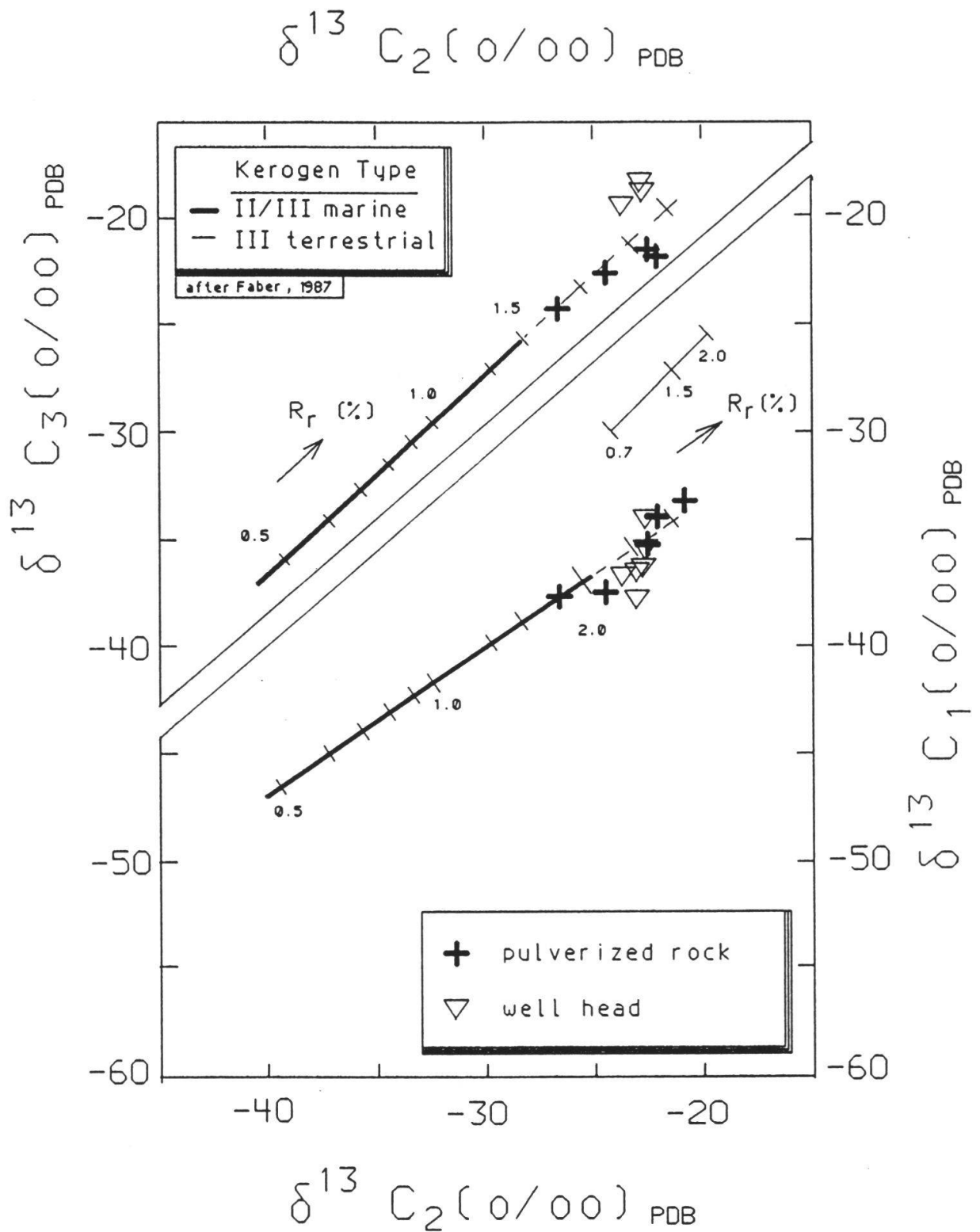
In Figures 5 and 6 the stippled areas represent gas- and isotope-ratios of hydrocarbons desorbed from surface soil samples of the Wellenberg site taken from a depth of 1.2 to 2.8 m (ERNST et al. 1989). Although partly coincidence is found between the soil gases and the samples discussed in this study, the variation of the gas ratio ( $30 \leq C_1/(C_2 + C_3) \leq 400$ ) in the soil gases is larger and the methane is slightly heavier in  $^{13}C$  and  $^2H$  compared to the well head gases (this study). Fractionated degassing of the soils and/or partially methane oxidation could explain this difference. However, the soil gas data could also be taken as indication of a gas from a more mature/more terrestrial source compared to the gases from well-head and pulverized rocks.

In summary, it is concluded, that the gas-, methane-hydrogen and methane through propane-carbon isotope ratios characterize the genetic origin of the gases analysed. The well- and rock gases are considered to have the same genetic origin. They are thermally derived from marine organic material in the overcooked maturity stage and indicate a deep source for the gases.



**Fig. 6:** Methane carbon and hydrogen isotope ratios of the well-head gases and gases from the pulverized rocks. The range of the data 'sorbed soil gases Wellenberg' is taken from ERNST et al. (1989).





**Fig. 7:** Carbon isotope ratios of methane through propane of the well-head gases and gases from the pulverized rocks compared to correlation lines of thermally derived gases from marine or terrestrial organic sources.

Table 4: Isotopic composition of hydrocarbon gas and CO<sub>2</sub> released on pulverizing whole rock samples  
(Analysis by Bundesanstalt für Geowissenschaften und Rohstoffe)

| Borehole<br>SA, Depth | Stratigraphy/<br>Lithology | N <sub>2</sub><br>V-% | O <sub>2</sub><br>V-% | CO <sub>2</sub><br>V-% | C <sub>1</sub><br>V-% | C <sub>2</sub><br>V-% | C <sub>3</sub><br>V-% | C <sub>1</sub> /ΣC <sub>n</sub> | δ <sup>13</sup> C <sub>1</sub><br>‰ | δ <sup>13</sup> C <sub>2</sub><br>‰ | δ <sup>13</sup> C <sub>3</sub><br>‰ | δ <sup>13</sup> CO <sub>2</sub><br>‰ | δDC <sub>1</sub><br>‰ |
|-----------------------|----------------------------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|---------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|--------------------------------------|-----------------------|
| 96.96 m               | Vm / Marl                  | 91.2                  | 6.2                   | 1.1                    | 1.1                   | 0.3                   | 0.1                   | 0.729                           | -34.0                               | -22.0                               | -22.2                               | -19.3                                | -162                  |
| 96.96 m               | Vm / Marl                  | 92.2                  | 3.9                   | 1.1                    | 2.2                   | 0.4                   | 0.1                   | 0.815                           | -35.7                               | -22.9                               | -21.8                               | -20.8                                | -154                  |
| 319.63 m              | T / Shale                  | 87.0                  | 6.7                   | 0.9                    | 5.1                   | 0.3                   | <0.1                  | 0.929                           | -37.8                               | -24.7                               | -22.9                               | -20.0                                | -150                  |
| 324.41 m              | T / Shale                  | 88.7                  | 10.6                  | 0.6                    | <0.1                  | <0.1                  | <0.1                  | 0.791                           | -33.9                               | -21.0                               | n.d.                                | -20.0                                | n.d.                  |
| 343.00 m              | Vm / Marl                  | 88.3                  | 10.3                  | 0.8                    | 0.5                   | <0.1                  | <0.1                  | 0.847                           | -38.0                               | -26.5                               | -24.7                               | -21.4                                | -116                  |

Vm = Valanginian marl, T = Tertiary

Table 5: Isotopic composition of free hydrocarbon gas and CO<sub>2</sub> from borehole HVB (well-head samples)  
(Analysis by Bundesanstalt für Geowissenschaften und Rohstoffe)

| Borehole<br>Sample | Date     | N <sub>2</sub><br>V-% | O <sub>2</sub><br>V-% | CO <sub>2</sub><br>V-% | C <sub>1</sub><br>V-% | C <sub>2</sub><br>V-% | C <sub>3</sub><br>V-% | C <sub>1</sub> /ΣC <sub>n</sub> | δ <sup>13</sup> C <sub>1</sub><br>‰ | δ <sup>13</sup> C <sub>2</sub><br>‰ | δ <sup>13</sup> C <sub>3</sub><br>‰ | δ <sup>13</sup> CO <sub>2</sub><br>‰ | δDC <sub>1</sub><br>‰ |
|--------------------|----------|-----------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|---------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|--------------------------------------|-----------------------|
| HVB A1             | 20.06.87 | 77.0                  | 14.7                  | <0.1                   | 8.1                   | 0.1                   | <0.1                  | 0.987                           | -35.7                               | -22.7                               | n.d.                                | -15.6                                | -144.0                |
| HVB A2             | 20.06.87 | 77.2                  | 22.5                  | <0.1                   | 0.3                   | <0.1                  | <0.1                  | 0.987                           | -33.1                               | n.d.                                | n.d.                                | -15.2                                | n.d.                  |
| HVB A3             | 30.06.87 | 64.5                  | 21.1                  | <0.1                   | 14.1                  | 0.2                   | <0.1                  | 0.988                           | -35.9                               | -23.2                               | n.d.                                | -16.0                                | -148.0                |
| HVB B1             | 26.06.87 | 26.6                  | 8.2                   | <0.1                   | 64.1                  | 1.0                   | <0.1                  | 0.984                           | -34.4                               | -22.6                               | -17.9                               | n.d.                                 | -165.0                |
| HVB B2             | 26.06.87 | 38.6                  | 12.4                  | <0.1                   | 48.3                  | 0.6                   | <0.1                  | 0.987                           | -35.3                               | -22.6                               | -18.1                               | n.d.                                 | -153.0                |
| HVB C1             | 04.07.87 | 38.2                  | 12.2                  | <0.1                   | 38.9                  | 0.6                   | <0.1                  | 0.988                           | -37.5                               | -23.6                               | -19.5                               | n.d.                                 | -153.0                |
| HVB C2             | 04.07.87 | 31.0                  | 9.8                   | <0.1                   | 58.3                  | 0.8                   | <0.1                  | 0.986                           | -36.1                               | -23.6                               | n.d.                                | n.d.                                 | -153.0                |

n.d. = not determined

## 5.5 Noble gases in fracture calcite

The extent to which hydrocarbons have interacted with fluids of different provenance plays an important role when placing constraints on the scale and mechanism of hydrocarbon transport. Noble gases within the mantle, the atmosphere and those produced radiogenically within the earth crust are distinct not only in their isotopic structure but also in their relative abundances. The measurement of the abundances and isotopic ratios of He, Ne and Ar within any fluid therefore enables the magnitude of contribution of noble gases from each of these sources to be resolved (e.g. BALLENTINE et al., 1990).

### 5.5.1 Experimental

He, Ne and Ar abundances and isotopic structure was determined for the fluid existing within the inclusions of fracture calcite on three samples from the Oberbauenstock site, namely one from the SA borehole and two from the HVB borehole. In addition, the U, Th and K concentration of the calcite and inclusions was determined. Each sample was gently disaggregated, ultrasonically cleaned in distilled water and dried at 100°C. Up to 1.0 g of calcite was picked from the material, ranging from 0.1 to 1mm in size. Half of

the sample was placed in a stainless steel vacuum mill and evacuated overnight. The sample was then crushed to release the fluid within the inclusions into the vacuum. Active gases (CH<sub>4</sub>, CO<sub>2</sub>,...) were removed, the remaining He, Ne and Ar separated, and aliquots taken for mass spectrometric determination of their abundances and isotopic composition. The remaining half of the cleaned and picked sample was dissolved in dilute nitric acid, and using a combination of ICP-MS and AA spectrometry, the U, Th and K concentration in each determined (Table 6).

### 5.5.2 Results

The measured He, Ne and Ar abundances within all samples are the same within analytical error at  $14 \times 10^{-6} \text{ cm}^3 \text{ } ^4\text{He (STP)/g}$ ,  $9 \times 10^{-9} \text{ cm}^3 \text{ } ^{20}\text{Ne (STP)/g}$ , and  $5 \times 10^{-6} \text{ cm}^3 \text{ } ^{40}\text{Ar (STP)/g}$ , with the exception of sample OB SA(206.98) which recorded a higher  $^{20}\text{Ne}$  concentration of  $2 \times 10^{-8} \text{ cm}^3 \text{ } ^{20}\text{Ne (STP)/g}$  (Table 6a). The corresponding He/Ne ratios of  $>1500$  compared with the atmospheric He/Ne ratio of 0.288 would indicate that atmospheric He contribution to these samples is negligible. The measured  $^3\text{He}/^4\text{He}$  ratios (R) is normalised to the atmospheric ratio (Ra) of  $1.4 \times 10^{-6}$ . The  $^3\text{He}/^4\text{He}$  ratios are corrected for any air contamination after CRAIG et al. (1978), giving sample (R/Ra)<sub>c</sub> values between 0.02 and 0.05 (Table 6b).

Crustal radiogenic and mantle driven  $^3\text{He}/^4\text{He}$  end members can be taken to have an R/Ra value of 0.02 and 8.0 respectively (MAMYRIN & TOLSTIKHIN, 1984; CLARKE et al., 1969). After correction for any atmospheric He, (R/Ra)<sub>c</sub> values above 0.1 would indicate a resolvable mantle component, while values between 0.02 and 0.1 may be attributed to variations in the radiogenic  $^3\text{He}/^4\text{He}$  end member ratio (HOOKER et al., 1985). The measured R/Ra values between 0.02 and 0.05 are therefore indistinguishable from the crustal radiogenic end member.

The isotopic composition of Ne within all samples is the same within analytical uncertainty. The  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios are indistinguishable from the atmospheric value of 9.80 and it therefore may be assumed that all of the  $^{20}\text{Ne}$  is derived from the atmosphere.  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios of about 0.0310 are significantly above the atmospheric value of 0.0290 with a resolvable radiogenic contribution to the  $^{21}\text{Ne}$ . Similarly the isotopic composition of Ar within all samples is the same within analytical uncertainty. The  $^{38}\text{Ar}/^{36}\text{Ar}$  ratios are indistinguishable from the atmospheric value of 0.1880 and it therefore may be assumed that all of the  $^{36}\text{Ar}$  is derived from the atmosphere.  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios of about 445 are significantly above the atmospheric value of 295.5, with a resolvable radiogenic contribution to the  $^{40}\text{Ar}$ .

$^{20}\text{Ne}$  and  $^{36}\text{Ar}$  measured in the samples are almost entirely atmosphere derived and can only reasonably have been introduced into the calcite by interaction between the inclusion fluid and water which has equilibrated with the atmosphere, such as meteoric or formation water. Considering the concentration of noble gases measured in the calcite (Table 6a), the solubility of  $^{20}\text{Ne}$  in air equilibrated water (e.g. sea water at 25°C =  $1.47 \times 10^{-7} \text{ cm}^3 \text{ } ^{20}\text{Ne (STP)/g H}_2\text{O}$ , SMITH & KENNEDY, 1983) and an estimated calcite volume of 10% within the Valanginian marl, the minimum volume of air equilibrated water required to introduce the  $^{20}\text{Ne}$  measured would occupy 2.3% of the total marl volume. Estimates of pore volumes between 1 and 5 % at the temperatures and pressures recorded by the fluid inclusions would suggest that while a minimum, such a volume of air equilibrated water may have been contained within the pore space of the marl, perhaps as formation water. The mass balance of atmosphere derived noble gases, while not excluding, does not support any large scale fluid circulation involving air equilibrated water.

Radiogenic noble gases within the fluid inclusion consist not only of noble gases associated with the emplacement but also of noble gases produced «in situ», by the radioactive decay of U, Th and K. However, the concentration of these radio-elements in the fracture calcite is small (Table 6b), and even over a period of 30 Ma will not contribute significantly to the radiogenic noble gas content measured. The radiogenic noble gases within the fluid inclusions were emplaced, therefore, during formation of the inclusions, and the Valanginian marl can be considered as a possible source. Radio-element concentrations measured in two samples from the Valanginian marl are U = 1.4ppm, Th = 7.1ppm (analysis by R. KEIL, PSI) and K  $\approx$  1‰ (NAGRA, 1988). At these concentrations, it would require a minimum of 3.7 Ma for a unit volume of marl to produce the radiogenic noble gases trapped in the fracture material within the marl. The ratio of U/Th/K determines the ratio of radiogenic  $^4\text{He}/^{21}\text{Ne}/^{40}\text{Ar}$  produced. The resolved radiogenic  $^4\text{He}/^{21}\text{Ne}/^{40}\text{Ar}$  ratios in the fracture material (not shown) are within experimental error of that calculated for the marl U/Th/K content. Despite the consistency, this correlation cannot unambiguously define the marl as the source of the radiogenic noble gases. However, neither the minimum time required to produce the radiogenic noble gases nor their composition contradict the Valanginian marl as a possible source.

In conclusion, the noble gases in the samples measured are remarkably homogeneous in their concentration and isotopic ratios within the fracture material. Atmosphere derived and radiogenic noble gases dominate the system, with no resolvable mantle component. The radiogenic noble gases may be accounted for by radiogenic production in the host Valanginian marl before the formation of the fluid inclusions / calcite veins. In addition, considering the volume of air equilibrated water as a source of the atmosphere derived noble gases, it would appear that the mass balance of the noble gases may be achieved internally. These results, while not ruling out noble gas input from outside the Valanginian marl, are consistent with a closed system.

Table 6a: Noble gas and radio-element concentration in the fracture calcite

| Borehole<br>Sample | $^4\text{He}$<br>$10^{-6}\text{cm}^3/\text{g}$ | $^{20}\text{Ne}$<br>$10^{-6}\text{cm}^3/\text{g}$ | $^{40}\text{Ar}$<br>$10^{-6}\text{cm}^3/\text{g}$ | U<br>ppb  | Th<br>ppb | K<br>ppm |
|--------------------|--|---|---|-----------|-----------|----------|
| SA (206.98)        | 13.7 (18)                                      | 0.0201 (38)                                       | 7.0 (14)  | 8.4 (8)   | 12.5 (13) | < 3      |
| HBV (6.75)         | 15.4 (20)                                      | 0.0088 (17)                                       | 5.0 (10)  | 7.8 (8)   | 65.7 (70) | < 11     |
| HBV (37.57)        | 13.7 (18)                                      | 0.0084 (16)                                       | 4.6 (9)   | 29.0 (30) | 307 (30)  | < 7      |

Figures in parentheses are 2  $\sigma$  errors quoted for the last significant figures(s).

Table 6b: He, Ne and Ar isotopic composition of fluids released on crushing fracture calcite.

| Borehole<br>Sample           | $^3\text{He}/^4\text{He}$<br>(R/Ra) <sub>c</sub> | $^{20}\text{Ne}/^{22}\text{Ne}$ | $^{21}\text{Ne}/^{22}\text{Ne}$ | $^{38}\text{Ar}/^{36}\text{Ar}$ | $^{40}\text{Ar}/^{36}\text{Ar}$ |
|------------------------------|--|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| SA (206.98)                  | 0.018 (1)  | 9.83 (4)                        | 0.03077 (3)                     | 0.1878 (6)                      | 444 (12)                        |
| HBV (6.75)                   | 0.020 (1)  | 9.76 (5)                        | 0.03098 (4)                     | 0.1879 (8)                      | 431 (16)                        |
| HBV (37.57)                  | 0.050 (3)  | 9.78 (4)                        | 0.03124 (5)                     | 0.1879 (7)                      | 461 (17)                        |
| Air (OIZIMA & PODOSEK, 1983) | 1.0  | 9.80                            | 0.0290                          | 0.1880                          | 295.5                           |

Figures in parentheses are  $2\sigma$  errors quoted for the last significant figure(s).

## 6. MICROTHERMOMETRIC INVESTIGATION OF FLUID INCLUSIONS

As shown above, a considerable amount of methane is found in the Valanginian marl, and a significant proportion of this gas is thought to be trapped in fluid inclusions of fracture calcites. A pilot programme was therefore set up using microthermometry for three samples (HBV 6.75 m, SA 123.03 m, SA 222.54 m). Microthermometric measurements were performed on the Chaix-Meca freezing-heating stage, designed to work in the  $-180$  to  $+600$  °C by POTY et al. (1976). Despite some difficulties in preparing the fracture calcites for the investigations, most of the questions relevant to gas transport could be answered.

In addition to rock-forming calcite, three generations of calcite fracture systems are differentiated by intersection criteria. Early calcite fractures are characterized by a high density of very small inclusions which, on a microscopic scale, give the calcite a slightly grey appearance. They are too small for fluid inclusion investigations. In contrast to this, the second calcite generation contains several fluid inclusion populations easily distinguishable by texture, form and size of fluid inclusions. Similar fluid inclusion populations were also detected in contemporaneously precipitated fissure quartz. The last calcite generation as well as the rock-forming calcites are more or less depleted in inclusions and therefore not useful for microthermometry. Detrital quartz grains in rocks contain inherited fluids from the parent material as well as hydrocarbon-bearing fluids from the Alpine metamorphic cycle.

The earliest inclusion populations trapped in the 2nd generation of fracture calcite and within the fracture quartz are small ( $< 2\text{-}16\mu\text{m}$ ) and are characterized by fairly dense methane ( $0.293\text{-}0.315\text{ g/cm}^3$ ). They contain a so-called «dry gas» ( $> 95\text{ wt.-% CH}_4$ ), less than  $2\text{ wt.-%}$  of higher hydrocarbons (HHC) and only a  $3\text{ - }4\text{ wt.-%}$  of water. Methane-bearing water-rich fluid inclusions ( $0.5\text{ to }1\text{ wt.-%}$  of  $\text{CH}_4$ ) with a mean homogenization temperature of  $163^\circ\text{C}$  were also found in the fracture quartz. The younger inclusion populations are larger (up to  $30\ \mu\text{m}$ ), richer in HHC and contain only  $60\text{ to }70\text{ wt.-% CH}_4$  (so-called «wet gas»).

According to MULLIS (1979) and FREY et al. (1980a), the fairly pure methane in the oldest inclusion populations indicates minimum formation temperatures of around  $200^\circ\text{C}$ . Whether such temperatures were actually reached in the present host rocks remains questionable. On the one hand, homogenisation temperatures from some water-





rich inclusions in fracture quartzes gave a mean value of only 163°C and, on the other hand, the investigation zone lies somewhat to the north of the beginning of the anchi-zone (at around 200°C according to MULLIS (1979) and FREY et al. (1980b)); the data in BREITSCHMID (1982) and FREY et al. (1980a) tend to indicate temperatures below 200°C. It is therefore possible that the methane was produced through «cracking» of organic material in even deeper-lying units and became trapped further up in fractures as fluid inclusions. This is also supported by the fact that the rock-forming calcites do not appear to contain any significant methane-rich inclusions.

Knowing both, composition and density of the fluid inclusions, the internal fluid pressure can approximately be determined at any given temperature (MULLIS, 1979 and 1987). Pressures calculated below refer to the system CH<sub>4</sub> (ANGUS et al., 1976) and the extrapolated ternary system H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> (JACOBS & KERRICK, 1981), yielding similar pressure values for fluid inclusions filled with ≈ 99 vol.-% of methane. At 25°C, the pressures in the earliest methane-rich fluid inclusions are 600-700 bars, 1200 -1400 bars at 170°C and 1300-1500 bars at 200°C. Assuming lithostatic pressure (highly over-pressured rocks) and a mean rock density of 2.5 g/cm<sup>3</sup>, an overburden of 5 - 6 km of rock (Penninic and Eastern Alpine nappes ?) would be required to generate such pressures during formation of inclusions. These inclusions must therefore have been formed during the Alpine metamorphism in this area. It is not clear how much younger the later methane-depleted inclusions are.

If one assumes 0.1-1 vol.-% methane-rich fluid inclusions with a density of 0.3 g/cm<sup>3</sup> in the fracture calcites, this would give absolute concentrations of 0.42-4.2 l of methane per litre of fracture calcite.

## **7. CONCLUSIONS AND IMPLICATIONS FOR HYDROCARBON EXPLORATION**

The presence of natural hydrocarbon gas, mainly methane, was observed in boreholes in the Valanginian marl at the Oberbauenstock site and in soil gas measurements at the Oberbauenstock and Wellenberg sites. A pilot programme was therefore set up to investigate the origin and the migration mechanisms of these gases.

Gas chromatography and isotope analyses were carried out on gases collected at the well-head, on gases released on pulverizing rock samples (marl and calcite fractures) and on vacuum core degassing.

The fracture infilling calcites contain up to 3 litres of hydrocarbon gas (STP) per litre of calcite, while, in the marl matrix, only minor amounts of gas are found. The total amount of methane gas in 1 km<sup>3</sup> of Valanginian marl (marl including the calcite fractures) is estimated at 100 to 300 million m<sup>3</sup> of gas (STP).

Most of the gas is trapped in fluid inclusions at high pressures. Hydrocarbon isotopes, vitrinite reflectance measurements and microthermometric investigations of the fluid inclusions indicate a thermogenic origin of the hydrocarbon gas from a highly mature marine source rock ( 1.7 ‰ < R<sub>r</sub> < 3 ‰). The fluid inclusions were formed during the Alpine orogeny at temperatures of 160-200°C and pressures of 1200 to 1500 bars. The ratios of the radiogenic noble gases in the fluid inclusions may be accounted for by radiogenic production within the host Valanginian marl, but do not rule out noble gas input from outside the Valanginian marl.

The hydrocarbon gas was transported within the rock by the Alpine tectonic uplift from great depth to its present position in the form of fluid inclusions. Because the gas did not fractionate significantly during these processes, the isotopic signature of its overcooked maturity stage is still well preserved.

In contrast to quartz, calcites have well-defined cleavage planes, which allow the gas to escape occasionally, e.g. due to chemical dissolution, neotectonic movements (Alpine uplift), earthquakes or decompression by erosion. Accumulation in open fracture systems and subsequent migration to the surface is thought to be responsible for at least some of the soil gas anomalies measured in the northern Helvetic Alps.

Gas seepage from this type of near-surface gas reservoir can cause a significant overprint on gas indicators or anomalies from deep gas reservoirs. The inherited signature from its deep highly mature origin could well coincide with the signature of gases migrating at present from deep reservoirs.

In hydrocarbon exploration strategies, (more) attention has to be paid to detailed rock and fracture material analyses for hydrocarbons.

To fully understand the genesis and migration of hydrocarbon gas at the potential sites for a radioactive waste disposal in the Valanginian marl, future Nagra work will include investigations of rocks and calcite veins from other stratigraphic units and tectonic settings in the study area.

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