Carbon and Nitrogen Isotope Measurements of Gas-Bearing Fluid Inclusions: A Tool For Tracing Gas Sources and Maturity of Source Rocks*

Volker Lüders¹ and Birgit Plessen¹

Search and Discovery Article #40963 (2012)**
Posted June 25, 2012

*Adapted from poster presentation at AAPG Annual Convention and Exhibition, Long Beach, California, April 22-25, 2012
**AAPG©2012 Serial rights given by author. For all other rights contact author directly.

¹Helmholtz Centre Potsdam GFZ, Potsdam, Germany (volue@gfz-potsdam.de; birgit.plessen@gfz-potsdam.de)

Abstract

Since gases in reservoirs may be accumulated from different sources it is of importance to trace regional migration paths especially in unexplored areas or commercially dry fields where no information about the composition, origin and fate of migrated gases can be obtained in due to the lack of petroleum samples from reservoirs or gas tests. In such frontier areas, fluid inclusions can provide pointers to commercial hydrocarbon accumulations because they may contain considerable amounts of gases, such hydrocarbons, CO₂, and/or N₂.

For the past decades, several studies of isotope ratios in fluid inclusions have been performed using different techniques for the extraction of gases from inclusions and for the determination of isotopic ratios. Most of the studies used off-line or online sample preparation, either by thermal decrepitation of fluid inclusions or mechanical crushing. Subsequent measurements of isotope ratios of released gases were either done by using isotope ratios mass spectrometry (IRMS) or gas chromatography-mass spectrometry (GC-MS). The amounts of sample material being used typically varied between 1 to 10 g, or even more.

Here we describe a new analytical method for simultaneous measurements of natural gases in fluid inclusions using a sample crusher and an Elemental analyzer (EA) combustion-IRMS system, including an EA, ConFlo III and DeltaplusXL mass spectrometer. The use of such an analytical setup provides a means to analyze the isotopic composition of simultaneously released N₂, CH₄, and CO₂ from fluid inclusions. Even small amounts of sample material (0.1 - 0.5 g) produce enough gas to obtain reproducible values.

A case study being performed in the North German Basin demonstrates the use of gas-bearing fluid inclusions, as remnants of gas migration in the unexplored southern part of the Lower Saxony Basin, to obtain information about probable source rocks and their maturities. It turned out that gases in fluid inclusions are either be derived from type II or type III kerogens. Strong variations in carbon isotopic composition of methane-bearing inclusions indicate that the parent source rocks had achieved different degree of maturity in local parts of the basin at the time when the gases where released. Furthermore, the data obtained from simultaneous measurements of carbon isotopic composition of methane and nitrogen isotopic composition in fluid inclusions yielded evidence of different origin of nitrogen in some reservoirs.
Carbon and Nitrogen Isotope Measurements of Gas-Bearing Fluid Inclusions: A Tool For Tracing Gas Sources and Maturity of Source Rocks

Introduction

The use of carbon isotopes in hydrocarbon exploration is widely applied and provides important information for the correlation between source rocks and hydrocarbons (e.g., Stahl, 1977; Chung and Sackett, 1979; Schueller, 1990 and 1984; Rice et al., 1989; Clayton, 1991). The δ13C(CH4) is a useful tool to assess the contribution of different sources of gases. However, no information about the composition, origin and fate of migrated gases can be obtained in unexplored areas or commercially dry fields due to the lack of petroleum samples from reservoirs or gas tests during drilling. In such frontier areas hydrocarbon-bearing fluid inclusions can provide pointers to commercial hydrocarbon accumulations (e.g., Kärnten et al., 1993; Goldstein and Reynolds, 1994; Georg et al., 2007).

This study demonstrates the use of gas-bearing fluid inclusions, as remnants of gas migration in parts of the North German Basin (NGB) in Europe, to obtain information about probable source rocks and their maturities.

Carbon isotopic composition of methane from natural gases

The carbon isotopic composition of methane being produced from boiled organic matter depends on the carbon isotopic signature of the precursor material and depositional conditions (e.g., temperature, time of gas generation, etc.). Biogenic gas formed during early stages of burial by methanogenic bacteria is enriched in 13C and typically shows light δ13C(CH4) values in the range between -110 and -60‰ (Fig. 1). With increasing temperatures bacterial activity decreases and finally ceases since nutrient supply for microbial activity is restricted (e.g., Wilhelms et al., 2001). Further increase in temperature at greater depth, thermal cracking and hydrogen disproportion in the kerogen leads to the formation of oil and volatiles, i.e., Hydrocarbons (Fig. 2). Thermal cracking first leads to the breaking of -C-C- bonds and subsequent breaking of more stable -C-H- bonds with increasing temperature (Sackett, 1978) resulting in fractionation of the δ13C(CH4) values. Thermogenic gas typically shows δ13C(CH4) values between -50 and -20‰ (e.g., Stahl, 1977; School 1980; Rice et al., 1989). However, methane being generated from nonmarine humic source rocks (type III kerogen, e.g., coals) shows less negative initial δ13C values when compared with gas being sourced from marine type II kerogen that have achieved equivalent degrees of maturity.

Analytical setup

Several techniques have been developed and tested so far for the extraction of fluids and gases from inclusions, and for the determination of isotope ratios. Most of these studies used off-line sample preparation, by either thermal decrepitation or mechanical crushing. Subsequent measurements of the isotope ratios of released gases were predominantly performed off-line by dual-inlet IRMS or GC-IRMS (Pienzen and Lüders, 2012). However, gas-rich inclusions hosted in diagenetic minerals often consist of complex mixtures of CO2 and CH4, and/or variable amounts of N2. Therefore, an analytical approach was needed for effective gas release and separation, and simultaneous on-line measurements in order to determine the isotope ratios of gases. The combination of a crusher, gas chromatography (GC) and elemental analyzer (EA) and continuous-flow IRMS. (Fig. 2) is the only technique that fulfills all these requirements because it allows the conversion of gas mixture into clean gases and on-line measurements of stable isotope ratios. The δ13N and δ15N (CH4, CO2) values of gases released from fluid inclusions hosted in selected samples are shown in Table 1. These samples originate from a hydrothermal gold-quartz vein (GH-171 and GH-151), a fracture-fill calcite/anhydrite mineralization in a well from the North German Basin, and quartz mineralization hosted by Upper Jurassic quartzite (Limberg, Lower Saxony Basin). The excellent reproducibility of the δ15N values for CH4 and CO2 indicates complete gas separation and oxidation of CH4 to CO2.

The general high signal stability of the mass spectrometer and good linearity even allows precise measurements of δ15N and δ13C values at low signal intensity of about 100 mV.

Table 1: δ15N and δ13C (CH4, CO2) isotopic composition of gases from fluid inclusions in quartz and anhydrite from various locations.

<table>
<thead>
<tr>
<th>Sample (Local)</th>
<th>Location</th>
<th>δ15N (‰)</th>
<th>δ13C (‰)</th>
<th>δ13C (‰)</th>
<th>δ15N (‰)</th>
<th>δ13C (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GH-171 quartz</td>
<td>n.d.</td>
<td>-9.9</td>
<td>1764</td>
<td>-10.6</td>
<td>1153</td>
<td></td>
</tr>
<tr>
<td>GH-151 quartz</td>
<td>n.d.</td>
<td>-9.4</td>
<td>1591</td>
<td>-10.8</td>
<td>2153</td>
<td></td>
</tr>
<tr>
<td>H-18-A anhydrite</td>
<td>14.7</td>
<td>810</td>
<td>-26.5</td>
<td>1174</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H-18-A anhydrite</td>
<td>15.2</td>
<td>526</td>
<td>-27.0</td>
<td>519</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H-18-A anhydrite</td>
<td>15.3</td>
<td>476</td>
<td>-26.3</td>
<td>1081</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H-18-A anhydrite</td>
<td>14.8</td>
<td>948</td>
<td>-26.9</td>
<td>1212</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Note: Peak intensities below 100 mV yield erratic isotope values, n.d. = not detected, i.e., peak intensities below 100 mV.
**Relationship between carbon isotope ratios and maturity of source rocks**

Stahl (1977) and Schoell (1980) have shown that dry gases generated from Carboniferous coal measures in the NGB show a clear relationship between carbon isotope fractionation and the maturity of their source rocks (Fig. 3). This relationship is also well constrained by pyrolysis experiments showing that the carbon isotopic composition of methane sourced from coals increases up to several per mil with increasing thermal rank of the parent kerogen. The same relationship holds also true for type II kerogen in the Val Verde Delaware Basin (Fig. 3).

This often well-expressed correlation between the \(\delta^{13}C(CH_4)\) values of the gas and the maturity of the organic matter in the parent source is commonly plotted in \(\delta^{13}C(CH_4)\) versus maturity diagrams where the maturity of the source rocks is indicated by vitrinite reflectance. In cases where gases are assumed to be unaffected by contamination during migration or by mixing, increasingly less negative \(\delta^{13}C(CH_4)\) values with increasing maturity have been generally observed (e.g. Stahl et al., 1977; Schoell, 1980; Berner and Farber, 1988).

Le Fig. 3 (modified after Schoell, 1980) shows the carbon isotope ratios of methane in natural gases in relation to the maturity of their source rocks. Gases from the Val Verde Delaware Basin are generated from marine source rocks (type II kerogen). Data for coal gas (type III kerogen) are from reservoirs in the North German Basin.

**Coal gas**

The measured \(\delta^{13}C(CH_4)\) values in quartz-hosted inclusions from the Upper Carboniferous strata in the NGB vary between -28.8 and -17.9‰ (Fig. 4). Increasing \(\delta^{13}C(CH_4)\) values are mostly correlated with increasing ranges of Ro in potential sources rocks.

When plotting the \(\delta^{13}C(CH_4)\) values of methane in gas-rich inclusions in a \(\delta^{13}C(CH_4)\) vs. % Ro of potential source rock diagram (Fig. 4), they fall along or close to the proposed trend line for the maturation evolution trend of \(\delta^{13}C(CH_4)\) from type III kerogen in Fig. 3. The exceptions are the samples Halb-52 and Bzg 1/74 quartz I where early stages of gas migration occurred prior to maximum burial (Fig. 4) and the \(\delta^{13}C(CH_4)\) values of the inclusions in quartz indicate lower maturity of the source rocks. In contrast, younger quartz fracture-fill mineralization (quartz II in Table 3) within the Bzg 1/74 well that precipitated at Mesozoic times during stages of maximal burial (Fig. 5) reflect \(\delta^{13}C(CH_4)\) isotopic composition that can be expected from a source rock that achieved maturity well above 4% vitrinite reflectance (Fig. 3).

**Origin of CO\(_2\)**

The \(\delta^{13}C\) values of CO\(_2\) trapped along with CH\(_4\) (xCH\(_4\)) are mostly slightly negative or even positive, suggesting that CO\(_2\) in the inclusions is of inorganic origin (e.g., water-rock interaction and dissolution of detrital, marine calcite). Increasing CO\(_2\) content in gas-rich inclusions mostly correlates with increasing \(\delta^{13}C(CH_4)\) values of CO\(_2\). Strong negative \(\delta^{13}C\) values of CO\(_2\), suggesting an organic CO\(_2\) origin, were only measured in inclusions where gas is derived from type II kerogen as indicated by also very negative \(\delta^{13}C(CH_4)\) values of methane (Fig. 6).

**Alteration of CH\(_4\) by TSR**

At temperatures well above 80°C most sulfate-reducing bacteria cease metabolism and TSR is the main process generating large quantities of H\(_2\)S in deep subsurface reservoirs. In the North German Basin natural gases with H\(_2\)S content up to 30% occur in deep Zechstein reservoirs (Stassfurt Carbonate 2). Experimental studies have shown that natural gas could react with anhydrite under high temperatures, and that H\(_2\)S, CO\(_2\), calcite, and water are the main products. TSR of natural gas with anhydrite is possible and high temperature is favorable to the simplified reaction:

\[
\text{CaSO}_4 + CH_4 \rightarrow \text{CaCO}_3 + H_2S + H_2O
\]  

(1)

TSR leads to the breaking of \(^{12}C-^{16}O\) bonds and the subsequent breaking of the more stable \(^{12}C-^{18}O\) bonds at higher temperatures resulting in fractionation of the \(\delta^{13}C(CH_4)\) values (Fig. 7). \(^{13}C\) gets enriched in H\(_2\)S and thus calcite cements may show very negative \(\delta^{13}C(CH_4)\) values in cases where CO\(_2\) from reaction 1 is trapped in fluid inclusions in non-carbonaceous mineral such as fluorite or anhydrite strong negative \(\delta^{13}C(CH_4)\) values can also be observed (Fig. 7).

In areas with complex gas fillings, studies of carbon isotopic ratios in fluid inclusions provide a means to decipher stages of fluid migration and possible timing of TSR.

---

**Fig. 3** δ\(^{13}C\) values of methane in natural gases in relation to the maturity of their source rocks.

**Fig. 4** Ranges of \(\delta^{13}C\) values of methane in fluid inclusions from fracture-fill mineralization hosted by Carboniferous sediments (North German Basin) in relation to the maturity of their source rocks (after Lüders et al. 2012).

**Fig. 6** Carbon isotope ratios of CO\(_2\) vs. CH\(_4\) of fluid inclusion gases.

**Fig. 7** Carbon isotope ratios of CH\(_4\) and CO\(_2\) gases from fluid inclusions in fault fracture fillings from Zechstein carbonate H\(_2\)S-rich reservoirs and \(^{12}C\) vs. \(^{18}O\) values of reservoir carbonates and calcite cements. Note: \(\delta^{13}C(CH_4)\) values increase with increasing H\(_2\)S content in the reservoirs.
Shale gas

As observed for coal gas, there is also a good correlation between the carbon isotopic composition of methane in natural gases and the maturity of their source rocks. This correlation is shown in Fig. 8 for natural gases being sourced from Lower Jurassic Posidonia shale (NGB) and from Paleozoic shale from the Delaware Valley-Verde Basin (USA). The trend line shown in Fig. 8 is the reference line for fractionation of the carbon isotopes of methane used to estimate the maturity of source rocks at the time of gas generation in Figs. 10 and 12.

Nitrogen

Nitrogen concentrations in natural gases may constitute a major risk for hydrocarbon exploration in sedimentary basins. The study of nitrogen isotope ratios may provide information about the origin of gas accumulations. Nitrogen concentrations in natural gases may constitutes a major risk for hydrocarbon exploration in sedimentary basins. The study of nitrogen isotope ratios may provide information about the origin of gas accumulations. Nitrogen isotope ratios of fluid inclusion gases can be measured by on-line continuous-flow isotope ratio mass spectrometry. Several fracture-fill mineralization studied here contain complex gas mixtures of CH (3), CO (2), and N (1) irrespective the origin of gas (i.e., coal vs. shale gas).

Conclusions

The use of a crushing device interfaced with an elemental analyzer combustion-IRMS system provides a powerful method for hydrogen and carbon isotope analysis in fluid inclusions. Several fracture-fill mineralization studied here contain complex gas mixtures of CH (3), CO (2), and N (1) irrespective the origin of gas (i.e., coal vs. shale gas).

Fig. 8 Carbon isotope ratios of methane in natural gases in relation to the maturity of their source rocks. Data are taken from Stahl (1979) and Schoell (1980).

Fig. 9 Left: Quartz mobilizes in Viskiian chert, Lautenthal, Harz Mts. (Germany). Right: Calcite fracture-fillings in Gzhelian shale, well Schadewalde E She 175, NGB (Germany).

Fig. 10 Ranges of δ13C values of methane in fluid inclusions from fracture-fill mineralization sourced from Carboniferous sediments (NGB, Harz Mts., and Rhenish Massif) in relation to the maturity of their source rocks. Gas of fluid inclusions in fracture-fill calcite from the She well may represent mixtures of coal and shale gas.

Fig. 11 Simplified map of the outline of the LSB also showing iso-reflectance contours (Ro%) on base Jurassic (after Koch & Armannsen, 1975 and Daudhoff et al. 1990) and Ro values of Posidonia shale from wells and Wealden coal. Sample sites of quartz mineralization hosted by Triassic and Jurassic strata are shown in squares and circles, respectively. OS: City of Osnabrück.

Fig. 12 Ranges of δ13C values of methane in fluid inclusions from fracture-fill mineralization in relation to the maturity of their source rocks (most likely Posidonia shale). Color codes of symbols refer to sample sites in Fig. 11. Ro values of two wells are shown in relation to the measured δ13C values of methane in fluid inclusions. Note that fluid filled fractures in horst halokinesis yield lower maturity than the measured Ro of 0.88%, probably reflecting continuous gas generation prior to maximal burial.

Fig. 13 δ13C values vs. δ18O values of methane in fluid inclusions from fracture-fill mineralization hosted by Paleozoic rocks from the NGB and Harz Mts. and Mesozoic rocks from the Lower Saxony Basin. The most positive δ13C values were measured in fluid inclusion gases from fracture-fill mineralization from wells offshore by Rotliegender lacustrine shale (Fig. 14).

Fig. 14 Distribution of Rotliegender salt lake sediments in the NGB and North Sea (after Gost et al., 1998) and ranges of measured δ13C values in fluid inclusions gases from fracture-fill mineralization hosted by Paleozoic rocks.