

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

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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 were 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

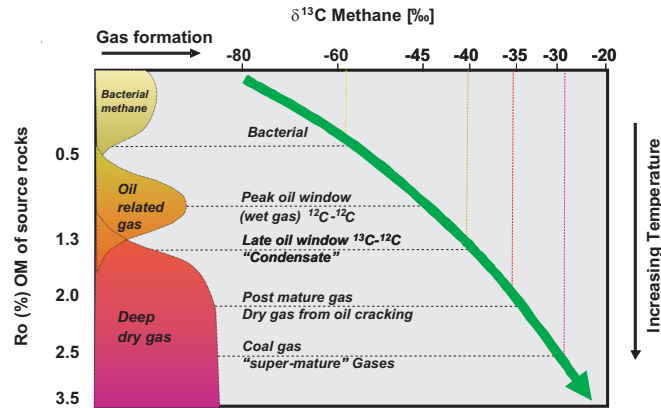


Fig. 1 Classification of natural gases and $\delta^{13}\text{C}$ isotopic composition of methane (modified after Schoell, 1980)

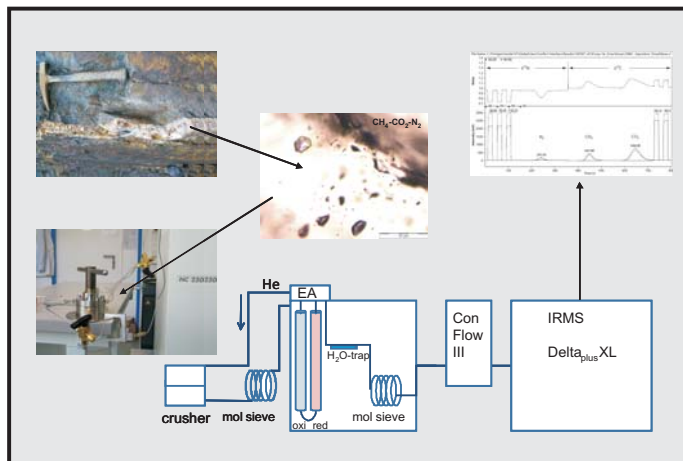


Fig. 2 Schematic diagram showing the crusher/EA/IRMS line for simultaneous measurements of N_2 , CH_4 , and CO_2 gases from fluid inclusions.

Table 1: $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ (CH_4 and CO_2) isotopic composition of gases from fluid inclusions in quartz and anhydrite from various locations.

Sample	mineral	$\delta^{15}\text{N}_{\text{N}_2}$	Intensity M28	$\delta^{13}\text{C}_{\text{CH}_4}$	Intensity M45	$\delta^{13}\text{C}_{\text{CO}_2}$	Intensity M45
		‰	mV	‰	mV	‰	mV
GH-172	quartz	n.d.	<100	-	-	-9.8	631
GH-172	quartz	3.4	158	-	-	-9.3	1764
GH-172	quartz	n.d.	<100	-	-	-9.5	734
GH-172	quartz	3.3	114	-	-	-9.7	1244
Mean						-9.6	
Stdev.						0.2	
GH-151	quartz	n.d.	<100	-	-	-10.6	1153
GH-151	quartz	n.d.	<100	-	-	-10.4	1591
GH-151	quartz	n.d.	<100	-	-	-10.8	2153
Mean						-10.6	
Stdev.						0.2	
H-18-A	anhydrite	15.4	1362	-27.2	1047	-	-
H-18-A	anhydrite	15.2	726	-27.4	1171	-	-
H-18-A	anhydrite	14.8	948	-26.9	1212	-	-
H-18-A	anhydrite	14.8	238	-26.8	221	-	-
H-18-A	anhydrite	15.3	476	-26.3	1081	-	-
H-18-A	anhydrite	15.2	526	-27.0	519	-	-
H-18-A	anhydrite	15.5	1097	-26.8	1171	-	-
H-18-A	anhydrite	14.7	810	-26.5	1174	-	-
Mean		15.1		-26.9			
Stdev.		0.3		0.4			
Limberg 1	quartz	-2.7	215	-33.1	1244	-1.7	3873
Limberg 2	quartz	-2.3	212	-33.4	1356	-1.5	3737
Limberg 3	quartz	-3.3	118	-32.7	880	-1.0	1209
Limberg 4	quartz	-2.8	121	-30.8	1193	-0.9	1892
Limberg 5	quartz	-3.8	128	-31.8	1072	-0.9	1707
Mean		-3.1		-32.2		-1.1	
Stdev.		0.7		1.1		0.3	

Note that peak intensities below 100 mV yield erratic isotope values. n.d.= not detected, i.e., peak intensities below 100 mV. Quartz samples GH-171 and GH-151 contain no CH_4 and anhydrite sample H-18-A contains no CO_2 .

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; Schoell, 1980 and 1988; Rice et al., 1989; Clayton, 1991). The $\delta^{13}\text{C}(\text{CH}_4)$ isotopic compositions of natural gases in individual reservoirs depends primarily on the initial carbon isotopic composition of kerogen in the source rocks (Tissot and Welle, 1984), but also on burial history, migration, mixing of gases from different sources, and locally in-reservoir alteration processes such as thermochemical sulfate reduction, or oxidation.

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. Karlsen et al., 1993; Goldstein and Reynolds, 1994; George 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 buried organic matter strongly 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 ^{12}C and typically shows light $\delta^{13}\text{C}(\text{CH}_4)$ values in the range between c. -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 ^{12}C - ^{12}C bonds and subsequent breaking of more stable ^{13}C - ^{12}C bonds with increasing temperature (Sackett, 1978) resulting in fractionation of the $\delta^{13}\text{C}(\text{CH}_4)$ values. Thermogenic gas typically shows $\delta^{13}\text{C}(\text{CH}_4)$ values between -50 and -20‰ (e.g., Stahl, 1977; Schoell 1980; 1988; Rice et al., 1989). However, methane being generated from nonmarine humic source rocks (type III kerogen, e.g., coals) shows less negative initial $\delta^{13}\text{C}$ 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-MS (Plessen and Lüders, 2012).

However, gas-rich inclusions hosted in diagenetic minerals often consist of complex mixtures of CO_2 and CH_4 and/or variable amounts of N_2 . 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) all these requirements because it allows the conversion of gas mixture into clean gases and on-line measurements of stable isotope ratios.

The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ (CH_4 , CO_2) values of gases released from fluid inclusions hosted in selected samples are shown in Table 1. These samples originate from hydrothermal gold-quartz veins (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 $\delta^{13}\text{C}$ values for CH_4 and CO_2 indicates complete gas separation and oxidation of CH_4 to CO_2 .

The general high signal stability of the mass spectrometer and good linearity even allows precise measurements of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values at low signal intensity of about 100 mV.

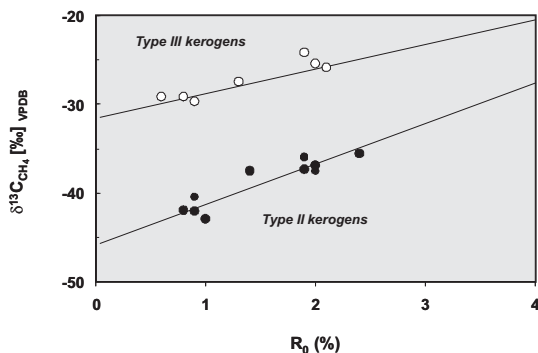


Fig. 3 $\delta^{13}\text{C}$ values of methane in natural gases in relation to the maturity of their source rocks.

Carbon isotope ratios of fluid inclusion gases

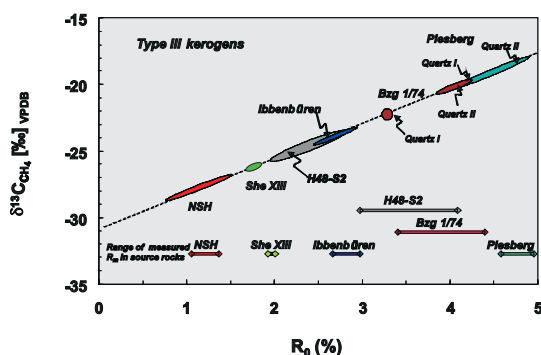


Fig. 4 Ranges of $\delta^{13}\text{C}$ values of methane in fluid inclusions from fracture-fill mineralization hosted by Carboniferous sediments (North German Basin) in relation to the maturity of their source rocks (after Lüders et al. 2012).

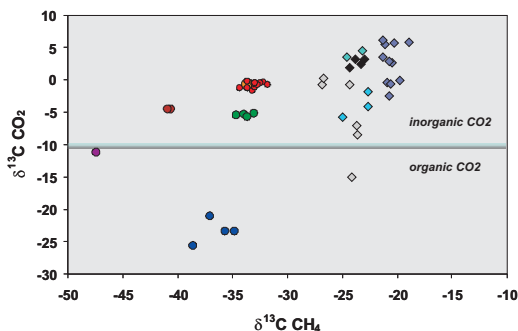


Fig. 6 Carbon isotope ratios of CO_2 vs. CH_4 of fluid inclusion gases.

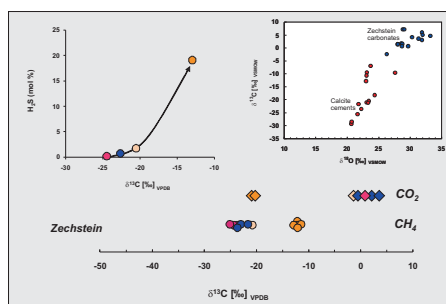


Fig. 7 Carbon isotope ratios of CH_4 and CO_2 gases from fluid inclusions in fluorite fracture fillings from Zechstein carbonate H_2S -rich reservoirs and $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ values of reservoir carbonates and calcite cements. Note: $\delta^{13}\text{C}(\text{CH}_4)$ values increase with increasing H_2S content in the reservoirs.

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 Paleozoic shale from the Val Verde Delaware Basin (Fig. 3)

This often well-expressed correlation between the $\delta^{13}\text{C}(\text{CH}_4)$ values of the gas and the maturity of the organic matter in the parent source is commonly plotted in $\delta^{13}\text{C}(\text{CH}_4)$ 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 $\delta^{13}\text{C}(\text{CH}_4)$ values with increasing maturity have been generally observed (e.g. Stahl et al., 1977; Schoell, 1980; Berner and Farber, 1988).

Left 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 $\delta^{13}\text{C}(\text{CH}_4)$ values in quartz-hosted inclusions from the Upper Carboniferous strata in the NGB vary between -28.8 and -17.9‰ (Fig. 4). Increasing $\delta^{13}\text{C}(\text{CH}_4)$ values are mostly correlated with increasing ranges of Ro in potential sources rocks.

When plotting the $\delta^{13}\text{C}$ values of methane in gas-rich inclusions in a $\delta^{13}\text{C}(\text{CH}_4)$ 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 $\delta^{13}\text{C}$ of CH_4 from type III kerogen in Fig. 3. The exceptions are the samples H48-S2 and Bzg 1/74 quartz I where early stages of gas migration occurred prior to maximum burial (Fig. 4) and the $\delta^{13}\text{C}(\text{CH}_4)$ 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 $\delta^{13}\text{C}(\text{CH}_4)$ isotopic composition that can be expected from a source rock that achieved maturity well above 4% vitrinite reflectance (Fig. 3).

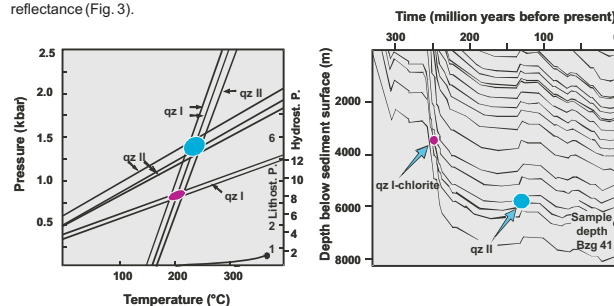


Fig. 5 Isochoric sections of aqueous and gaseous inclusions in two generations of quartz from the Bzg1/74 well (NGB) and projection of possible time of entrapment in the burial curve.

Origin of CO_2

The $\delta^{13}\text{C}$ values of CO_2 trapped along with CH_4 ($\pm \text{N}_2$) 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 $\delta^{13}\text{C}$ values of CO_2 . Strong negative $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}$ 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_2S in deep subsurface reservoirs. In the North German Basin natural gases with H_2S 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_2S , 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:



TSR leads to the breaking of ^{12}C - ^{13}C bonds and the subsequent breaking of the more stable ^{13}C - ^{12}C bonds at higher temperatures resulting in fractionation of the $\delta^{13}\text{C}(\text{CH}_4)$ values (Fig. 7). ^{12}C gets enriched in HCO_3^- and thus calcite cements may show very negative $\delta^{13}\text{C}$ values (Fig. 7). In cases where CO_2 from reaction 1 is trapped in fluid inclusions in non-carbonaceous mineral such as fluorite or anhydrite strong negative $\delta^{13}\text{C}(\text{CO}_2)$ 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.

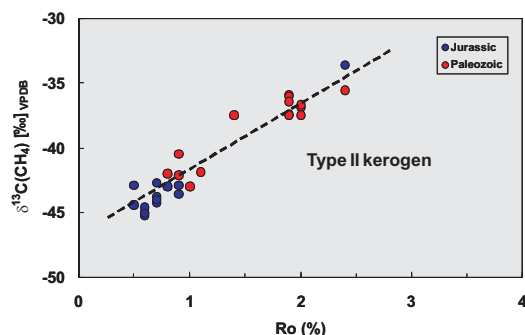


Fig. 8 Carbon isotope ratios of methane in natural gases in relation to the maturity of their source rocks. Data are taken from Stahl (1979) and Schoell (1980).



Fig. 9 Left: Quartz mobilization in Viséan chert, Lautenthal, Harz Mts. (Germany). Right: Calcite fracture-fillings in Gzhelian shale, well Schadewalde E She 1/75, NGB (Germany).

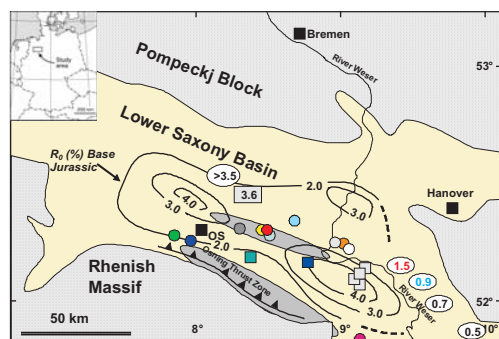


Fig. 11 Simplified map of the outline of the LSB also showing iso-reflectance contours (Ro %) on base Jurassic (after Koch & Arneemann, 1975 and Deutloff et al. 1980) and Ro values of Posidonia shale from wells and Wealden coal. Sample sites of quartz mineralization hosted by Triassic and Jurassic strata are shown in squares and circles, respectively. OS: City of Osnabrück.

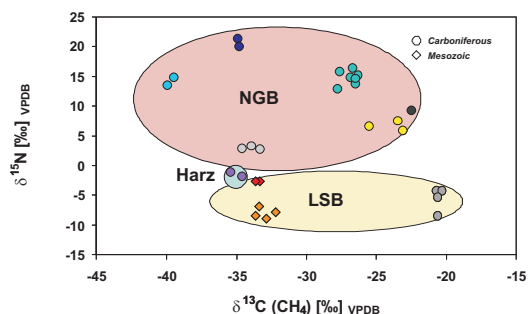


Fig. 13 $\delta^{15}\text{N}$ values vs. $\delta^{13}\text{C}$ values of methane in fluid inclusions from fracture-fill mineralization hosted by Paleozoic rocks from the NGB and Harz Mts. and Mesozoic rocks from the Lower Saxony Basin. The most positive $\delta^{15}\text{N}$ values were measured in fluid inclusion gases in fracture-fill mineralization from wells overlie by Rotliegend lacustrine shale (Fig. 14).

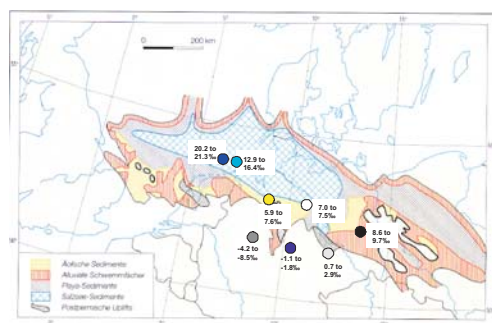


Fig. 14 Distribution of Rotliegend salt lake sediments in the NGB and North Sea (after Gast et al., 1998) and ranges of measured $\delta^{15}\text{N}$ values in fluid inclusion gases from fracture-fill mineralization hosted by Paleozoic rocks.

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 on Fig. 8 for natural gases being sourced from Lower Jurassic Posidonia shale (NGB) and from Paleozoic shale from the Delaware Val-Verde Basin (USA). The trend line shown in Fig. 8 is the reference line for fractionation of the carbon isotope ratios of methane is used to estimate the maturity of source rocks at the time of gas generation in Figs. 10 and 12.

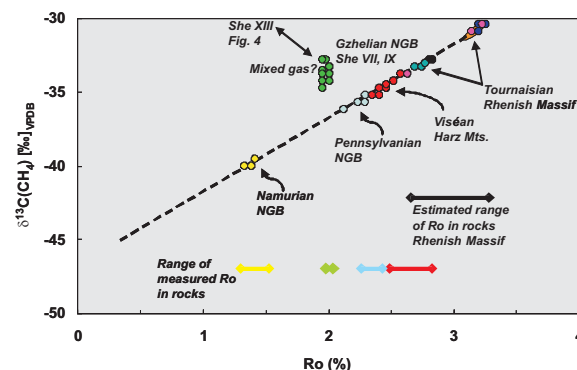


Fig. 10 Ranges of $\delta^{13}\text{C}$ values of methane in fluid inclusions from fracture-fill mineralization sourced from Carboniferous sediments (NGB, Harz Mts., and Rhenish Massif) in relation to the maturity of their source rocks. Gases of fluid inclusions in fracture-fill calcite from the She well may represent mixtures of coal and shale gas.

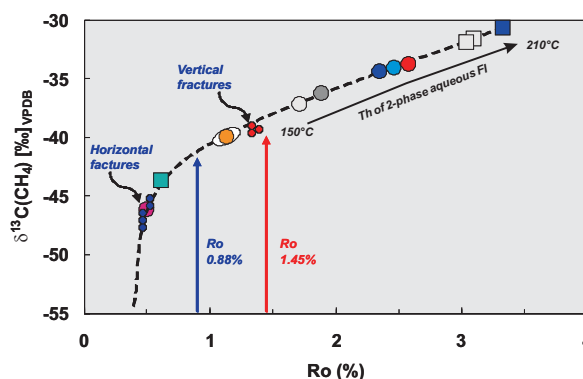


Fig. 12 Ranges of $\delta^{13}\text{C}$ values of methane in fluid inclusions from fracture-fill mineralization in relation to the maturity of their source rocks (most likely Posidonia shale). Color codes of symbols refer to sample sites in Fig. 11. Ro values of two wells are shown in relation to the measured $\delta^{13}\text{C}$ values of methane in fluid inclusions. Note that fluid inclusions hosted in horizontal fractures yield lower maturity than the measured Ro of 0.88%, probably reflecting continuous gas generation prior to maximal burial.

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 its origin. Nitrogen isotope ratios of fluid inclusion gases can be measured by on-line continuous-flow isotope ratio mass spectrometry. Several fracture-fill mineralization studies here contain complex gas mixtures of CH_4 , CO_2 , and N_2 or CH_4 - N_2 irrespective of the origin of gas (i.e., coal vs. shale gas).

The $\delta^{15}\text{N}$ values of fluid inclusions are highly variable (Fig. 13). Negative $\delta^{15}\text{N}$ values in fluid inclusion gases are probably related to condensation or alteration of marine shale. Positive $\delta^{15}\text{N}$ values up to about 10‰ may result from fluid-rock interaction between saline brines and ammonium-rich mica in Paleozoic shale. Strong positive $\delta^{15}\text{N}$ values <15‰, however, may be indicative for nitrates being derived from Rotliegend lacustrine shale.

Conclusions

The use of a crushing device interfaced with an elemental analyzer combustion-IRMS system provides a means to analyze the isotopic composition of simultaneously released N_2 , CH_4 , and CO_2 from fluid inclusions. Even small amounts of sample material (0.1–0.5 g) produce enough gas to obtain reproducible values. The $\delta^{13}\text{C}$ stable isotopic composition of fluid inclusions can be used to trace source rocks of methane and carbon dioxide and provide information regarding their maturity. The $\delta^{15}\text{N}$ values yield important information about the origin of nitrogen in gas accumulations.

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