Evaluation of the Gas Content in Archived Shale Samples: A Carbon Isotope Study

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Received: 19 September 2019; Accepted: 14 November 2019; Published: 15 November 2019

Abstract: We examined 14 archived samples of shale for the chemical and 13C isotopic composition of residual gases produced as part of rock-crushing operations at a hammer mill. Results were compared with data on maturity from Rock-Eval pyrolysis and vitrinite reflectance measurements. The samples originated from three different formations (Mikulov Marls, Ostrava Formation, and Liteň Formation) located in the Czech Republic. For comparison, we examined a gas-prone shale sample from the Polish Silurian. We used changes in the chemical and isotopic composition of released gases to evaluate the isotope fractionation during gas loss and retroactively calculated the initial content of gas in the shale samples. The gas content estimates (in L of gas per ton of rock) correspond with the maturity parameters of the shales. Calculated isotope fractionation for the gas release was −3‰ for both methane and ethane. The archived samples primarily lost methane (up to 90%), with subsequent changes in the content of ethane and higher hydrocarbon levels.

Keywords: shale gases; carbon isotopes; chemical composition; diffusion

1. Introduction

Shales were long considered to be seals rather than hydrocarbon source rocks. The significant technological improvement in hydraulic stimulation led to the exploitation of natural gas from unconventional deposits that include gas shales, among others. Initially, shale gas was defined as gas that is recovered from organic-rich shale with low rates of porosity and permeability [1,2]. Unlike conventional gas deposits where migrating hydrocarbons are accumulated in stratigraphic/structural traps, shale gas is a self-stored, self-generated gas, stored within pores/fractures or adsorbed onto the surface of organic components found within the shale [1].

Parameters such as total organic carbon (TOC), kerogen type, and thermal maturity of organic matter are routinely used to evaluate the source rock potential of strata [3,4] and to estimate the hydrocarbon potential of rock. The TOC represents residual organic carbon that includes both soluble bitumen and insoluble kerogen. The degree of organic matter conversion is given by thermal maturity and can be predicted from the results of pyrolysis (Rock-Eval, RE), random vitrinite reflectance (Rr), and bitumen characteristics [4]. The type and quality of organic matter is essential to estimate the amount and composition of generated hydrocarbons [5].

For natural gas, carbon and hydrogen isotope compositions of hydrocarbon gases are the principal geochemical characteristics; these parameters are influenced by isotope composition of organic precursors and by kinetic isotope effects during the generation of oil and gas [5,6]. Another process of isotope fractionation is underway during gas desorption and migration [7,8], when
changes in the carbon—as well as hydrogen—isotope composition can be measured and modeled with success [7–11].

Isotope desorption experiments are frequently used for the study of gas migration from rocks [8,9] and gas production from coal bed [6], such as the canister method, which is a well-established standard method of production studies [12]. Sample crushing is an additional improvement of desorption studies to minimize the effects of in situ processes on the gas isotope composition [13].

 Archived samples lose the gas they contain via desorption and diffusion during storage. Since this process resembles the late period of shale gas generation, we realize that the evaluation of changes in the isotopic and chemical composition of released gases facilitates an estimate of the unknown initial gas content and composition.

The objectives of the present study were (i) to evaluate the gas content in archived samples of shale, as well as changes in the chemical and isotopic composition of the samples, and (ii) to estimate the initial gas content and its relationship with the properties of the source rock.

2. Materials and Methods

To achieve the aim of the work, 14 samples of shale were selected, representing three potential shale gas formations within the Czech Republic; they were analyzed for gas content, chemical composition, and carbon isotope composition of light hydrocarbons including methane to butane. For comparison, gas-prone shale from Poland was evaluated using the same procedures.

2.1. Shale Samples

The selected formations represent good potential source rocks in the Czech Republic [14–17]. Shale samples from the Mikulov Marls (type A) and the Ostrava Formation (type B) were archived as rock chips for about 20 years. Samples from Liteň Formation (type C) were collected from a fresh section two years before the study (Table 1).

The Upper Jurassic Mikulov Marls represent the autochthonous cover of the Bohemian Massif with known thickness of up to 1500 m [17]. The marls contain colonial planktonic/benthonic algae with a minor portion of re-worked and oxidized terrestrial plant debris; they represent kerogen type II and belong to an immature to oil window range based on Rock-Eval pyrolysis and biomarkers [12]. In terms of mineralogical composition, this is a highly homogenous formation with the predominance of carbonates (37.0%–74.8%), clays (16%–60%), and quartz (6.7%–28.8%), and it is classified as argillaceous marlstone [18].

The Ostrava Formation (Namurian A) represents a marginal foreland basin deposited in a wide spectrum of sedimentary environments ranging from purely continental settings to zones of transition into marine settings [17]. The thermal maturity of the known Ostrava Formation ranges from 0.46% to 2.32% Rr and samples are assigned to immature to wet gas. The organic matter is composed of coalified plant residues and products of its incomplete combustion and decarboxylation, with a small amount of alginite, representing type III kerogen [15].

The Lower Silurian Liteň Formation was deposited during marine transgression and consists mainly of dark shales interbedded with claystones; it is influenced by volcanic activity. Silurian dark shales of the Barrandian Basin contain fragments of graptolites and chitinozoans. The occurrence of bitumen in the Liteň Formation was also described [16]. The reflectance of graptolite and chitinozoa re-calculated to a vitrinite reflectance equivalent ranges from approximately 0.7% to 1.0% Rr, corresponding to the oil window [16].

2.2. Analytical Methods

The original core samples were homogenized and pyrolyzed using Rock-Eval 6 to obtain the following data: TOC (%), Tₘₐₓ (°C), S₁, S₂ (mg HC/g rock), S₃ (mg CO₂/g rock), and derived parameters HI (mg HC/g TOC) and OI (mg CO₂/g TOC). Polished surfaces were prepared from rock chips for the random reflectance (Rₚ) measurement. This was carried out in oil under non-polarized light using the
Opton Zeiss microscope photometer with 50× and 100× objectives and optical standards of 0.58%, 0.89%, 1.71%, and 3.12%.

Samples for the measurement of elemental and carbon isotope composition were homogenized to 60 μm and acidified by 10% hydrochloric acid to remove carbonates; then, they were washed repeatedly with distilled water and dried. The samples so treated were measured for the content of organic C and δ¹³C using flash combustion in a Fisons 1108 elemental analyzer coupled with a Delta V isotope ratio mass spectrometer (both products were from Thermo Scientific) in a continuous flow regime with NBS 22 (for δ¹³C measurement) and acetanilide (for elemental analysis) as reference materials. The standard error of carbon content measurement is about 3% from the measured value; the external reproducibility of δ¹³C measurement was less than 0.1‰.

Samples for gas measurement were firstly crushed to obtain particles less than 2 mm in size; the dust was removed. Particles were further used for chemical and isotopic analysis. The volume, as well as the chemical composition, was determined by gas chromatography with a flame ionization detector (FID; GC 96, Labio). An internally constructed hammer mill (Figure 1) was filled with rock particles (0.6 to 0.8 g), closed, and washed out with helium as a carrier gas; then, the rock was crushed using a handheld hammer. After the rock was crushed, the mill was installed in the loop of a six-way valve (Valco P Series) and all of the gas content was introduced into a column (PoraPlot Q 0.53 mm inner diameter (ID), 30 m) with helium as a carrier gas (gas flow 4 mL/min). The chromatograph oven was maintained at 35 °C for 3 min and heated up to 120 °C with a gradient of 15 °C per min. The chromatograph was calibrated by a standard gas mixture (1% of methane, ethane, and propane in air, Linde Gas) with known FID reference factors for higher hydrocarbons. The inner volume of the hammer mill was about 2 mL. To transfer all the gas content from the mill to chromatograph, more than 1 min of loop elution was necessary, which resulted in peak splitting of separated hydrocarbons.

Figure 1. Sketched hammer mill. Below (1), the mill has an inner diameter of 8 mm. There is a mill hammer (2) inside. A sample of the rock (3) is placed in the lower part of the mill, sealed with an O-ring (4). The tubes (inner diameter: 1/16 inch) end with Swagelok tube fittings with septa (5). The mill is complete with a sealing nut (6).

Each sample was crushed and measured twice—one for the gas content and, consequently, a second time for ¹³C isotope measurement. For isotope analysis, we only used a part of the mill volume to maintain a good peak resolution on Trace GC (PoraPlot Q capillary 0.3 mm ID, 30 m with 1.8 mL/min flow rate). The chromatograph oven was maintained at 35 °C for 3 min and heated up to 120 °C with a gradient of 15 °C per min. The six-way valve (Valco P Series) was installed on the Trace GC
inlet with a sampling loop (200–300 μL). The loop was evacuated, and part of the mill gas content (from 10–15%) was transferred to the loop. After loop change, the gas content was introduced to a GC inlet, Isolink combustion unit, and Delta V isotope mass spectrometer (all Thermo Scientific). Reference methane mixtures (T iso2, L iso1 produced by Isometric Instruments, Victoria, Canada) were used for calibration. Limited loop volume reduced the sample size, but the δ13C measurement was well reproducible (repeated sample crushing with following isotope analysis differed in δ13C by 0.5‰, Figure 2).

![hydrocarbon combustion line](image)

**Figure 2.** Hydrocarbon combustion line. The sample loop is evacuated and connected to the hammer mill, and part of the mill content is transferred to the loop. The gas from the loop is injected into the gas chromatograph. The loop can be immersed in liquid nitrogen to concentrate higher hydrocarbons. Hydrocarbons are separated inside Trace GC.

### 2.3. The Mechanism of Gas Release

Stored shale samples lost part of the available gas via desorption and diffusion. Diffusion flux \( N_i \) is given by Fick’s first law, which only depends on the interaction of the solute substance \( i \) within the solvent environment [19]. The diffusion coefficient \( D_i \) defines the molar flux through a surface per unit concentration gradient out of plane.

\[
N_i = -D_i \text{ grad } c_i. \tag{1}
\]

For methane, the air diffusion coefficient is \( 1.6 \times 10^{-5} \text{ m}^2\text{s}^{-1} \) [20]. Diffusion coefficients of higher hydrocarbons are lower according to their higher molecular mass and molecular size. Values can be derived from the methane diffusion coefficient \( D_{\text{AM}} \) and molecular masses according to Graham’s law [20].

\[
\frac{D_{\text{AM}}}{D_2} = \sqrt{\frac{M_2}{M_{\text{CH}_4}}} \tag{2}
\]

The corresponding diffusion coefficients for ethane, propane, and butane would be \( 1.6 \times 10^{-5} \text{ m}^2\text{s}^{-1} \) divided by 1.15, 1.4, and 1.6. The diffusion of gases in porous media is directed by effective diffusion coefficients \( D_{\text{eff}} \) which are many orders of magnitude less than the diffusion coefficient \( D_{\text{AM}} \) for methane in pure air [19], because of the tortuosity of porous media and retardation.

\[
D_{\text{eff}} = D_{\text{AM}} \times R \times \tau, \tag{3}
\]

where \( \tau \) is the tortuosity factor (\( \tau < 1 \)), and \( R \) is the retardation coefficient (\( R \gg 1 \)). The diffusing substance can adsorb onto the internal surface of the porous medium. The adsorption/desorption process has a complicated effect on the degassing rate due to the delay of mass transport [11]. Hydrocarbon mobility through the rock is strongly reduced by organic matter content [8,9]. Considering a low adsorption affinity of methane to organic matter in comparison with higher
hydrocarbons [9], higher hydrocarbons would be significantly retarded in diffusion compared to methane. In this way adsorption/desorption processes further enlarge the retardation of the diffusion of higher hydrocarbons vs. methane in comparison with Graham’s law [20].

The actual isotopic ratio $R = ^{13}\text{C}/^{12}\text{C}$ changes during a single unidirectional process of diffusion by a fractionation factor $\alpha = \frac{D_mH}{D_mL}$ (where $D_m$ is the diffusion coefficient of substance $m$ with heavy H and light L isotopes, $\alpha < 1$). The experimental isotope enrichment factor $\varepsilon$ during kinetic fractionation can be determined using the Rayleigh equation [21].

$$1000 \times \ln \frac{R}{R_0} = 1000 \times \ln \left(\frac{\delta^{13}\text{C}/1000 + 1}{\delta^{13}\text{C}_0/1000 + 1}\right) = \varepsilon \times \ln \frac{C}{C_0} \tag{4}$$

where $R$ refers to the ratio $^{13}\text{C}/^{12}\text{C}$, $\delta^{13}\text{C}_0$ and $\delta^{13}\text{C}$ refer to the initial isotope ratio of a compound and the isotope ratio at time $t$, respectively, and $C_0$ and $C$ are the initial concentration and the concentration at time $t$, respectively. Ratio $C/C_0$ is the fraction of an unreacted (or not released in this case) compound from the surface, frequently assigned as $f$. In analogy with the $\%$ notation of $\delta$, the enrichment factor $\varepsilon$ is evaluated as the enrichment of the residual compound against the initial composition in $\%$ units; $\varepsilon = (\alpha - 1) \times 1000$. During kinetic fractionation, the light isotopes are preferentially released from the rock surface, which is progressively enriched in heavy isotopes.

To express changes in the chemical composition of the residual gas during migration, we used a simplified heuristic approach. In gas mixtures, methane is the most abundant component, forming about 90 vol.% or more [1]. Higher gaseous hydrocarbons (ethane, propane, and butane) contribute only in units of percentage. Moreover, methane is less retarded by adsorption/desorption phenomena in pore transport, in comparison with higher hydrocarbons [9,22]. As the first approximation in the calculation of the gas loss, we suppose that methane is the only gas lost from the rock. The proceeding methane loss generates changes in the chemical composition of remaining gas components (see Figure 3).

To find a common solution for the entire sample subset (i.e., for the formations A, B, and C), we assume that we analyzed one sample in a different stage of the gas loss. For the modeling of the changes in gas composition with proceeding methane loss, an estimation of the initial gas composition was necessary. We approximated the gas composition by the actual gas composition from a similar rock formation or by composition from existing drilling mud. We used a model initial composition No. 1 (90% of C1, 4% of C2, 3% of C3, 2% of C4, and 1% of C5) for set A and B, and mixture No. 2 (95% of C1, 2.5% of C2, 1% of C3, 1% of C4, and 0.5% of C5) for set C. The chemical composition of mixtures after modeled methane losses was compared with the chemical composition of gases released from samples to estimate their methane loss.

For example, the loss of 50% of initial methane from mixture No.1 develops a new mixture with the composition of 81.8% C1, 7.3% C2, 5.5% C3, 3.6% C4, etc. Such a mixture would have a $C/C_0$ ratio (Equation (4)) equal to 0.5. When we plot the modeled composition data together with measured data, we can estimate probable methane loss and residual methane concentration C for the samples (Figure 3). The initial methane concentration $C_0$ is substituted by the initial value of models, i.e., 90% or 95%. Finally, we can calculate the ratio of $C/C_0$ and isotope fractionation for gas loss according to Equation (4). Measured gas content data (Table 2) were plotted against $C/C_0$ and extrapolated to 1 to get the initial gas content $V_0$ in Table 3.
3. Results

Data from Rock-Eval ($T_{\text{max}}$, TOC, $S_1$, $S_2$, HI, OI) and reflectance measurements ($R_r$) were complemented with those obtained from the elemental analysis (organic carbon content and $\delta^{13}$C of organic carbon). According to the $S_1$ and $S_2$ values, samples of Mikulov Marls were just on the immature/mature border of the source rock classification ($S_1 < 0.07$–$0.23$ mg of HC/g rock, $S_2 = 3.8$–$8.2$ mg HC/g rock) with a production index (PI) less than 0.10, which corresponded to the low maturity of organic matter [3].

Samples of Ostrava Formation had lower values of $S_1$ (0.04–$0.12$ mg of HC/g rock) and $S_2$ (0.5–$3.5$ mg HC/g rock) parameters, but a slightly higher production index (PI) compared with Mikulov Marls. This was due to the higher maturity of Ostrava Formation samples (0.64–$1.20\%$ $R_r$, $T_{\text{max}} = 434$–$464$ °C) compared with 0.62–$0.72\%$ $R_r$ and $T_{\text{max}}$ not over 434 °C in Mikulov Marls. Samples from Liteň Formation with $T_{\text{max}} 497$ and $519$ °C were those most thermally mature. Higher thermal maturity was also reflected in increased graptolite reflectance ($1.79\%$ $R_r$). The different kerogen types presented in each of the studied formations were evident in the HI versus $T_{\text{max}}$ graph (Figure 4). A comparison of
the bulk parameters proved the highest hydrogen index and the lowest maturity for Mikulov Formation, low HI for Ostrava and Liteň Formations, and the highest maturity for Liteň Formation.

Figure 4. The modified van Krevelen plot with hydrogen index (HI) versus thermal maturity (T<sub>max</sub>), which enables discerning the prevailing kerogen type of the studied source rocks.

Due to the high homogeneity of the depositional environment, the samples within the subgroups A, B, and C were considered as representative of the same thermal maturity level and the same original organic matter (δ<sup>13</sup>C), despite the fact they originated from different depths (Table 1).

We tested samples for the gas content, as well as chemical and ¹³C isotope composition (see Table 2). The volume of the gas released from the sample in the mill was calculated as a sum of volumes from C₁ to C₄. The volume of the released gas was very variable, as was the chemical composition of gases. The C₁ content of samples was lower than C₁ of model mixtures (from 80% to 20%); the content of C₂–C₄ was higher (from 2 to 29%). Generally, the gas composition of released gases follows the effect of the methane loss on the composition of the gas mixture; increasing methane loss increases the contribution of higher hydrocarbons up to tens of percent (Figure 3). Experimental data were close to modeled gas composition with a few exceptions. One sample from B and one sample from C had a significantly higher concentration of C₂ and C₃ than the model (Figure 3). Considering the chemical composition of the model for the initial gas composition (90% of C₁, 4% of C₂, 3% of C₃, 2% of C₄, and 1% of C₅ for B; 95% C₁ for C), an initial composition of such a sample would probably be more abundant in methane than the model supposed. Unexpected were the values of the C₃ concentration, which were generally higher than the C₂ values (Table 2). This resulted from the simplified assumption of methane loss only. Obviously, samples also lost ethane, which resulted in the suppression of C₂ concentration and an increase in C₃ content.

From the measured δ<sup>13</sup>C, we calculated ¹³C fractionation during methane release (diffusion accompanied by desorption, according to Equation (4); see Figure 5A). The necessary C and C₀ values for methane were calculated directly from the difference of the initial model concentration (C₀) and estimated methane loss (C = C₀ – loss). The evident loss of ethane was in contradiction with the assumption of methane loss only. The isotopic composition of ethane changed with the changes in chemical composition, and we clearly observed a similar process to methane loss. To keep the assumption of methane loss valid, we assumed that methane released first, and ethane released successively. In this case, we could use the calculated ethane content after methane loss as the initial C₂₀ concentration before ethane loss. Measured concentrations of C₂ were nearly always lower than
model values (with two or three exceptions, which are visible in Figure 3, highlighting the calculated changes in composition). The difference between the model value (i.e., $C_{20}$) and measured $C_2$ content was the estimate of the ethane loss. In this way, we could evaluate the $C/C_0$ ratio and calculate the fractionation for ethane release (Figure 5B).

![Graph](image-url)

**Figure 5.** $^{13}$C isotope fractionation for the migration of methane (A) and ethane (B) as calculated from gas chromatography and mass spectrometry measurements (Ostrava Formation).

The apparent fractionation enrichment $\varepsilon$ is related to the gas loss via diffusion (and desorption); the intercept assigns the initial autochthonous isotope composition of methane and ethane. Isotope fractionation data and the estimates of initial $\delta^{13}C_0$ are summarized in Table 3.

**Table 1.** Geochemical parameters of the studied shales. Source rock (SR) classification based on measured total organic carbon (TOC) calculation values according to Reference [23]. HI—hydrogen index; SR—source rock; PI—production index; Rr—random reflectance.

| Sample | $C_{org}$ (% | $\delta^{13}C_0$ (‰) | TOC Calculated (%) | $T_{max}$ (°C) | $S_1$ (mg HC/g rock) | $S_2$ (mg HC/g rock) | HI (mg HC/g TOC) | OI (mg CO$_2$/g TOC) | SR type | PI = $S_1/(S_1 + S_2)$ | Rr (‰) |
|--------|--------------|----------------------|---------------------|---------------|-----------------------|---------------------|-------------------|----------------------|---------|----------------------|--------|
| A      | 2.56         | $-26.7$              | 1.46                | 432           | 4.31                  | 0.11                | 295               | 47                   | Very good | 0.02                 | 0.69   |
| A      | 2.44         | $-27.2$              | 1.39                | 434           | 3.78                  | 0.09                | 272               | 22                   | Very good | 0.02                 | 0.72   |
| A      | 2.47         | $-26.8$              | 1.23                | 433           | 4.30                  | 0.07                | 350               | 33                   | Very good | 0.02                 | 0.68   |
| A      | 3.57         | $-26.7$              | 0.96                | 434           | 8.17                  | 0.23                | 851               | 90                   | Very good | 0.03                 | 0.65   |
| A      | 0.74         | $-24.3$              | 2.4                 | 424           | 12.79                 | 0.23                | 533               | 29                   | Fair     | 0.02                 | 0.66   |
Table 2. Chemical and $\delta^{13}C$ isotopic composition of gases extracted from the crushed archived shales.

| Sample | Depth (m) | Gas Volume ($m^3 \cdot t^{-1}$) | C1 (%) | $\delta^{13}C_1$ (‰) | C2 (%) | $\delta^{13}C_2$ (‰) | C3 (%) | $\delta^{13}C_3$ (‰) | C4 (%) | $\delta^{13}C_4$ (‰) |
|--------|----------|-------------------------------|-------|----------------|-------|----------------|-------|----------------|-------|----------------|
| A      | 3342     | 0.00050                       | 48.5  | $-19.6$       | 14.8  | $-20.6$       | 24.4  | 10.9           |       |               |
| A      | 3491     | 0.00065                       | 74.1  | $-22.4$       | 9.6   | $-21.4$       | 7.2   | 6.3            |       |               |
| A      | 2997     | 0.00045                       | 48.4  | $-18.8$       | 17.8  | $-17.9$       | 20.7  | 10.3           |       |               |
| A      | 3411     | 0.00055                       | 55.5  | $-18.4$       | 12.6  | $-16.9$       | 18.3  | 10.1           |       |               |
| A      | 2546     | 0.00090                       | 81.3  | $-26.5$       | 10.4  | $-24.6$       | 4.6   | 1.8            |       |               |
| B      | 4575     | 0.00040                       | 55.5  | $-23.7$       | 14.1  | $-22.3$       | 17.3  | 10             |       |               |
| B      | 4034     | 0.00017                       | 38.0  | $-18.8$       | 20.0  | $-19.8$       | 24.4  | 14             |       |               |
| B      | 1374     | 0.00015                       | 29.2  | $-14.6$       | 29.2  | $-21.5$       | 35.3  | 6.3            |       |               |
| B      | 4760     | 0.00030                       | 32.3  | $-16.0$       | 13.9  | $-20$         | 13    | 22.8           |       |               |
| C      | 0.00014  | 58.2                          | 58.2  | $-22.0$       | 8.6   | $-19.4$       | 10    | 10             |       |               |
| C      | 0.0006   | 67.0                          | 67.0  | $-21.3$       | 9.2   | $-21$         | 10.5  | 23             | 7.8   |               |
| C      | 0.0125   | 95.0                          | 95.0  | $-27.9$       | 2.0   | $-22$         | 1     | 0.8            |       |               |
| C      | 0.0078   | 86.0                          | 86.0  | $-26.0$       | 8.9   | 1.5           | 1.8   |               |       |               |
| Ex     | 0.0239   | 44                            | 44    | $-24.2$       | 26    | $-25.2$       | 12    | $-25$         | 10    | $-24$         |

Table 3. Apparent diffusion fractionation $\epsilon$ for C1 and C2 with calculated estimates of the initial isotope composition $\delta^{13}C_0$.

| Formation | $\delta^{13}C$ rock (‰) | $\delta^{13}C_0$ (‰) | $\epsilon$ C1 (‰) | $\delta^{13}C_0$ (‰) | $\epsilon$ C2 (‰) | $\epsilon$ C3 (‰) | $\epsilon$ C4 (‰) | $V_0$ Gas ($m^3 \cdot t^{-1}$) |
|-----------|--------------------------|-----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|---------------------------|
| B         | $-24.1$                  | $-25.7$               | $-2.9$            | $-2.9$           | $-22$             | $-3.7$           | 0.00165           |
| A         | $-26.9$                  | $-25.5$               | $-3$              | $-21.6$         | $-2.7$           | 0.0017           |
| C         | $-30.6$                  | $-28.3$               | $-2.7$            | $-22.5$         | $-3.1$           | 0.0132           |
| Ex *      | $-29$                    | $-31$                 | $-3$              | $-26.8$         | 0.200            |

* An arbitrary value of $-3$‰ was used for the calculation of $\delta^{13}C_0$.

The initial gas volume $V_0$ (in m$^3$ of gas per ton of rock) was estimated from the extrapolated chromatography data to C/C$_0 = 1$. The gas content of formation C was approximately 10 times higher than for formations A and B. The comparative gas-prone sample from Poland contained significantly more gas than samples from formation C despite the uncertainty of the estimate. We tested only one sample of comparative shale Ex; thus, methane loss was estimated from the gas composition (Table 2).

The initial isotope composition $\delta^{13}C_0$ derived for methane and ethane (together with some measured $\delta^{13}C$ values for propane) can be associated with the source rock (Figure 6).
Figure 6. The relationship between δ¹³C of the source rock and the shale gas components estimated from extrapolation of ¹³C fractionation to initial δ¹³C values (A). Diagram of 1/Cn versus δ¹³C for the same initial values according to Reference [24] (B).

The data found in Figure 6A indicate a close relationship between the source organic and gaseous products with a small isotopic separation between successive n-alkane homologues. The relationship between alkanes (Figure 6B) is linear for Ostrava Formation and the comparative sample from Poland. Samples from Mikulov and Liten Formations present so-called isotopic reversal, where the δ¹³C value of propane is less negative than the ethane value [25]. Isotopic reversal is interpreted by mixing of different sources [24], by water–hydrocarbon reactions [25], or by mixing of primary and secondary generated hydrocarbons [10].
4. Discussion

4.1. Estimate of Gas at the Site

We do not know the initial volumes of the gas at the site; thus, our estimates (Table 3) can be confronted only with other independent geochemical data (Table 1). According to References [3,4], studied shale samples have a potential for hydrocarbon production. The organic matter content was higher than a minimum of 0.5%; Rock-Eval index $S_2$ (thermal kerogen cracking) was within the range of units. In addition, methane $\delta^{13}C$ values corresponded to the maturity of samples [26].

However, the $S_1$ index (volatile organic compounds) and production index $PI = S_1/(S_1 + S_2)$, were low, which corresponded to a minimal degree of hydrocarbon production. In this way, it was consistent with a small volume of the gas released (in L per ton of rock). The organic matter in shales (A and B) was immature ($T_{max} < 430 \degree C$, 450 $\degree$C) and could not produce measurable amounts of hydrocarbons. Shales from Liteň (type C) had a higher $T_{max}$, which corresponded to higher maturity and the possibility of higher gas production (Table 3).

For comparison, we included a gas-prone sample from Poland. While this sample was comparable with group B in terms of thermal maturity, its PI index was higher (Table 1). This was also consistent with the content of gas released, which was well above the samples of group B.

4.2. Carbon Isotope Fractionation during the Sample Degassing

We assumed that, for a given set of shales (A, B, or C), the hydrocarbon production proceeded to the same extent according to geochemical conditions, and the single samples differed by degassing loss only. The collected samples released gas based on their porosity, organic content, and duration of diffusion; sample size would also be important. As we could not evaluate samples separately with so many variables, we considered the entire set as a single sample with different degrees of degassing.

In this way, the calculated isotope fractionation was similar to the results of the coal canister method [12]. Determined isotope enrichment $\varepsilon = -3$‰ for the methane release neared the $-2$‰ value for the methane desorption from coal [12,22] and the experimental values from Reference [9] ($-1.6$ to $-2.8$‰).

The study referred to in Reference [8] reported values from $-3.3$ to $-1.3$ ‰ ($-4$ ‰ as a maximum for coal and mudstone). The isotope enrichment determined for ethane release $\varepsilon = -2.7$ to $-3.7$‰ was larger than that measured for rock experiments ($-0.8$ to $-1.6$‰) [9]. Although quite different isotope fractionation values for both methane ($-9.2$‰) and ethane ($-2.8$‰) were reported in the experimental study in Reference [27], it is generally accepted that carbon isotope fractionation should decrease with increasing carbon number [9,28]. Results from diffusion modeling in Reference [11] were also similar. However, the secondary process as desorption could have had a significant effect on isotope fractionation, as was observed during coal bed gas production experiments [22]. We supposed that such secondary processes modified our ethane isotope fractionation, which was higher than literature values.

The observed isotopic reversal for propane $^{13}C$ (Figure 6B) had no simple explanation. Considering the low maturity of measured samples, we could not suppose the formation of ethane/propane rollover, as it proceeds during gas production from highly mature shales [29], or by mixing of primary and secondary generated gases [10]. We have only few data on $\delta^{13}C$ of propane available (Table 2), and solutions as admixtures of another gas or possible effects of preferential adsorption of $^{12}C$ against $^{13}C$ as reported in Reference [28] cannot be differentiated.

Propane isotopic reversal can also arise from the formation of the “heavy” ethane as we observed for the samples from Liten Formation (subset C). These samples had the highest TOC content (Table 1), which affected both the adsorption properties of shales and the carbon isotope fractionation during desorption. Isotope fractionation decreases during desorption with a decreasing content of TOC in the sample [8], while increasing the adsorption capacity increases isotope fractionation during methane desorption [11]. Desorption affects the isotopic composition of the expelled gas because the light isotopologue is preferentially desorbed. Finally, the gas residuum (which is released after rock crushing) is isotopically enriched.
5. Conclusion

Diffusion and adsorption/desorption processes affect the chemical and isotopic composition of residual gases in shale samples. We attempted to reconstruct the original gas content of shales from the gas residuum released from archived crushed-rock samples. Samples from the same formation, i.e., with the same geochemical parameters, differ in their gas content and composition because of different rock properties and sample history. To find a common solution for the entire set, we assume that we analyzed one sample in a different stage of gas loss. The main findings of the study were as follows: the $^{13}$C isotope fractionation $\varepsilon$ for diffusion ranged between $-2.7\%\text{o}$ and $-3\%\text{o}$ for methane and between $-2.7\%\text{o}$ and $-3.7\%\text{o}$ for ethane. Estimated $\delta^{13}$C values of indigenous gas components (methane, ethane, and propane) were very near to the source rock value. The dominant processes influenced the estimates of $\delta^{13}$C values as follows: (i) the gas-abundant sample had a more negative $\delta^{13}$C of methane than the source rock because of diffusion, and (ii) the organic-rich rocks desorbed ethane slowly, which shifted the $\delta^{13}$C value of ethane to a value that was less negative than that for the source rock. Estimates of the original gas volume produced in situ were consistent with the maturity parameters of shales. Most of the shales were immature, and the gas volume ranged between 1 and 200 L per ton of rock. Methane was the dominant component of any lost gas. Archived shales lost 20% to 95% of the original methane. This resulted in an unusual chemical composition of the residual gases, which contained mostly higher hydrocarbons, with a quantity of tens of vol.%.

Author Contributions: Conceptualization, B.F.; methodology, B.F. and G.E.; sampling and resources, G.E. and G.M.; analysis, G.E., B.F., C.B., J.I., and L.Z.; investigation, G.E. and B.F.; writing—original draft preparation, B.F. and G.E.; review and editing, B.F.

Funding: This research received no external funding.

Acknowledgments: The involvement of B.F. as part of this study was supported under a project funded by the Czech Geological Survey, project ID 331390. The study received institutional support from Masaryk University Brno and Mendel University Brno. The Editor and two anonymous reviewers are gratefully acknowledged for their useful and constructive comments.

Conflicts of Interest: The authors declare no conflicts of interest.

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