



# Article Conversion of Organic Matter of Carbonate Deposits in the Hydrothermal Fluid

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**Abstract**: This present paper investigates the conversion of organic matter in carbonate rocks of the Semiluksko-Mendymsky horizon Volga-Ural Basin under hydrothermal conditions with excess water in subcritical conditions at 613–653 K and 170–200 Bar. It has been found that the content of hydrocarbon extracts increases (relatively) which indicates the oil-generating potential of the studied deposits. Besides, it has been shown that organic matter undergoes oxidation reactions under hydrothermal conditions, as indicated by the presence of oxidized structures in the extracted hydrocarbons. Moreover, our results indicate that increasing the temperature and pressure of the used hydrothermal fluid leads to an increase in the content of n-alkanes  $C_{25}$ - $C_{30}$  and asphaltenes in the extracts. On the other hand, it has been found that saturated, aromatic hydrocarbons and resins content decreases at this stage. The obtained data about the geochemical parameters dependencies of the hydrocarbons obtained from the studied carbonate rock on temperature and pressure associated to hydrothermal effect show possible pathways of migration, genesis, and formation of hydrocarbon deposits.

**Keywords:** hydrothermal fluid; carbonate rock; subcritical region; hydrocarbon extract; analysis of composition and properties

# 1. Introduction

A substantial decrease in conventional oil and gas reserves [1–5] led to the establishment of three potential development trends in global energy [6]. The first trend is related to the involvement of alternative fuel resources in the area [7–13]; the second is related to deeper processing of conventional hydrocarbon feedstock to obtain marketable products with high added value [14–21]; and the third is related to the increasing interest in unconventional oil and gas resources [22–26].

Innovative technologies for the development of hard-to-recover hydrocarbon resources represents a highly relevant topic nowadays [27–29]. Alternative hydrocarbon resources, such as carbonate deposits containing organic matter, are widespread in Russia, China, Jordan, Brazil, Morocco, Australia, Estonia, USA, Canada, Zaire, Italy, France, etc. In the literature, preliminary assessments show that the resource potential of carbonate deposits exceeds several times the reserves of conventional oil in traditional reservoirs. However, extracting hydrocarbons from organo-mineral complexes of carbonate deposits faces serious issues which are currently receiving more and more attention all over the world.

Carbonate deposits containing organic matter in Russia are found on the East European platform and the Urals, on the northeastern slope of South Timan, in the Perm region, Udmurtia, Tatarstan, and Bashkiria, and are confined to the Semiluki horizon of the Lower Frasniansubstage [30–33]. Their analogs are also found in the Sargaevskiy,



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Buregskiy, and Askynskiy horizons of the Frasnian Stage, and partially in the Famennian Stage in the territory of the Kama-Kinelskpaleotrough. A wide range of literature has reported the lithological composition of these deposits which includes limestones, siliceous marls and siliceous argillites, silicites, and silica [34,35]. Nevertheless, recent findings regarding carbonate deposits of the Semiluki age on the territory of Tatarstan suggest that their composition differ from the higher and lower-lying rocks in mineral composition by low-permeability filtration-volumetric properties and by the presence of organic matter in the form of kerogen and heavy petroleum hydrocarbons.

Innovative methods of extracting hydrocarbon resources from unconventional carbonate reservoir rocks are widely based on scientific knowledge about geological and geochemical processes that cause the generation of petroleum hydrocarbons from the organic matter of rocks and their migration in the sedimentary cover with the formation of industrially significant accumulations. It is worth noting that theoretical and experimental studies proved the ability of the hydrothermal fluid located near the critical point of water to change the composition of organic matter in rocks. It was shown that hydrothermal processes play a vital role in the spatial distribution and formation of both carbonate reservoirs and in certain deep reservoirs. In these reservoirs, hydrothermal fluid-rock interaction may result in permeability creation (due to carbonate dissolution) or permeability destruction (due to the deposition of cementing minerals). Thermal maturation of organic matter in sedimentary rocks presents relevant issue in this area, since it is controlled by multiple parameters [36–41].

In fact, water plays a crucial role in physical transformations and chemical reactions occurring in a supercritical aqueous fluid at temperatures and pressures above 647 K and 220 Bar, where it participates not only as a solvent but also as a reagent. These changes are widely believed to be the main factors causing the formation of petroleum hydrocarbons from the organic matter of rocks [42–47]. Thermal enhanced oil recovery by steam injection treatment is recognized as being one of the most promising methods for the development of unconventional oil deposits (where water is used in the form of a hydrothermal fluid [42,48–50]).

Currently, many companies, institutes, and research groups in different countries are engaged in the creation of innovative technologies for the extraction and processing of hydrocarbons from carbonate rocks [31,34,35,51–58]. Thus, the present work is devoted to study the composition of the extracted hydrocarbons (petroleum hydrocarbons) from Semiluksko-Mendymsky horizon carbonate rock containing organic matter under hydrothermal conditions at different temperatures and pressures.

### 2. Materials and Methods

# 2.1. Materials

The object of the present research was a sample of siliceous-clayey carbonate rock containing organic matter from the sediments of the Semiluksko-Mendymsky horizon of the South Tatar arch lying at a depth of more than 1700 m. Deposits of the Semiluksky horizon present a belt that stretches along the Urals from north to south, from the Pechora Sea to the Caspian Syneclise. Many scientists, guided by the content of hydrocarbons in these deposits exceeding 3225 g/m<sup>3</sup>, refer them to oil source rocks [59]. According to X-ray diffraction analysis, the carbonate rock contained 62% quartz, 16% dolomite, 12% calcite, 9% feldspars, and 1% clay minerals.

#### 2.2. Experiments

The experiments were carried out in a batch reactor, a heated cylindrical thick-walled vessel made of Hastelloy C-276 material with a volume of 1000 cm<sup>3</sup>, equipped with a thermocouple, an electric drive, and a manometer. The temperature control of the reactor (R-101) was carried out using a heating jacket H-101 and a cooling coil.

10 g of crushed carbonate rock with an excess amount of distilled water (330 g), was loaded manually through the upper nozzle of the reactor; the filling factor was 0.6. With an

increase in the temperature of the experiment to 613 and 653 K, the pressure in the reactor increased to 170 and 200 Bar, approaching the critical point of water (647 K and 214 Bar), the duration of the experiment was 1 h.

## 2.3. Analysis

Thermal analysis of carbonate rock before and after the experiments was carried out on a synchronous thermal analyzer STA 6000 (Perkin Elmer) in the presence of nitrogen with a temperature range from 288 to 1273 K and a scanning rate from 0.1 °/min to 100 °/min. Thermal analysis values were calculated from the weight loss data: F ( $\Delta m_{473-673 \text{ K}}/\Delta m_{673-873 \text{ K}}$ ) and *p* ( $\Delta m_{673-873 \text{ K}}/\Delta m_{873-1073 \text{ K}}$ ). The weight loss data were used to calculate the indicators of the fractional composition F and *p* of the corresponding weight fraction of alkyl substituents in aromatic structures.

The extraction of petroleum hydrocarbons from the carbonate rock before and after the experiments was carried out in a Soxhlet apparatus using a mixture of solvents: chloroform, toluene, and isopropyl alcohol in a ratio of 1:1:1. The obtained extracts were separated in accordance with SARA analysis into four fractions: saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes.

The study on the individual hydrocarbon composition of n-alkanes and acyclic isoprenoids of saturated hydrocarbons was carried out by gas-liquid chromatography on a Perkin Elmer Clarus 500 chromatograph using a flame ionization detector on a capillary column, 25 m in length and 0.2 mm in diameter.

The analysis of the individual composition of aromatic hydrocarbons was carried out by GC/MS on a Thermo Fisher Scientific instrument with an ISQ LT Single Quadrupole mass selective detector based on a Chromatek-Kristall 5000 chromatograph with Xcalibur software. A CR-5 ms quartz capillary column 30 m in length and 0.25 mm in inner diameter with a deposited methylsiloxane phase (0.25  $\mu$ m) was used.

The structural group composition of resins and asphaltenes was determined by FTIR spectroscopy on a Vector 22 IR spectrometer (Bruker) in the range of 4000–450 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. IR spectra were compared in terms of optical density D at the maxima of the corresponding absorption bands.

The surface area of the carbonate rock was determined from nitrogen adsorption or desorption isotherms using a Quantachrome NOVA<sup>®</sup> 1200 analyzer (Anton Paar QuantaTec Inc., Boynton Beach, Florida, USA). To calculate the total volume and average pore diameter, BET and BJH methods were used and in order to calculate the volume of micropores we have used the Halsey t-method.

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## 3. Results and Discussion

The results of thermal analysis of carbonate rock before and after the experiments are shown in Figures 1 and 2. The initial rock is characterized by a high value of the contained organic matter (8.67% wt.). The results of thermal analysis of rock samples indicate that with an increase in the temperature and pressure of the hydrothermal fluid from 613 K to 653 K and pressure from 170 to 200 Bar, respectively, the content of the contained organic matter in the rock becomes higher.



Figure 1. Weight loss of carbonate rock before and after experiments.



Figure 2. Thermal analysis of carbonate rock before and after experiments.

The obtained data indicate a change in the values of the content of organic matter (OM) in the carbonate rock and the F and *p* values after hydrothermal experiments. The organic matter of the initial rock is characterized by a relatively high value of the fractional composition index F (0.54). After hydrothermal treatment at 653 K and 200 Bar, the index F decreases to 0.45, and the content of organic matter increases to 9.29%, which indicates an increase in the oxidation rate of the hydrocarbon components of the rock. During hydrothermal treatment of the rock under milder conditions at 613 K and 170 Bar, the OM content decreases to 8.25 wt.%. At the same time, the fractional composition of OM enriches in heavy condensed structures, as evidenced by a decrease in mass loss of the rock sample in the range of 0–200 °C, indicating the presence of low-boiling hydrocarbons (gasoline fractions). Carbonate rock after hydrothermal treatment at 613 K and 170 Bar is characterized by a markedly lower fractional composition F (0.37) and OM content (8.25). The indicator of the fractional composition of the hydrothermally converted rock changes in the range of values (0.37–0.45). Correspondingly, a change in the chemical composition of organic matter towards enrichment in heavy compounds occurs.

In contrast to the hydrocarbon extract of the initial carbonate rock, the extracts from the rock after hydrothermal treatment are characterized by a lower amount of saturated (HC), aromatic hydrocarbons (AR HC) and resins (R) (Figure 3). The extract from the initial carbonate rock, in which the resinous-asphaltene components account for 66.02 wt.%. Hydrothermal treatment of carbonate rock leads to 21.23 and 21.32 wt.% content of saturated and aromatic hydrocarbons, and to 46.43 and 47.08 wt.% of asphaltenes, respectively. In



addition, changing the temperature and pressure from 613 K and 170 Bar to 653 K and 200 Bar, leads to increasing the yield of asphaltites in the rock from 3.12 to 3.39–5.05 wt.%.

Figure 3. Yield and component composition in extracts from carbonate rock before and after experiments.

An increase in the temperature of the hydrothermal fluid initiates radical chain nucleation reactions involving aromatic hydrocarbons, resin, and asphaltene molecules, with the most vulnerable C-H bond located in the  $\beta$ -position to the benzene nucleus. The chain termination occurs due to the recombination of aromatic radicals with the accumulation of resin (R) and asphaltene (A) molecules in the hydrothermal fluid. By increasing temperature, the reactions proceed mainly by the radical-chain mechanism (i.e., dealkylation of naphthenic and aromatic structures, resins, and dehydrogenation of naphthenes to aromatic compounds with their subsequent condensation into resins). The hydrogen proton formed as a result of dehydrogenation reactions of naphthenic and naphthenoaromatic structures participates in the reactions of inhibition of the radical-chain mechanism and in the reactions of OM conversion. Despite the ongoing condensation reactions of aromatic hydrocarbons with the formation of resins, the amount of the latter in the extract decreases, which indicates a low thermal stability of the resins themselves. It should be noted that an increasing the process temperature and pressure may intensify the revealed patterns.

Figure 4 graphically shows the changes in the geochemical coefficients of the carbonate rock organic matter depending on the thermodynamic parameters of the hydrothermal fluid.  $\Sigma$  (C<sub>16</sub>-C<sub>22</sub>)/ $\Sigma$  (C<sub>23</sub>-C<sub>29</sub>) represents the content ratio of the sum of linear alkanes with the number of carbon atoms from 16 to 22 to the sum of linear alkanes with the number of carbon atoms from 23 to 29.  $C_{27}/C_{17}$  represents the ratio of the content of linear alkane with the number of carbon atoms 27 to the content of the linear alkane with the number of carbon atoms 17.  $(Pr + Ph)/(C_{17} + C_{18})$  represents the ratio of the content of the sum of pristane (Pr) and phytane (Ph) to the content of linear alkanes with the number of carbon atoms from 17 to 18.  $\Sigma$  (C<sub>27</sub>-C<sub>31</sub>)/ $\Sigma$  (C<sub>15</sub>-C<sub>19</sub>) represents the ratio of the content of the sum of linear alkanes with the number of carbon atoms from 27 to 31 to the content of the sum of linear alkanes with the number of carbon atoms from 15 to 19.  $Pr/C_{17}$  represents the ratio of the content of pristane (Pr) to the content of linear alkane with the number of carbon atoms from 17.  $Ph/C_{18}$  represents the ratio of phytane content (Ph) to the content of linear alkane with carbon atoms from 18.  $\Sigma$  (C<sub>11</sub>-C<sub>14</sub>)/ $\Sigma$  (C<sub>15</sub>-C<sub>18</sub>) represents the ratio of the content of the sum of linear alkanes with the number of carbon atoms from 11 to 14 to the content of the sum of linear alkanes with the number of carbon atoms from 15 to 18.  $\Sigma$  (C<sub>13</sub>-C<sub>15</sub>)/ $\Sigma$  (C<sub>25</sub>-C<sub>27</sub>) represents the ratio of the content of the sum of linear alkanes with the number of carbon atoms from 13 to 15 to the content of the sum of linear alkanes with the number of carbon atoms from 25 to 27.  $\Sigma$  (C<sub>12</sub>-C<sub>21</sub>)/ $\Sigma$  (C<sub>22</sub>-C<sub>30</sub>) represents the ratio of the content of the sum of linear alkanes with the number of carbon atoms from 12 to 21 to the content of the sum of linear alkanes with the number of carbon atoms from 22 to 30.  $2C_{19}/\Sigma$  ( $C_{18}$ - $C_{20}$ ) represents the ratio of the doubled content of linear alkane with the number of carbon atoms of 19 to the content of the sum of linear alkanes with the number



**Figure 4.** Geochemical coefficients of saturated hydrocarbons in extracts from carbonate rocks before and after experiments.

Geochemical coefficients are calculated based on the data of gas chromatographic analysis of saturated hydrocarbons and clearly show the redistribution of the dominant compounds in their composition after hydrothermal treatment.

The presence of the carbonate rock containing organic matter in a hydrothermal fluid changes the composition of saturated hydrocarbons. The content of n-alkanes of the composition  $C_{23}$ - $C_{29}$ ,  $C_{15}$ - $C_{18}$  increases, with an increase in the temperature and pressure of the process, and the content of n-alkanes of the composition  $C_{11}$ - $C_{14}$  significantly decreases. High molecular weight homologues prevail over low molecular weight, which follows from the values of the ratio  $\Sigma$  ( $C_{13}$ - $C_{15}$ )/ $\Sigma$  ( $C_{25}$ - $C_{27}$ ) decreasing by more than two times. The predominance of the amount of linear alkanes over iso-alkanes (Pr + Ph)/( $C_{17}$  +  $C_{18}$ ) also noticeably increases, which indicates a high reactivity of the tertiary carbon atom in iso-alkanes. However, a decrease in the values of the Pr/ $C_{17}$  index and a decrease in the values of the Pr/Ph ratio indicate a high reactivity of pristane (Pr). Under these hydrothermal conditions, the opposite picture is observed with phytane (Ph).

The practical value of geochemical coefficients lies in their predictive assessment of the composition of saturated hydrocarbons as a potential hydrocarbon feedstock for fuel and energy. Thus, hydrothermal technologies aimed at the extraction/generation of oil hydrocarbons from oil source deposits are of interest.

As seen from Figure 4, the extracts of carbonate deposits after hydrothermal treatment are characterized by a lower  $Pr/n-C_{17}$  ratio and a high  $Ph/n-C_{18}$  ratio, as compared to the initial rock extract. Moreover, the organic matter of carbonate rocks after hydrothermal

exposure has almost similar values of the Pr/Ph index, which are equal to 0.8–1.0, following a decrease in the  $(Pr + Ph)/(C_{17} + C_{18})$  value from 2.34 to 1.84 and 1.62, while the  $C_{27}/C_{17}$  index decreases by half, which indicates the predominance of n-alkanes in the composition.

The decrease in the ratio of the content of iso-alkanes to n-alkanes ( $Pr/C_{17}$ ,  $Ph/C_{18}$ ,  $Pr + Ph/C_{17} + C_{18}$ ) is due to the ongoing oxidation reactions with atmospheric oxygen, when the rate of decrease in the concentration of iso-alkanes is higher than the rate of decrease of linear alkanes. It can be assumed that formed radicals of aromatic rings serve as the initiators of the radical chain reaction for n-alkanes. Due to the removal of alkyl substituents of aromatic hydrocarbons, resins and asphaltenes, as a rule, lower n-alkanes (mainly methane and n-alkanes of the composition  $C_4$ - $C_{12}$  form). However, with an increase in the temperature of the hydrothermal fluid, the amount of the latter, relative to n-alkanes of the composition  $C_{15}$ - $C_{27}$ , decreases. Thus, in a closed system containing hydrothermal fluid at 653 K and 200 Bar, the transformation of alkanes in the carbonate rock mainly occurs via the reactions of chain continuation or growth with recombination reactions.

Figure 5 shows the relative content of hydrocarbons and sulfur-containing compounds in aromatic fractions before and after hydrothermal experiments. In the initial aromatic fraction, benzothiophenes (BTP) predominate and phenanthrenes (Ph) are present.



**Figure 5.** Distribution of various types of aromatic hydrocarbon compounds in extracts from carbonate rocks before and after experiments.

In aromatic hydrocarbon extracts from carbonate rock, the content of naphthalenes (N) decreases and the content of dibenzothiophenes (DBTP) increases with increasing temperature and pressure of hydrothermal treatment. The increase in the content of trimethylbenzenes (TMB) and dibenzothiophenes is probably due to the processes of cyclization and aromatization of saturated hydrocarbons.

The values of structural parameters according to IR spectroscopy data are presented in Table 1. It has been found that resins in carbonate rocks extracts after hydrothermal treatment are distinguished by increased values of aliphaticity (Al  $(D_{2857} + D_{2925})/(D_{2857} + D_{2925} + D_{1630})$ ) against the background of similar values of aromaticity (Ar  $(D_{3050}/D_{2897}))$ , and low values of branching (Br  $(D_{2957}/D_{2925})$ ).

IR Spectral Coefficients	Initial Rock		613 K, 170 Bar		653 K, 200 Bar	
	Resins in Extracts	Asphaltenes in Extracts	Resins in Extracts	Asphaltenes in Extracts	Resins in Extracts	Asphaltenes in Extracts
Ar	1.02	0.49	1.02	0.56	0.99	0.55
Ox	0.36	0.20	0.4	0.24	0.39	0.21
С	0.85	0.16	0.48	0.20	0.42	0.18
Br	0.70	0.60	0.60	0.60	0.61	0.61
Al	0.84	0.78	0.89	0.79	0.87	0.78

Table 1. Structural parameters according to IR spectroscopy.

With an increase in the temperature of the hydrothermal fluid from 613 to 653 K, the aliphaticity and branching of asphaltenes does not change. On the contrary, their aromaticity and condensation (C ( $D_{3050}/D_{1600}$ )) increase, indicating the occurrence of naphthenic dehydrogenation reactions and condensation of aromatic structures leading to the formation of asphaltenes and their carbonization. With an increase in the temperature of the experiment, the values of oxidation (Ox ( $D_{1710}/(D_{1710} + D_{1630})$ )) of the resins increase and the values of condensation (C) decrease, which indicates the reaction of oxidative dehydrogenation.

Studies have shown changes in the pore space of carbonate rocks in the hydrothermal fluid (Table 2). With a temperature increase in the hydrothermal fluid to 613 K, the total volume and average pore diameter increase, which leads to an increase in the specific surface area. In the carbonate rock, the pore volume and diameter increase from 0.1204 cm<sup>3</sup>/g and 4.209 nm to 0.1248 cm<sup>3</sup>/g and 4.228 nm, and micropores are formed, which leads to an increase in the specific surface area up to  $3.491 \text{ m}^2/\text{g}$  for BET and up to  $2.906 \text{ m}^2/\text{g}$  for BJH. A further increase in the temperature and pressure of the hydrothermal fluid to 653 K and 200 Bar leads to a decrease in pore volume to 0.1164 cm<sup>3</sup>/g and specific surface area to  $0.752 \text{ m}^2/\text{g}$  according to BET and to  $0.622 \text{ m}^2/\text{g}$  according to BJH.

Table 2. The pore space of carbonate rocks.

Structural Parameters	Initial Rock	613 K, 170 Bar	653 K, 200 Bar
BET specific surface, m <sup>2</sup> /g	1.569	3.491	0.752
BJH Total pore volume, sm <sup>3</sup> /g	0.1204	0.1248	0.1164
BJH Average pore diameter, nm	4.209	4.228	4.221

In a hydrothermal fluid, an increase and decrease in the specific surface area of a carbonate rock containing organic matter correlates with the free pore volume and pore diameter, which depends on the content of organic matter and the yield of the hydrocarbon extract. In a hydrothermal fluid at 653 K and 200 bar, we observe the greatest increase in the content of organic matter in the rock from 8.6 to 9.2 wt%. and an even higher yield of hydrocarbon extract from 3.1 to 5% wt., which led to a decrease in pore volume and, as a consequence, to a decrease in specific surface area. In a hydrothermal fluid at 613 K and 170 bar, the yield of the extract from the carbonate rock remained practically unchanged (3.3 wt%), while the content of organic matter, on the contrary, decreased from 8.6 to 8.5. Within a sharp decrease in paraffin-naphthenic and aromatic compounds in the composition, the proportion of resin and asphaltene molecules (SARA) significantly increases with an increase in aromatic and condensed fragments in them. Thus, the organic component of the rock is compacted, which leads to an increase in pore volume and, as a consequence, to an increase in the specific surface of the rock.

## 4. Conclusions

The conversion of organic matter of a siliceous-clayey carbonate rock in the hydrothermal medium at 613 K and 170 Bar leads to a decrease in the amount of saturated and aromatic hydrocarbons in the extract from 33.9 to 21.2 wt.%, resins from 37 to 24.5 wt.% and an increase in the content of asphaltenes from 29 to 54.3 wt.%, which indicates the predominance of polycondensation reactions. In the composition of saturated hydrocarbons after hydrothermal treatment, the prevalence of n-alkanes with the number of carbon atoms from 19 to 26 over iso-alkanes is observed. It shows high reactivity of the C-C bonds at the tertiary carbon atom under these conditions. In aromatic hydrocarbons with an increase in the content of trimethylbenzenes from 1.9 to 28.2 wt.% and dibenzothiophenes from 8.6 to 12.3 wt.%, the content of naphthenes decreases from 23.6 to 11% wt. and benzothiophenes (from 61 to 44.3% wt). The dehydrogenation of alkyl-substituted cyclohexanes leads to an increase in the content of alkylbenzenes in the hydrocarbon extract. An increase in the ratio of the intensity of absorption bands of oxygen-containing groups to aromatic rings (Ox) in asphaltenes and resins of the hydrocarbon extract, and an increase in the degree of their condensation (C) prove that polycondensation proceeds through oxidative polymerization. The temperature and pressure increase in the hydrothermal fluid to 653 K and 200 Bar leads to an increase in the amount of the hydrocarbon extract in the organic matter from 3.1 to 5.1 wt.%, and to a more intense course of the reactions described above. An increase in the number of hydrocarbons in organic matter leads to a decrease in pore volume from 0.1204 to 0.1164 cm<sup>3</sup>/g, and, as a consequence, to a significant decrease in the specific surface area of siliceous-clayey carbonate rock from 1.569 to  $0.752 \text{ m}^2/\text{g}$  according to BET.

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