energies

MDPI

Article

Characteristics and Significance of Acid-Soluble Organic Matter in Marine Carbonate Source Rocks

Danting Feng [1], Xiaofeng Wang [1,*], Wenhui Liu [1,2], Dongdong Zhang [1], Jie Wang [2], Houyong Luo [1] and Peng Liu [3]

[1] State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, China
[2] Petroleum Exploration and Production Research Institute, SINOPEC, Beijing 100083, China
[3] College of Safety Science and Engineering, Xi'an University of Science and Technology, Xi'an 710054, China
* Correspondence: wangxf@nwu.edu.cn

Abstract: Since the 1950s, major breakthroughs have been made in the field of carbonate oil and gas exploration, and large reservoirs have been found in carbonate strata in many countries; however, the validity of highly evolved carbonate source rocks has been controversial. Because of the loss of organic carbon during acid-solution processing in conventional total organic carbon (TOC) determination, we decided to use a new method of reducing acid-solution losses in order to more effectively quantify acid-soluble organic matter in carbonate rock samples. Different levels of acid-soluble organic matter were present in different types of samples, and there was no positive correlation between the content of acid-soluble organic matter and conventionally measured TOC values. However, the thermal evolutionary maturity of samples with high acid-soluble organic matter content is relatively low, and the high hydrocarbon generation conversion rate of acid-soluble organic matter and conventional TOC in carbonate rocks is an important reason for the low residual TOC in highly evolved carbonate rocks. The new method is helpful in re-evaluating the abundance of organic matter in carbonate rocks and in providing evidence for studying hydrocarbon generation and the hydrocarbon capacity of carbonate source rocks.

Keywords: carbonate rock; source rock evaluation; TOC; acid-soluble organic matter; organic acid salt

check for updates

Citation: Feng, D.; Wang, X.; Liu, W.; Zhang, D.; Wang, J.; Luo, H.; Liu, P. Characteristics and Significance of Acid-Soluble Organic Matter in Marine Carbonate Source Rocks. *Energies* **2023**, *16*, 2017. https://doi.org/10.3390/en16042017

Academic Editor: Edo Boek

Received: 2 December 2022
Revised: 29 January 2023
Accepted: 16 February 2023
Published: 17 February 2023

Copyright: © 2023 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/).

1. Introduction

Marine carbonate rocks are important strata for oil and gas storage and exploration, and 60% of global oil and gas production comes from marine carbonate rocks [1–3]. Compared with rocks in most of the world, marine carbonate strata in China are older and have been more deeply buried, and most units are highly mature or over-mature; this leads to great difficulty in oil and gas exploration [4,5]. However, in recent years, as exploration has progressed, carbonate rocks have exhibited good exploration prospects and have gradually become important oil and gas resource-replacement areas in China [1,2,6]. Large-scale oil/gas fields have been discovered in the lower Paleozoic carbonate rocks of the Ordos Basin, the Sichuan Basin, and the Tarim Basin in China; in particular, great progress has been made in the exploration of Ordovician subsalt natural gas in the Ordos Basin. Against this background, the question of whether carbonate rocks with low residual organic-matter abundance, which are widespread in lower Paleozoic strata, can act as effective hydrocarbon sources has attracted much attention [7–11]. The original abundance of organic matter, the characteristics of the assemblage of hydrocarbon-forming organisms, the forms of occurrence of organic matter, and the hydrocarbon-generating potential of carbonate source rocks have become a hot issue of widespread concern [5,12–15].

At present, total organic carbon (TOC) is the main index used to evaluate the abundance of organic matter in source rocks. It is generally believed that the types of organic matter stored in carbonate source rocks are favorable for hydrocarbon generation, and the lower limit of TOC for carbonate rocks to become effective hydrocarbon sources is therefore

markedly lower than that of shale [16–18]. However, the lower limits of TOC of carbonate source rocks suggested in previous studies differ by orders of magnitude, and there is currently no unified standard (Table 1).

Table 1. TOC lower limits of TOC carbonate source rocks proposed in various studies.

Scholar	TOC Lower Limit/%	Scholar	TOC Lower Limit/%
Hunt [19]	0.29	Liu B. Q. et al. [20]	0.05
Palacas [21]	0.40	Chen P. J. et al. [18]	0.1
Tissot et al. [22]	0.30	Hao S. S. et al. [23]	0.2
Fu J.M. et al. [17]	0.1–0.2	Liang D. G. et al. [24]	0.5
Xia X.Y. et al. [25]	0.4–0.5	Peng P. A. et al. [26]	0.1

TOC is an inappropriate indicator of source rock quality, because organic matter abundance is a measure of the amount of hydrocarbon-producing organic matter in the sediment, which may also include non-generating kerogen (i.e., dead carbon) and bitumen in oil-prone mature samples [27,28]. There are obvious discrepancies between the TOC data obtained by the traditional method and the actual amount of TOC; these discrepancies indicate that TOC data may not be a reliable means of source rock evaluation [29]. The discrepancies may arise from the particular characteristics of organic matter in carbonate rocks.

Organic matter in carbonate rocks can be divided into kerogen and soluble organic matter. There are many forms of soluble organic matter, including adsorbed organic matter, organic matter in inclusion, and organic matter enclosed in carbonate minerals [30–34]. These various forms of organic matter may be related to the sedimentary and diagenetic complexity of carbonate rocks [35,36].

During conventional TOC determination, the carbonate minerals in the rock are removed using 5% hydrochloric acid, and the sample is repeatedly washed with distilled water until neutral. The organic carbon present in the residue is measured, but the acid solution is discarded. Previous studies have found that the acid solution contains a large amount of organic matter dissolved in the aqueous phase of the acid solution; this is called acid-soluble organic matter. The loss of acid-soluble organic matter means that some organic matter is not included in the organic carbon measurement, which is an important reason for the low TOC test results [12,37]. The loss of acid-soluble organic matter has little effect on the TOC value of organic-rich argillaceous source rocks, but it has a great influence on the source rocks of gypsum-salt strata with low organic matter abundance [38]. For modern carbonate sediments, Roberts et al. found that 44% of organic carbon was lost as a result of acid hydrolysis and water washing during conventional TOC determination [39].

Organic acid salts are the main component of acid-soluble organic matter, which has been proven to be a potential hydrocarbon source for carbonate rocks [14,38]. Chong and McKay extracted a series of carboxylic acids from Green River oil shale, including monocarboxylic acids, dicarboxylic acids, aliphatic and unsaturated acids, branched-chain fatty acids, and aromatic acids [40]. Only a small fraction of the acids existed in the form of free acids, and most of the acids were combined with, or coprecipitated with, calcium carbonate minerals in the form of salts. Other acids seemed to have been trapped inside minerals until they were dissolved [41].

To avoid the loss of (acid-soluble) organic matter during TOC testing of carbonate source rocks, Liu Peng et al. added standard samples of organic matter to the matrix ($CaCO_3$ and SiO_2) to simulate the mineral composition of natural carbonate rocks and tried to re-evaluate the organic matter abundance of carbonate rocks using a new method. That study established a method in which montmorillonite is used to thicken the acid-soluble carbonate hydrocarbon source rock solution, thus reducing the amount of rinsing with distilled water required and effectively avoiding the loss of acid-soluble organic matter [13]. We used the new method of total organic matter (TOC^+) analysis of Liu et al. to determine the content of TOC^+ and acid-soluble organic matter in different types of carbonate samples from China and the USA. The loss of (acid-soluble) organic matter was confirmed from the

TOC^+ and TOC values, and the relationship between the abundance of acid-soluble organic matter and conventional TOC in geological samples was analyzed. We also discussed the controlling factors of the formation and evolution of acid-soluble organic matter in carbonate strata.

At present, the traditional TOC determination method cannot truly reflect the organic-matter abundance of carbonate rock samples. This may be a key factor limiting the evaluation of marine carbonate rocks in China, and therefore a new and reliable method for the evaluation of organic matter abundance of carbonate rocks is needed. The experiments in this paper calculate all the organic matter lost in the traditional TOC test into organic carbon, thus providing new ideas for the evaluation of hydrocarbon source rocks in marine carbonate rocks and theoretical support for carbonate oil and gas exploration.

2. Samples and Methods

2.1. Samples

The samples used in the experiment were carbonate rocks from the Ordovician Majiagou Formation of the Ordos Basin, China; the Permian Maokou Formation of the Sichuan Basin, China; the Cambrian Xiaoerbulake Formation of the Tarim Basin, China; and the Eagle Ford Formation of Texas, USA. Basic information on the samples is provided in Table 2. All the samples were crushed to 100 mesh before analysis.

Table 2. Basic information on the studied carbonate source rock samples [42–45].

Sample	Strata	Stage of Thermal Evolution	TOC Distribution Range (%)	Mineral Content of Carbonate Rock (%)	Depositional Environment	Organic Matter Type
Majiagou Formation	Ordovician	High-over mature (1.6–2.5%)	0.01–1.67	40.2–99.1	Restricted open carbonate platform	Type I
Maokou Formation	Permian	Low mature-mature (0.8–1.5%)	0.16–2.36	9.4–69.4	Open carbonate platform; slope facies	Type II
Xiaoerbulake Formation	Cambrian	High-over mature (1.8–2.5%)	0–0.61	45–78	Carbonate gentle slope facies	Type I/II
the Eagle Ford carbonate rocks	K	Low mature-mature (0.6–1.2%)	0.09–6.16	>45	Littoral shallow marine environment	Type II

2.2. Instruments and Experimental Methods

Montmorillonite has a laminated crystal structure, which expands in water to form a thixotropic grid-like gel [46]. This property means that montmorillonite can be used to thicken the carbonate source rock solution after acid treatment, and measurements of the organic carbon data can be obtained by using an elemental analyzer.

Before using montmorillonite, trace carbon that may exist in impurities should be removed. The treatment method includes the following six steps.

First, grind the montmorillonite samples after crushing, and pass them through a 100 mesh sieve. Second, wash repeatedly with distilled water, and remove the suspended matter from the surface of the solution. Third, add excess of 3% dilute hydrochloric acid several times, stir until no bubbles are generated, leave the solution to stand, and take the supernatant. Fourth, heat the montmorillonite suspension in a water bath at 40 °C. Add 30% hydrogen peroxide until no bubbles are produced, and then wash with distilled water until neutral. Fifth, add distilled water to the montmorillonite from which organic matter has been removed, stir the sample fully using a glass rod, leave it to stand for 8 h, and then transfer one third of the upper part of the precipitate into a container. Repeat this step

several times. Sixth, slowly dry the resuspended and purified montmorillonite in an oven, and regrind to 1 mm size.

The new method of measuring TOC uses the following procedure (Figure 1), which is slightly modified from that of Liu et al. [13].

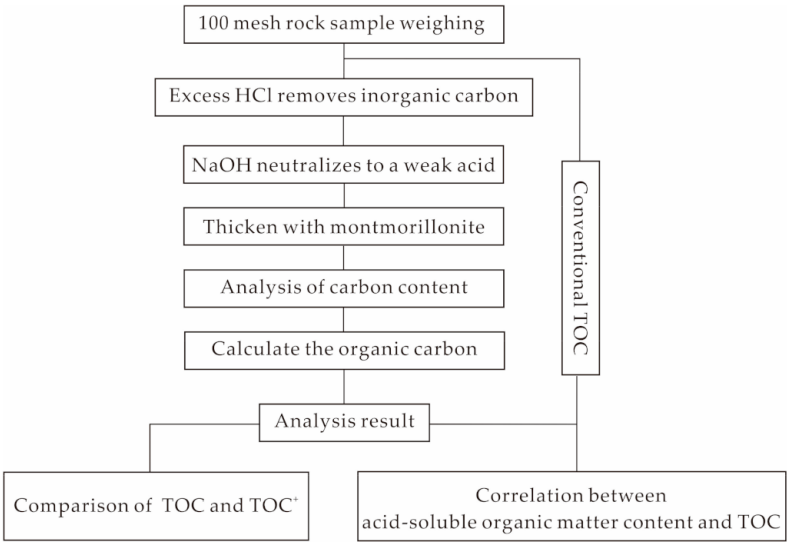


Figure 1. Flow chart of the experimental procedure (modified from Liu Peng [13]).

First, crush the carbonate rock sample to 1 mm size, weigh out approximately 1 g of the sample, and place this measured amount in a conical flask. Second, add concentrated hydrochloric acid into the conical flask repeatedly, and stir thoroughly until no bubbles are generated. Third, add a proper amount of montmorillonite to the conical flask to thicken, and stir thoroughly to mix the solution and residue evenly.

The elemental carbon in the "clay paste" is analyzed by using an elemental analyzer, and the total organic carbon content of the original sample is calculated from the results. The conversion formula is as follows:

$$TOC^{+}(\%) = \frac{(m_3 - m_1) \times n}{m_2 - m_1} \quad (1)$$

where m_1 is the mass of the empty conical flask; m_2 is the mass of the conical flask after the sample has been added; m_3 is the mass of the conical flask after montmorillonite has been added; and n% is the result of carbon elemental analysis. All TOC values measured by the new method are expressed as TOC^{+}. Blank montmorillonite was measured, and the results were corrected accordingly.

The elemental analysis tests were performed on a vario PYRO cube elemental analyzer (Germany), which was connected online to an Isoprime 100 continuous flow stable isotope mass spectrometer. This step can analyze $\delta^{13}C$ isotopic ratios while testing the organic carbon content. The measurement precision is estimated to be ±0.5‰ for $\delta^{13}C$ with respect to the Vienna Peedee Belemnite (VPDB). Conventional organic carbon testing was completed on a CS-344 carbon sulfur analyzer (LECO Company, United States), following the analytical process described in the National Standard of P.R. China (GB/T 19145-2003). The experimental analysis was completed at the Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Science at Lanzhou. All reagents used were pure analytically, and all reagents were used after secondary distillation.

Liu Peng et al. used standard samples to test the new method for measurement of the abundance of organic matter in carbonate rocks. When montmorillonite was added to samples with low theoretical levels of organic carbon, the already low concentration

of organic carbon was further diluted. When the test value was close to the instrument detection limit, there was a large error [13]. Combined with the basic information from the samples, for samples with TOC values of less than 0.2%, the analytical error is relatively large, and the results should be used for reference only.

3. Results and Discussion

3.1. Comparison of TOC Results Obtained Using Different Methods

A comparison of the results obtained using the conventional TOC determination method and the new method demonstrates that the TOC^+ values of most samples are markedly higher than the conventional TOC values (Figure 2), indicating that loss of acid-soluble organic matter occurs to varying degrees during the acid treatment process. In this study, the TOC^+ values were slightly lower than those of conventional TOC analysis in some samples because of experimental errors.

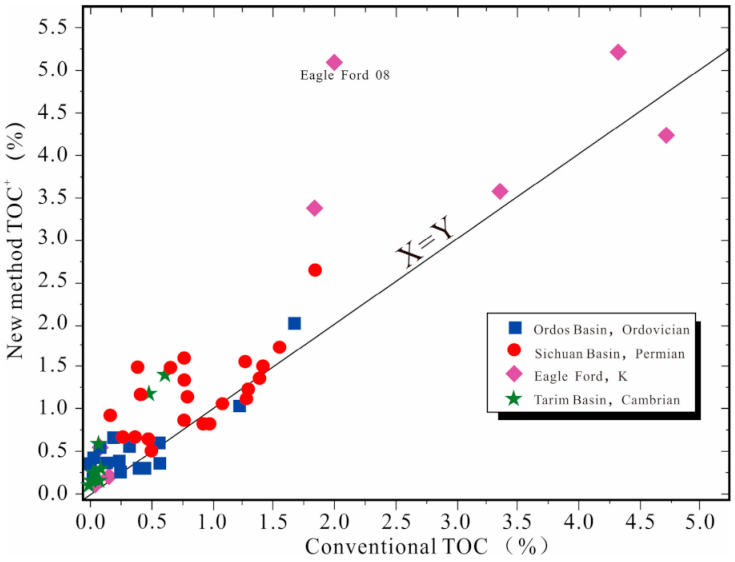


Figure 2. Comparison of the TOC values of carbonate source rocks from different regions measured using different methods.

In addition to TOC^+ analysis, organic carbon isotope ratios were measured for most of the samples. The organic carbon isotopic values for the samples analyzed with the new method are between −24.7‰ and −35.8‰, with the main peak between −26‰ and −30‰ (Figure 3). These isotopic values are typical of organic carbon, indicating that the treatment method is reliable and that there was no contamination by inorganic carbon.

In the carbonate rocks of the Cambrian Xiaoerbulake Formation of the Tarim Basin, the TOC values of most samples from the Penglaiba outcrop are less than 0.2%. The average TOC^+ content of these samples measured by the new method is 0.28%, indicating that the acid-soluble organic matter content in these samples is low. The TOC values of the three samples from the same formation obtained from the Sugaitbulak outcrop are different from the TOC^+ values, demonstrating that the content of acid-soluble organic matter in these samples is relatively high (Table 3).

The maturity of the samples from the Permian Maokou Formation of the Sichuan Basin and the Eagle Ford Formation is relatively low, and TOC^+ for these rocks is markedly higher than conventional TOC. The TOC value of the Eagle Ford 08 carbonate rock sample measured by the conventional method is 2.0%, and the TOC^+ measured by the new method is as high as 5.09%, indicating that more than half of the organic matter may have been lost during conventional TOC testing.

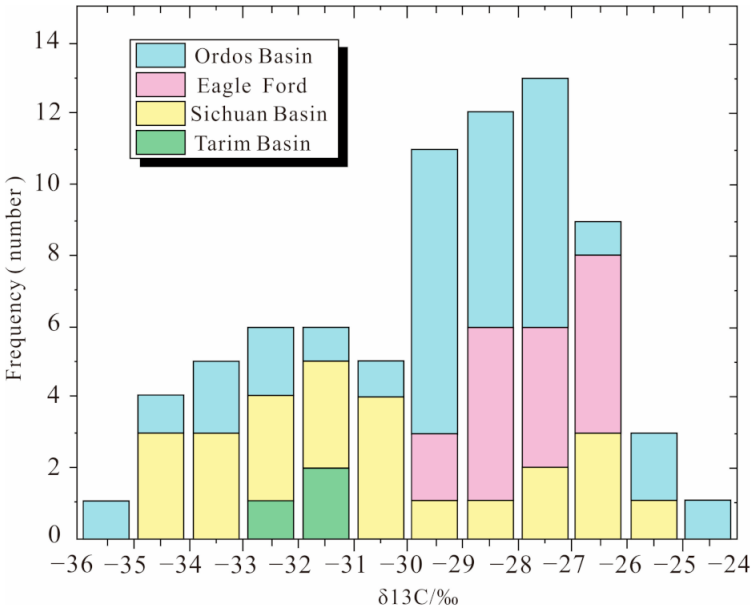


Figure 3. Organic carbon isotopic composition of carbonate source rocks from different regions.

Table 3. Organic-matter abundance and carbon isotope measurements of carbonate rocks of the Xiaoerbulake Formation from the Sugaitbulak Outcrop, Tarim Basin.

Samples	Lithology	Formation	TOC (Conventional)/%	TOC⁺ (New Method)/%	$\delta^{13}C$/‰
Tsgt-3	Oily bituminous limestone	Xiaoerbulake Formation	0.08	0.60	−31.9
Tsgt-4	Shale interlayers	Xiaoerbulake Formation	0.61	1.41	−31.3
Tsgt-5	argillaceous limestone	Xiaoerbulake Formation	0.47	1.18	−32.1

In summary, the loss of acid-soluble organic matter is an important reason for the large errors in conventional organic carbon testing. Carbonate rocks that have experienced high thermal evolution and possess low TOC may also be source rocks; however, owing to the way in which they are formed, their residual TOC is low. The loss of acid-soluble organic matter leads to an underestimation of the hydrocarbon generation potential of highly thermally evolved carbonate source rocks. However, not all marine carbonate rocks with low TOC and high thermal evolution were once effective source rocks. The enrichment and the distribution of acid-soluble organic matter (organic acid salts) in carbonate rocks were controlled by the sedimentary environment, the facies belt, the type and amount of organic matter, and even diagenetic evolution [10].

3.2. Relationship between Acid-Soluble Organic Matter Content and TOC

The organic matter in source rocks from marine hydrocarbon sources in China can be divided into three types: insoluble, soluble, and acid-soluble organic matter [47]. Organic acid salts are an important component of acid-soluble organic matter. Organic acid salts are organic matter formed by the reaction of organic acids and metal ions during geological processes; this matter is preserved in the form of salts in the rock. The main organic acid salt is carboxylate salt, which has a structure compatible with carbonate minerals. This salt can be transported together with carbonate, and it can be coprecipitated in an appropriate environment [48]. Acid-soluble organic matter contains other substances in addition to organic acid salts, such as hydrocarbons, aldehydes, alcohols, ketones, and

other compounds. However, acid-soluble organic matter does not contain exclusively organic acid salts, and many macromolecular organic acid salts are not lost, as they are difficult to dissolve in an acid solution [10].

Sun Minzhuo used chemical methods to extract organic acid salts from carbonate rocks from the Tarim Basin and confirmed the presence of those salts from the characteristic absorption peaks of organic acid salts in infrared spectra. Lei Tianzhu used ether to extract soluble organic matter from the acidolysis solution and, using chromatography, identified organic compounds mainly composed of short-chain fatty acids, alkyl furanones, aromatic acids, and aromatic anhydrides [12,15]. The greatest difference between the new TOC^+ analysis method used in this paper and the traditional method is that the acid-soluble organic matter is included in the detection range, thus avoiding the loss of organic matter in the acid treatment process.

The difference between the new method and conventional TOC can be assessed by means of the relative percentage content of acid-soluble organic matter. Our results show that there is no direct correspondence between the TOC measured by conventional methods and the content of acid-soluble organic matter (Figure 4); the content of acid-soluble organic matter in low-TOC samples is also considerable. Acid-soluble organic matter (organic acid salts) has been suggested to have some potential for hydrocarbon generation, and this has been confirmed by simulation experiments.

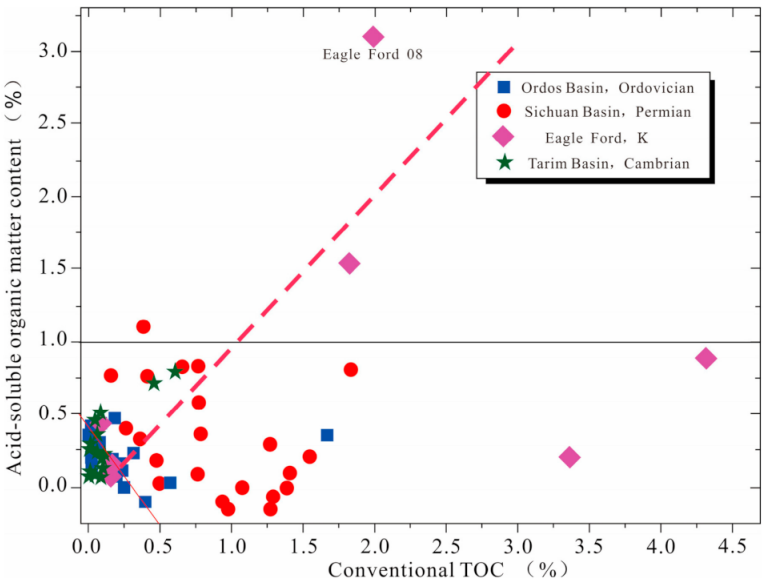


Figure 4. Correlation diagram of acid-soluble organic matter content and TOC of carbonate source rocks in different areas.

Organic acid salts can form hydrocarbons under pyrolysis conditions, and they tend to be stable and without decomposition. These organic acid salts will be released as small molecular hydrocarbons (gas hydrocarbons) in an acidic medium or under abnormal thermal and catalytic action [14,49]. During this process, large amounts of ketone compounds and carbon monoxide will be produced, and the decomposition of the ketones and calcium carbonate will lead to the production of CO_2. Carbon isotope fractionation will result in changes to the carbon isotope characteristics of the CO_2, which can thus be used as an effective indicator of the generation of hydrocarbons from organic acid salts under certain conditions [50,51]. Therefore, organic acid salts can give rise to high-temperature hydrocarbon generation, with large amounts of gas generation in the late stage and a high hydrocarbon generation conversion rate. These salts may be the main hydrocarbon generation material in the high thermal evolution stage of carbonate source rocks, and their hydrocarbon generation potential cannot be ignored [49].

In addition, the acid-soluble organic matter content in most of the samples in this study is less than 1% (Figure 4), a fact that may be related to the maturity, lithology, carbonate mineral content, and sedimentary environment of the rock (see Section 3.3).

The lithology of the first member (p_1m_1) of the Maokou Formation is dark gray to grayish-black limestone, and the color gradually becomes lighter from bottom to top. The rock is often gray-black marl intercalated with carbonaceous shale containing eyelid-eyeball-shaped structures. The TOC^+ results show that the acid-soluble organic matter content of the carbonate rocks of the Permian Maokou Formation in the Sichuan Basin is 0–1.1%, and some samples are rich in acid-soluble organic matter. Excluding samples with negative acid-soluble organic matter content resulting from errors, there is an obvious negative correlation between the acid-soluble organic matter content of the samples and conventional TOC (Figure 5).

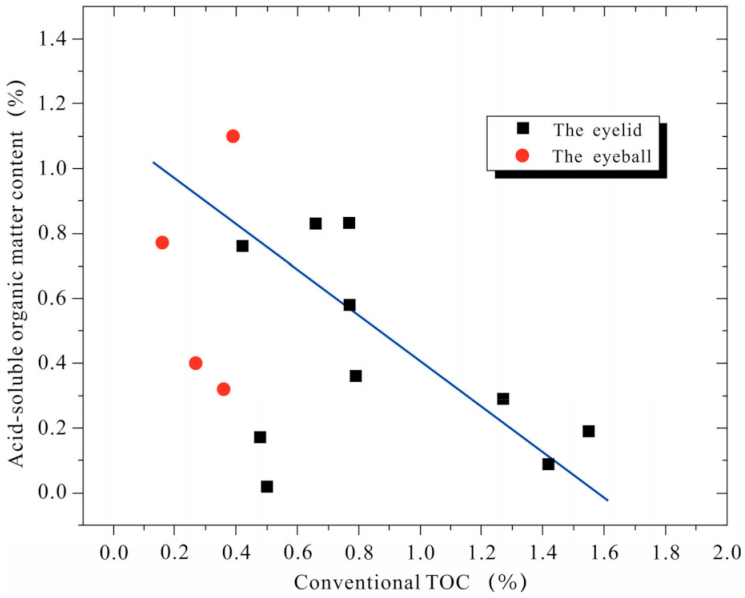


Figure 5. Correlation diagram of acid-soluble organic matter content and TOC in the Permian Maokou Formation, Sichuan Basin.

The "eyeballs" consist predominantly of micritic limestone with a high carbonate mineral content and a low conventional TOC content, corresponding to a relatively high acid-soluble organic matter content. The "eyelids", which have a high clay content, possess high conventional TOC and relatively low acid-soluble organic matter levels; this also confirms that the abundance of acid-soluble organic matter may be related to the content of carbonate minerals. The difference in organic matter content between the eyeball and the eyelid is related to the redox conditions of the sedimentary environment. The eyeballs were formed in a relatively oxidized depositional environment under oxidizing conditions in which organic matter was easily decomposed to form organic acids, becoming preserved in large quantities. These conditions were conducive to the formation of acid-soluble organic matter. The eyelids were formed in a reducing environment in which organic matter was well preserved, and the TOC is therefore relatively high [52–55]. Liu et al. confirmed the existence of organic acid salts in source rocks formed in different sedimentary environments in the Ordos Basin by means of infrared spectroscopy and conducted the quantitative analysis. They also suggested that there might be a negative correlation between the content of organic acid salts in source rocks and the TOC [14].

3.3. Factors Affecting the Abundance of Acid-Soluble Organic Matter

3.3.1. Thermal Evolution

The thermal evolution of carbonate source rocks is important for the evaluation of their hydrocarbon generation potential. The content of acid-soluble organic matter is related to the degree of the thermal evolution of organic matter, i.e., the content of acid-soluble organic matter in the samples from the relatively low-maturity Maokou Formation and the Eagle Ford Formation is relatively high, and the content of acid-soluble organic matter in the samples from the Xiaoerbulake Formation and the Majiagou Formation is relatively low. This difference may be related to the thermal evolution of acid-soluble organic matter, in that acid-soluble organic matter has a high hydrocarbon conversion rate, which is why acid-soluble organic matter is not abundant in highly evolved carbonate rocks, although the carbon isotope composition of the rock will be that of organic carbon. Wang et al. selected calcium stearate as the reactant and evaluated the hydrocarbon generation potential of organic acid salts through thermal simulation experiments [50]. The results showed that the hydrocarbon generation conversion rate of organic acid salts was high, and $CaCO_3$ minerals were produced during the experiment. The average $\delta^{13}C$ value was −24.9‰, indicative of an organic source.

Organic acid salts will form large amounts of ketones in the medium- to low-temperature evolution stage. An analysis of the ketone content of source rocks with different environments and different degrees of evolution demonstrated that there are relatively more organic acid salts in lower-maturity samples [12], confirming that the content of acid-soluble organic matter (organic acid salts) in carbonate rocks is negatively correlated with the degree of the thermal evolution of the organic matter.

3.3.2. Carbonate Minerals

The amount of acid-soluble organic matter as a proportion of the total organic matter in the Eagle Ford samples has an obvious positive correlation with the carbonate content of the rock (Figure 6), similarly to the Maokou Formation. Liu performed acidolysis on samples from the Cretaceous Eagle Ford Formation [56]. The "Rock-Eval" method can be used with temperature-programmed heating and can provide information on the amount of free hydrocarbons (S_1), hydrocarbon generated by thermal cracking (S_2), CO_2 produced during pyrolysis (S_3), and hydrocarbons generated by the oxidation of residual organic carbon (S_4). Pyrolysis analysis of samples that had been treated with acid hydrolysis indicated that the S_1, S_2, S_3, and TOC losses during pyrolysis were positively correlated with the proportion of rock loss during acidolysis, indicating that the organic matter in the acid solution was associated with carbonate minerals. The inorganic components mentioned above may be present on the surface of carbonate minerals in an adsorbed state or may exist as organic acid salts in carbonates.

The form of occurrence of organic acid salts in carbonate minerals is related to the unique diagenesis of carbonate rocks. When carbonate crystals are formed in early diagenesis, they occur in an irregular lattice in the form of twin crystals, resulting in the presence of many crystal cavities between the crystal cages [29]. Organic acid salts and other polar organic substances become trapped in these cavities. The carbonyl groups on organic acid salts cause the salts to have strong polarity, and thus they can be stably preserved in the caveolae of twins by δ-charge attraction. Differences in the pH of sedimentary water bodies, the carbonate crystal lattice, and late diagenesis lead to differently occurring forms of organic acid salts [14].

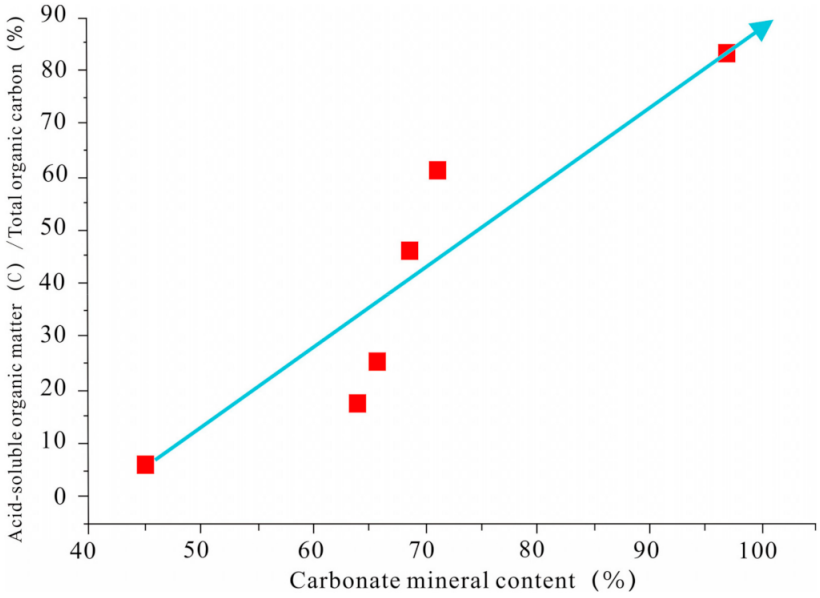


Figure 6. Relationship between carbonate mineral content and TOC loss rate in Eagle Ford samples.

The Eagle Ford Formation contains a high percentage of authigenic carbonate minerals, which are sensitive to temperature and fluid circulation and thus susceptible to dissolution, recrystallization, and metasomatism during inorganic–organic interactions. When the organic matter contained in shale matures, a large amount of organic acid fluid is produced [57]. These fluids promote the growth of calcite, resulting in continuous dissolution and precipitation or recrystallization [58]. If organic acids are abundant in a formation and the environment is alkaline, the rocks with a higher carbonate mineral content may be more favorable for the formation and preservation of organic acid salts, and the loss of acid-soluble organic matter after acid hydrolysis will also be greater. Li Yi analyzed the content of organic acid salts in carbonate rocks in the Xiaoerbulake Formation of the Tarim Basin and found that the content was weakly related to carbonate minerals: the higher the carbonate content, the greater the amount of organic acid salts [59].

3.3.3. Depositional Environment

The sedimentary environment has an important influence on the properties of the original organic matter, and the hydrocarbon generation potential of the original rock depends on the abundance of organic matter and the type of organic facies [60,61]. A carbonate–gypsum sedimentary environment can provide suitable formation conditions for organic acid salts, and organic acid salts are therefore mainly formed in this environment [10].

There are also many examples of the carbonate-evaporite paragenesis system as an important hydrocarbon source rock in China and in other countries [62,63]. The hydrocarbon source of the paste salt formation system is deposited in an environment with normal seawater salinity, and the biological assemblages and hydrocarbon-forming substances are the same as those of conventional marine hydrocarbon source rocks. The main hydrocarbon-forming organisms of marine-quality hydrocarbon source rocks are planktonic algae, benthic organisms, and bacteria [47]. Cyanobacteria and green algae are the dominant high-salinity organisms [64].

The species assemblages that can survive in high-salinity environments are non-diverse compared with those of normal environments and include mainly cyanobacteria, salt-tolerant dinoflagellates, phototrophic sulfur-reducing bacteria, halophilic archaea, halobacteria, and eubacteria; however, these assemblages have strong hydrocarbon generation potential and can provide sufficient high-quality hydrocarbon-generating parent materials for source rocks in gypsum-salt strata [37,64]. The high-quality hydrocarbon-generating substances originally present in gypsum-salt rocks may have undergone a

hydrocarbon-generating transformation during the unit's geological history. Most of the organic carbon is discharged from the source rocks in the form of hydrocarbons, and this leads to low residual TOC [10,40].

The TOC of conventional source rocks in slope facies is low, but organic acid salts can act as a supplement to compensate for the lack of hydrocarbon generation. Therefore, slope-facies sedimentary rocks are relatively rich in organic acid salts [15], but not all carbonate rocks are rich in organic acid salts, and not all organic acids can be converted into organic acid salts and preserved.

The content of acid-soluble organic matter may also be related to the lithology, the organic acid content in the formation, vitrinite reflectance, and other factors. There are many kinds of acid-soluble organic matter, with great differences in their chemical properties. Acid-soluble organic matter is a special type of hydrocarbon-generating parent material [65,66]. Its abundance and its hydrocarbon-generating mechanism are affected by many factors, and its hydrocarbon-generating potential cannot be ignored. The evaluation of the potential of marine carbonate source rocks requires the determination of their hydrocarbon-generating organic matter and a comprehensive analysis of favorable facies zones for the development of acid-soluble organic matter [10]. TOC cannot simply be applied to evaluate carbonate source rock, and lowering the evaluation standard and using a higher organic carbon recovery coefficient is not sufficient to solve the problem of source rock evaluation. The contribution of acid-soluble organic matter (organic acid salt) must be considered during the evaluation of marine carbonate source rocks.

There are still many unsolved problems regarding the hydrocarbon generation mechanism of carbonate rocks, the evaluation and identification of source rocks, and the occurrence and formation conditions of acid-soluble organic matter. The extent to which organic acid salts contribute to the generation of hydrocarbons is unknown; in-depth research will help us to better understand the factors influencing the formation of, and hydrocarbon generation in, carbonate source rocks and will provide guidance for oil and gas exploration of carbonate strata.

4. Conclusions

(1) In this study, the characteristics and significance of acid-soluble organic matter in marine carbonate source rocks are discussed. The problem of low TOC measurements caused by the loss of large amounts of organic matter during traditional TOC pretreatment is solved, and a new idea for the evaluation of marine carbonate source rocks is provided.

(2) For most samples, the TOC^{+} values measured by the new method are higher than the conventional TOC values. The loss of organic matter during conventional TOC testing of some carbonate rock samples from the Eagle Ford Formation accounted for more than half of the total organic matter.

(3) There is no obvious positive correlation between the content of acid-soluble organic matter and TOC. Furthermore, there is a pronounced negative correlation between the content of acid-soluble organic matter of carbonate rocks in the Permian Maokou Formation in the Sichuan Basin and conventional TOC. Additionally, the relative proportion of acid-soluble organic matter to total organic matter has an obvious positive correlation with the mineral content of carbonate rocks.

(4) The content of acid-soluble organic matter is affected by many factors. There is a certain negative correlation between the content of acid-soluble organic matter and the thermal maturity of organic matter, but low-maturity carbonate rocks are not necessarily rich in organic acid salts. The development of acid-soluble organic matter should be considered along with other influencing factors.

Author Contributions: Writing—original draft preparation, review, and editing, D.F.; sample and methodology, X.W., H.L. and P.L.; funding acquisition, W.L., X.W. and D.Z.; investigation, J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Grant No. 41972134) and Major special projects of Changqing Oilfield (ZDZX2021-03).

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: We sincerely appreciate the experimental analysis at the Key Laboratory of Petroleum Resources Research, Institute of Geology and Geophysics, Chinese Academy of Science at Lanzhou. We are grateful for the thoughtful suggestions from Xiaofu Li during the revision of this manuscript.

Conflicts of Interest: The authors declare that they have no conflict of interest.

References

1. Liu, S.G.; Sun, W.; Li, Z.W.; Deng, B.; Zhong, Y.; Song, J.M.; Ran, B.; Luo, Z.L.; Han, K.Y.; Jiang, L.; et al. Distribution characteristics of marine carbonate reservoirs and their tectonic controlling factors across the Sichuan Superimposed Basin. *Lithol. Reserv.* **2016**, *28*, 1–17. [CrossRef]
2. Jin, Z.J. Particularity of petroleum exploration on marine carbonate strata in China sedimentary basins. *Earth Sci. Front.* **2005**, *12*, 15–22. [CrossRef]
3. Yang, Z.; Zhang, G.X.; Wu, S.G.; Zhu, Y.H.; Wu, C.; Zhang, L.; Liu, S.F.; Yan, W.; Sun, M.; Zhang, Y.M.; et al. Geological distribution of the Miocene carbonate platform in the Xisha Sea area of the South China Sea, and its implications for hydrocarbon exploration. *Appl. Sci.* **2022**, *12*, 11831. [CrossRef]
4. Zhao, W.Z.; Wang, Z.C.; Zhang, S.C.; Wang, H.J. Accumulation conditions and enrichment zones of deep marine oil and gas in superimposed basins of China. *Chin. Sci. Bull.* **2007**, *52*, 9–18. [CrossRef]
5. Geng, X.H.; Geng, A.S.; Xiong, Y.Q. Review on the evaluation of lower Paleozoic carbonate source rocks in China. *Bull. Mineral. Petrol. Geochem.* **2004**, *23*, 344–349. [CrossRef]
6. Zhao, W.Z.; Hu, S.Y.; Liu, W.; Wang, T.S.; Li, Y.X. Petroleum geological features and exploration propect in deep marine carbonate strata onshore China: A further discussion. *Nat. Gas Ind.* **2014**, *34*, 14–23. [CrossRef]
7. He, Z.L.; Jin, X.H.; Wo, Y.J.; Li, H.L.; Bai, Z.R.; Jiao, C.L.; Zhang, Z.P. Hydrocarbon accumulation characteristics and exploration domains of ultra-deep marine carbonates in China. *China Pet. Explor.* **2016**, *21*, 3–14. [CrossRef]
8. Zhao, W.Z.; Wang, Z.Y.; He, H.Q.; Zhang, M.J.; Wang, H.J.; Wang, Y.P.; Qin, Y. Gas formation mechanism of marine carbonate source rocks in China. *Sci. China Ser. D Earth Sci.* **2005**, *35*, 638–648. [CrossRef]
9. Huang, J.Z.; Lü, Z.G. How to judge carbonate rock as source rock: A case of Sichuan Basin. *Mar. Orig. Pet. Geol.* **2011**, *16*, 8–14. [CrossRef]
10. Liu, W.H.; Borjigin, T.; Wang, X.F.; Li, M.W.; Hu, G.; Wang, J.; Lu, L.F.; Zhao, H.; Chen, Q.L.; Luo, H.Y. New knowledge of hydrocarbon generating theory of organic matter in Chinese marine carbonates. *Pet. Explor. Dev.* **2017**, *44*, 159–169. [CrossRef]
11. Huo, Z.P.; Pang, X.Q.; Zhang, B.S.; Chen, J.F.; Fan, B.J.; Li, S.M. Evidences on effective carbonate source rock of low organic matter abundance and its lower limit of TOC. *Geol. Rev.* **2013**, *59*, 1165–1176. [CrossRef]
12. Lei, T.Z.; Xia, Y.Q.; Qiu, J.L.; Jin, M.; Meng, Q.X.; Fang, L.H. Organic matter loss during the acidolysis of hydrocarbon source rock. *Nat. Gas Geosci.* **2009**, *20*, 957–960. [CrossRef]
13. Liu, P.; Wang, X.F.; Fang, X.; Zheng, J.J.; Li, X.F.; Meng, Q. A new method to measure the value of organic abundance in carbonate rocks. *Acta Sedimentol. Sin.* **2016**, *34*, 200–206. [CrossRef]
14. Liu, Q.Y.; Jin, Z.J.; Liu, W.H.; Lu, L.F.; Meng, Q.X.; Tao, Y.; Han, P.L. Presence of carboxylate salts in marine carbonate strata of the Ordos Basin and their impact on hydrocarbon generation evaluation of low TOC, high maturity source rocks. *Sci. China Ser. D Earth Sci.* **2013**, *56*, 2141–2149. [CrossRef]
15. Sun, M.Z.; Meng, Q.X.; Zheng, J.J.; Wang, G.C.; Fang, X.; Wang, Z.D. Analysis of organic acid salts of marine carbonate rocks in Tarim Basin. *J. Cent. South Univ.* **2013**, *44*, 216–222. [CrossRef]
16. Zhou, Z.Y.; Jia, R.F. Organic geochemical and petrological characteristics of carbonate rocks as a source rock for petroleum. *Geochimica* **1974**, *4*, 278–298. [CrossRef]
17. Fu, J.M.; Shi, J.Y. Theory and practice of petroleum evolution(II)—The practical model of petroleum evolution and its significance. *Geochimica* **1977**, *2*, 87–104. [CrossRef]
18. Chen, P.J. Comment on several topics in the geochemistry carbonate source rock. *Exp. Pet. Geol.* **1985**, *7*, 3–12. [CrossRef]
19. Hunt, J.M. The Origin of Petroleum in Carbonate Rocks. In *Developments in Sedimentology*; Elsevier: Amsterdam, The Netherlands, 1967; Volume 9, pp. 225–251. [CrossRef]
20. Liu, B.Q.; Liang, D.G.; Fang, J.; Jia, R.F.; Fu, J.M. Organic matter maturity and oil/gas prospects in middle-upper Proterozoic and lower Paleozoic carbonate rocks in northern China. *Chin. J. Geochim.* **1986**, *1*, 55–70. [CrossRef]
21. Palacas, J.G. Petroleum in carbonate rocks. In *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*; American Association of Petroleum Geologists: Tulsa, OK, USA, 1984; pp. 1–208. [CrossRef]
22. Tissot, B.P.; Welte, D.H. *Petroleum Formation and Occurrence*; Springer: Berlin/Heidelberg, Germany, 1984. [CrossRef]

23. Hao, S.S.; Jia, Z.Y. *Hydrocarbon Formation and Distribution in Carbonate Rocks*; Petroleum Industry Press: Beijing, China, 1989. Available online: https://xueshu.baidu.com/usercenter/paper/show?paperid=2cc08aed7272fc122a779fa762eb1e0e&site=xueshu_se (accessed on 3 March 2022).
24. Liang, D.G.; Zhang, S.C.; Zhang, B.M.; Wang, F.Y. Understanding on marine oil generation in China based on Tarim Basin. *Earth Sci. Front.* **2000**, *7*, 534–547. [CrossRef]
25. Xia, X.Y.; Dai, J.X. A critical review on the evaluation of hydrocarbon potential of marine carbonate rocks in China. *Acta Pet. Sin.* **2000**, *21*, 36–41. [CrossRef]
26. Peng, P.A.; Liu, D.Y.; Qin, Y.; Yu, C.L.; Zhang, S.W.; Sui, F.G.; Li, J.Y. Low limits of organic carbon in carbonate as oil and gas source socks. *Geochimica* **2008**, *37*, 415–442. [CrossRef]
27. Deaf, A.S.; El-Soughier, M.I.; Gentzis, T.; Makled, W.A. Hydrocarbon source rock potential of the lower Eocene carbonates from the Abu Darag sub-basin, Gulf of Suez, Egypt: Integrated organic geochemical and petrographic analyses. *Mar. Pet. Geol.* **2021**, *132*, 105235. [CrossRef]
28. Rashid, A.; Siddiqui, N.A.; Bavoh, C.B.; Haque, A.E.; Usman, M.; Kasim, S.A.; ElGhali, M.A.K.; Ridha, S. Organic matter distribution and characteristics among rock formations in Malaysia: Implications on hydrocarbon generation potential. *Appl. Sci.* **2022**, *12*, 9470. [CrossRef]
29. Hu, S.Q.; Zhang, H.W.; Zhang, R.J.; Jin, L.X.; Liu, Y.M. Quantitative interpretation of TOC in complicated lithology based on well log data: A case of Majiagou Formation in the Eastern Ordos Basin. *China Appl. Sci.* **2021**, *11*, 8724. [CrossRef]
30. Fu, J.M.; Jia, R.F. Main forms of disseminated organic matter in carbonate rocks, their evolutionary characteristics and significance in oil-gas evaluation. *Geochimica* **1984**, *1*, 1–9+105. [CrossRef]
31. Zhou, Z.Y.; Ye, J.S.; Sheng, G.Y.; Jia, R.F. Organic matter enclosed in carbonate minerals and its implication in petroleum generation. *Geochimica* **1983**, *3*, 276–284. [CrossRef]
32. Zhang, S.C.; Tong, Z.Y. The composition and hydrocarbon-generation evolution of organic matter associated with carbonate minerals. *Acta Sedimentol. Sin.* **1992**, *10*, 76–82. [CrossRef]
33. Wang, Z.Y.; Cheng, K.M. The hydrocarbon generation mechanism and the three-stage type model of hydrocarbon generation for carbonate source rocks. *Sci. China Ser. D: Earth Sci.* **1997**, *3*, 60–64. [CrossRef]
34. Xie, Q.L.; Zhou, Z.Y.; Lu, M.Y. Organic matter enclosed in carbonate minerals—A kind of important hydrocarbon-producing matter. *Acta Mineral. Sin.* **2000**, *20*, 59–62. [CrossRef]
35. Zeng, F.G. A study on hydrocarbon-generating mechanism and model for lower Palaeozoic marine carbonate rocks. *Geol. Geochem.* **1998**, *26*, 79–84. Available online: http://qikan.cqvip.com/Qikan/Article/Detail?id=3212361 (accessed on 9 September 2021).
36. Qin, S.F.; Qin, Y.; Zhong, N.N. Classification on occurrence of organic matter in carbonate rocks. *Pet. Explor. Dev.* **1996**, *23*, 23–27. [CrossRef]
37. Liu, W.H.; Hu, G.; Tenger; Wang, J.; Lu, L.F.; Xie, X.M. Organism assemblages in the Paleozoic source rocks and their implications. *Oil Gas Geol.* **2016**, *37*, 617–626. [CrossRef]
38. Zhao, H.; Liu, W.H.; Li, Y.J.; Liu, Q.Y.; Zhou, B.; Luo, H.Y.; Wang, J.; Lu, L.F.; Meng, Q.Q.; Wu, X.Q. A preliminary study on hydrocarbon generation and evaluation of marine gypsum/salt-bearing source rocks. *Mar. Orig. Pet. Geol.* **2019**, *24*, 3. [CrossRef]
39. Roberts, A.A.; Palacas, J.G.; Frost, I.C. Determination of organic carbon in modern carbonate sediments. *J. Sediment. Petrol.* **1973**, *43*, 1157–1159. [CrossRef]
40. Chong, S.-L.; Mckay, J.F. Extractable metal salts of carboxylic acids in Green River oil shale. *Fuel* **1984**, *63*, 303–309. [CrossRef]
41. Vandegrift, G.F.; Winans, R.E.; Scott, R.G.; Horwitz, E.P. Quantitative study of the carboxylic acids in Green River oil shale bitumen. *Fuel* **1980**, *59*, 627–633. [CrossRef]
42. Ren, D.C. *The Natural Gas Resources Potential Evaluate of the Middle Majiagou Formation in the East Side of the Ordos Basin*; Chengdu University of Technology: Chengdu, China, 2017. Available online: https://www.zhangqiaokeyan.com/academic-degree-domestic_mphd_thesis/020314349881.html (accessed on 6 June 2022).
43. Zhang, P.X.; He, X.P.; Gao, Q.F.; Gao, Y.Q.; Sun, B.; Cai, X.; He, G.S.; Zhang, Z.P.; Liu, N.N. Geological characteristics and enrichment pattern of Permian Mao 1 Member shale gas reservoirs at the southeastern margin of Sichuan Basin. *Oil Gas Geol.* **2021**, *42*, 146–157. [CrossRef]
44. Wang, Z.X.; Lü, X.X.; Qian, W.W. Geochemical characteristica of the Cambrian marine carbonate elements and its petroleum geological significance: Case study of Xiaoerbulake Formation in Keping area of Tarim Basin. *Nat. Gas Geosci.* **2017**, *28*, 1085–1095. [CrossRef]
45. Gao, H.; He, M.Q.; Zhao, P.Y.; Dou, L.B.; Wang, C. Comparison of geological characteristics of Chang 7 shale oil in Ordos Basin and typical shale oil in North America. *Exp. Pet. Geol.* **2018**, *40*, 133–140. [CrossRef]
46. Lei, S.M.; Hao, Q.; Xiong, B.H.; Zeng, X.B. Characteristics of montmorillonite and its application prospect. *Resour. Environ. Eng.* **2006**, *20*, 565–569. [CrossRef]
47. Liu, W.H.; Wang, J.; Tenger; Qin, J.Z.; Rao, D.; Tao, C.; Lu, L.F. Multiple hydrocarbon generation of marine strata and its tracer technique in China. *Acta Pet. Sin.* **2012**, *33*, 115–125. [CrossRef]
48. Wu, T.H.; Guan, P.; Liu, W.H. Organic acid salt as the possible hydrocarbon source matter in carbonate rocks. *Nat. Gas Ind.* **2005**, *25*, 11–13. [CrossRef]
49. Zhou, S.X.; Xia, Y.Q.; Luo, B.J.; Cheng, X.H.; Cui, M.Z.; Li, Y.; Wang, C.J. Study on laboratory simulation of the hydrocarbon formation from salts of fatty acids. *Acta Sedimentol. Sin.* **1997**, *15*, 118–121. [CrossRef]

50. Wang, Q.T.; Liu, W.H.; Pei, L.X.; Cai, Z.H.; Luo, H.Y.; Wang, X.F.; Zhang, D.D.; Liu, J.Z. Hydrocarbon generation from calcium stearate: Insights from closed-system pyrolysis. *Mar. Pet. Geol.* **2021**, *126*, 104923. [CrossRef]
51. Lei, T.Z.; Xia, Y.Q.; Jin, M.; Qiu, J.L.; Liu, Z.Y.; Fang, L.H. The geological significance and characteristics of aromatic fraction during organic acid salt generating hydrocarbon. *Acta Sedimentol. Sin.* **2010**, *28*, 1250–1253. [CrossRef]
52. Lei, H. Genesis and reservoir microscopic characteristics of Eyelid-Eyeball-Shaped limestone in the 1st member of Maokou Formation, Sichuan Basin. *China Univ. Geosci.* **2021**, *4*. [CrossRef]
53. Zhang, Y.; Cao, Q.G.; Luo, K.P.; Li, L.L.; Liu, J.L. Reservoir exploration of the Permian Maokou Formation in the Sichuan Basin and enlightenment obtained. *Oil Gas Geol.* **2022**, *43*, 610–620. [CrossRef]
54. Gao, G.H.; Cao, J.; Luo, B.; Xiao, D.; Zhang, Y.; Chen, C. Evidence of the middle Permian marine mixed type source rocks in the northwestern Sichuan Basin and its contribution to large gas reservoirs in Shuangyushi area. *Acta Pet. Sin.* **2020**, *41*, 433–445. [CrossRef]
55. Hu, D.F.; Wang, L.J.; Zhang, H.R.; Duan, J.B.; Xia, W.Q.; Liu, Z.J.; Wei, Q.C.; Wang, K.; Pan, L. Discovery of carbonate source rock gas reservoir and its petroleum geological implications: A case study of the gas reservoir in the first Member of Middle Permian Maokou Formation in the Fuling area, Sichuan Basin. *Nat. Gas Ind.* **2020**, *40*, 23–33. [CrossRef]
56. Liu, P.; Wang, X.F.; Li, X.F.; Zhang, T.; Liu, W.H. Geochemical characteristics of released organic matters by acid decomposition of hydrocarbon source rocks from different sedimentary basins. *Geofluids* **2019**, *2019*, 4816218. [CrossRef]
57. Liang, C.; Cao, Y.C.; Liu, K.Y.; Jiang, Z.X.; Wu, J.; Hao, F. Diagenetic variation at the lamina scale in lacustrine organic-rich shales: Implications for hydrocarbon migration and accumulation. *Geochem. Cosmochim. Acta.* **2018**, *229*, 112–128. [CrossRef]
58. Yahaira, G.-B.A.; Eduardo, G.-P.; Alejandro, C.-C.; Josué, E.-C.J. Diagenetic studies of the Eagle Ford and Indidura Formations in the Sabinas basin: Implications for source rock maturation. *J. S. Am. Earth Sci.* **2022**, *120*, 104092. [CrossRef]
59. Li, Y. Analysis of hydrocarbon generation petential of marine carbonate in the upper Sinian-lower Cambrian strata in Aksu area, Tarim Basin. *China Univ. Geosci.* **2021**, *12*. [CrossRef]
60. Gao, J.J.; Li, M.Z.; Hu, T.L.; Ge, B.X. Hydrocarbon generation potential of carbonate rocks in shallow platform. *Oil Gas Geol.* **1996**, *17*, 128–133. [CrossRef]
61. Xia, X.Y.; Hong, F.; Zhao, L.; Zhang, W.Z. Organic facies type and hydrocarbon potential of carbonates in Majiagou lower Ordovician in Ordos Basin. *Acta Sedimentol. Sin.* **1999**, *4*, 638–643+650. [CrossRef]
62. Edgell, H.S. Proterozoic salt basins of the Persian Gulf area and their role in hydrocarbon generation. *Precambrian Res.* **1991**, *54*, 1–14. [CrossRef]
63. Tänavsuu-Milkeviciene, K.; Sarg, J.F. Evolution of an organic-rich lake basin—Stratigraphy, climate and tectonics: Piceance Creek basin, Eocene Green River Formation. *Sedimentology* **2012**, *59*, 1735–1768. [CrossRef]
64. Gocke, K. Seasonal variations of bacterial abundance and biomass and their relation to phytoplankton in the hypertrophic tropical lagoon Cienaga Grande de Santa Marta, Colombia. *J. Plankton Res.* **2004**, *26*, 1429–1439. [CrossRef]
65. Wang, X.F.; Feng, D.T.; Liu, W.H.; Bao, H.P.; Zhang, D.D.; Wei, L.B.; Luo, H.Y.; Li, Y.N. Hydrocarbon generation characteristics and evaluation methods of highly maturity carbonate source rocks. *J. Northwest. Teach. Univ. Nat. Sci.* **2022**, *52*, 954–967. [CrossRef]
66. Carothers, W.W.; Kharaka, Y.K. Aliphatic acid anions in oil-field waters; implications for origin of natural gas. *Am. Assoc. Pet. Geol. Bull.* **1978**, *62*, 2441–2453. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.