Contents lists available at ScienceDirect

Arabian Journal of Chemistry

journal homepage: www.ksu.edu.sa

Review article

Geochemical characteristics of the shale gas reservoirs in Guizhou Province, South China

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ARTICLE INFO

Keywords:
Shale gas
Organic-rich shale
Organic matter
Marine shale
Marine-continental transitional shale
South China

ABSTRACT

We analyzed a large amount of published petrological, mineralogical, and geochemical data from the Niutitang, Wufeng-Longmaxi, Dawuba, Liangshan, and Longtan organic-rich shales. These include marine shales and marine-continental transitional shales. The main marine organic-rich shales include the Niutitang, Wufeng-Longmaxi, and Dawuba shales, while the main marine-continental organic-rich transitional shales include the Liangshan and Longtan shales. The marine organic-rich shales were generally deposited under anoxic conditions, and are generally brittle siliceous-rich lithofacies, which is a type I organic-matter dominated. In contrast to the marine organic-rich shales, the marine-continental transitional organic-rich shales were most likely deposited under dysoxic to oxic conditions. They are generally less brittle argillaceous-rich lithofacies, that are type III organic-matter dominated. Of the five organic-rich shales, the Niutitang and Wufeng-Longmaxi organic-rich shales are over-mature shales, and the Dawuba, Liangshan, and Longtan organic-rich shales are high-maturity to over-mature shales. The spots with siliceous rock floor on the western edge of the Xuefeng uplift is a favorable area for future exploration of shale gas in the Niutitang organic-rich shale. The Chishui terrestrial basin and center of the aulacogen are the faverable areaa for shale gas expolation and development of the Wufeng-Longmaxi and Dawuba organic-rich shales, respectively. More basic geological research work is needed to select favorable areas for the Liangshan and Longtan organic-rich shales. To accurately guide future shale gas exploration and development, more research is needed on the relationship between the sedimentary environment, the lithofacies, and the reservoir properties of the shales.

1. Introduction

In recent years, Chin's annual natural gas imports have consistently exceeded 40 % of its consumption, indicating a high degree of external dependency. From 2012 to 2022, China's shale gas production increased from 0.03 to 24.00 billion cubic meters, with its share in natural gas production exceeding 10 % for three consecutive years (https://www.nea.gov.cn/). China has achieved significant success in the exploration and development of shale gas, becoming the world's second-largest producer of shale gas (Long et al., 2021), and shale gas in China primarily produced from the Sichuan Basin. However, it still falls short of meeting societal demands (Zou et al., 2022). Currently, shale gas exploration is expanding to the deep and ultra-deep shale gas reservoirs within the Sichuan Basin and to the peripheral regions, marking a pivotal period of significant breakthroughs. The peripheral regions have become important substitutes for increasing shale gas resource and production (Zhang et al., 2021a; Zhang et al., 2021b; Zou et al., 2021; Guo et al., 2022; Hu et al., 2022).

Guizhou Province is located in South China (Fig. 1a), and has been divided into 13 tectonic zones according to its complicated tectonic evolution (Fig. 1b). The Chishui craton basin zone belongs to the Sichuan Basin, while the remaining 12 tectonic units are all located on the periphery of the Sichuan Basin (Guizhou Geological Survey, 2017). The sedimentary strata of Guizhou Province are well-developed,

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https://doi.org/10.1016/j.arabjc.2024.105616
Received 22 October 2023; Accepted 8 January 2024
Available online 11 January 2024

encompassing formations from the Neoproterozoic to the Quaternary, with a cumulative sedimentary thickness reaching tens of thousands of meters (Guizhou Geological Survey, 2017). In these sedimentary rock formations, there are multiple sets of organic-rich shales with significant exploration potential, including both marine shale and marine-continental transitional shale (Fig. 2). Preliminary surveys and evaluations conducted from 2012 to 2013 revealed the substantial shale gas resources in Guizhou Province (Qin et al., 2012; Zhang, 2012; Yi and Zhao, 2014; Geng et al., 2018; Zhu et al., 2019; Zhao et al., 2022). Guizhou Province ranked third among the 34 Provincial-level Administrative Regions in China, based on shale gas resources data from the Ministry of Natural Resources of the People's Republic of China (https://www.mnr.gov.cn). Subsequently, many geologists and engineers focused on shale gas exploration and development in this region (Wei et al., 2012; Sun et al., 2017; Zhang et al., 2016; Wu et al., 2017; Xia et al., 2018, 2020, 2021a, 2021b; Sun et al., 2019, 2021; Zhu et al., 2019; Li, 2020; Han et al., 2021; Zhao et al., 2021; Lan et al., 2022). However, the productivity of shale gas is still unsatisfactory. Compared to the Sichuan Basin, the sedimentary setting, developmental characteristics, and reservoir properties of organic-rich shale in Guizhou Province exhibit significant differences. The distribution of sedimentary strata is therefore highly heterogeneous in Guizhou Province, and contemporaneous heterotopic facies are common among organic-rich shales (Fig. 2, Guizhou Geological Survey, 2017; Fu et al., 2021; Xia et al., 2022). The characteristics of the minerals, lithofacies, and organic matter are also various among different organic-rich shales, and these varieties significantly affect the enrichment and recoverability of the shale gas. Thus, summarizing the distribution of the organic-rich shales, and characterizing their reservoir properties and exploration prospects, is therefore important.

This review considers the large volume of published petrological, mineralogical, and geochemical data, including data from the Lower Cambrian Niutitang, Ordovician-Silurian Wufeng-Longmaxi, Lower Carboniferous Dawuba, Lower Permian Liangshan, and Upper Permian Longtan organic-rich shales in Guizhou Province. The review also considers some experimental results to identify the differences between the different organic-rich shales. This study improves the understanding of the shale gas reservoirs and their properties in Guizhou Province, and can serve as a reference for shale gas evaluation in this province and other peripheral regions of the Sichuan Basin.

2. Organic-rich shales in Guizhou Province

The organic-rich shales in Guizhou Province occur in the Lower Ediacaran Doushantuo Formation, the Upper Ediacaran Laobao Formation, the Lower Cambrian Niutitang Formation (also called the Jiumenchong Formation or the Zhalagou Formation in Southeast Guizhou, and the Qiongzhusi Formation in Northwest Guizhou), the Ordovician-Silurian Wufeng-Longmaxi Formation, the Lower Carboniferous Dawuba Formation (which is also called the Xiangbai Formation in some regions), the Middle Carboniferous Jiusi Formation, the Lower Permian Liangshan Formation, and the Upper Permian Longtan Formation

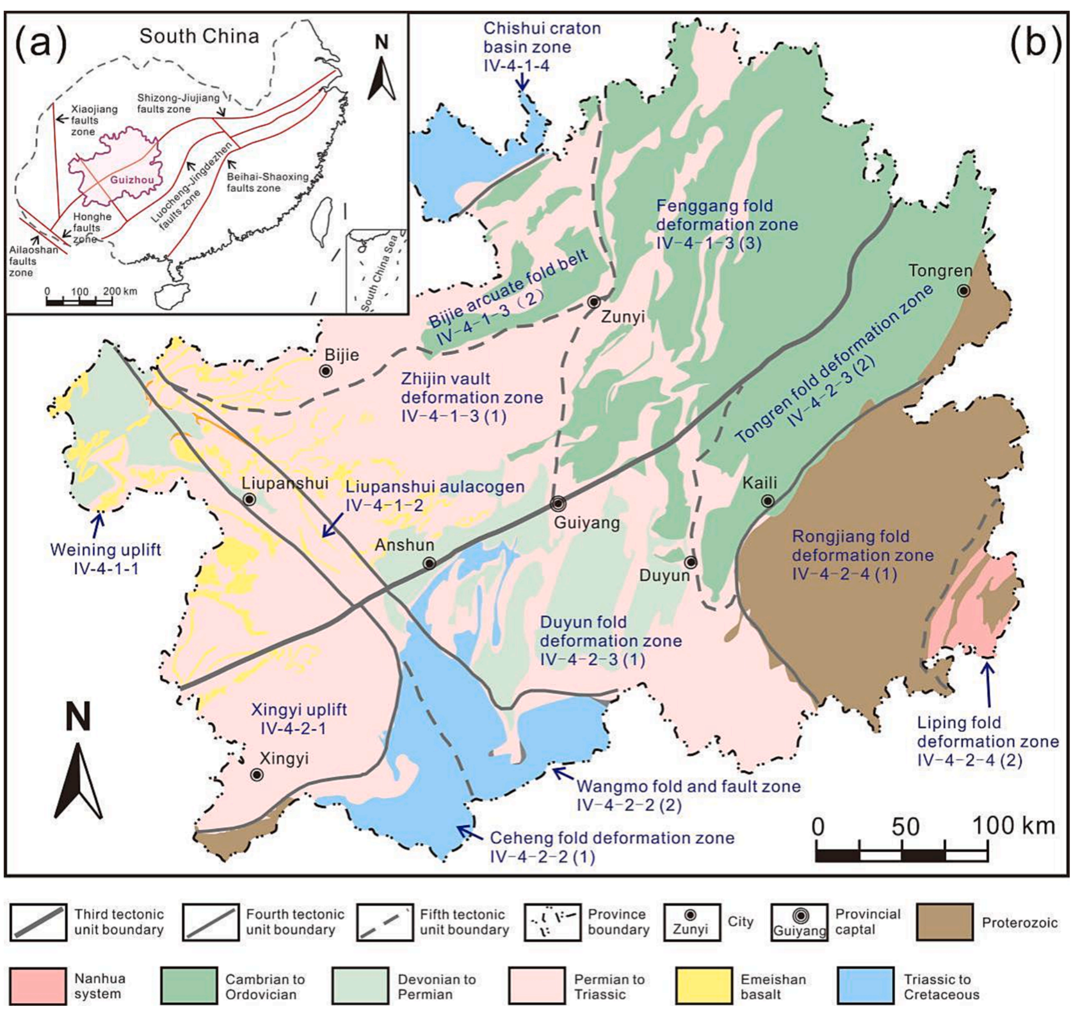

Fig. 1. Geological setting. a) The location of Guizhou Province in South China (after Guizhou Geological Survey, 2017), and b) The geological map of Guizhou Province showing its tectonic zones.

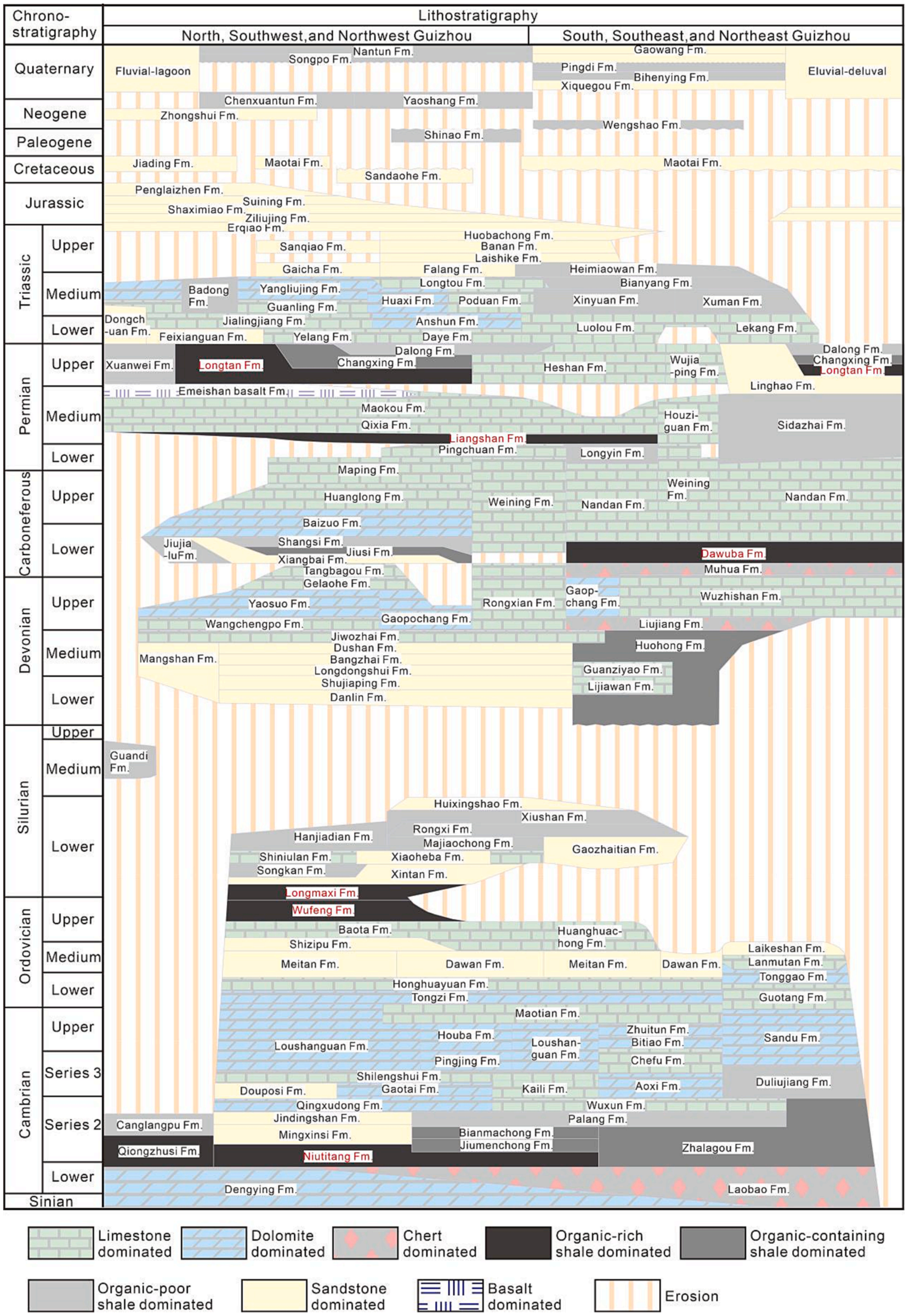

Fig. 2. Lithostratigraphic correlation chart of the strata from the Sinian to the Quaternary in Guizhou Province, showing the Niutitang, Wufeng-Longmaxi, Dawuba, Liangshan, and Longtan organic-rich shales (after Guizhou Geological Survey, 2017). Fm is Formation.

(Fig. 2). Of these organic-rich shales, the Niutitang, the Wufeng-Longmaxi, the Dawuba, the Liangshan, and the Longtan organic-rich shales are the main shale gas targets, see Fig. 2 (Cao et al., 2018; Zhu et al., 2019; Li, 2020; Han et al., 2021; Lu et al., 2021; Xia et al., 2021a; Zhao et al., 2021; Zou et al., 2021).

The Niutitang Formation unconformably overlies the dolomite of the Ediacaran Dengying Formation and conformably overlies the chert of the Ediacaran Laobao Formation (Fig. 2), while the Dengying and Laobao Formations are heterotopic deposits (Dai et al., 2013; Fu et al., 2016; Xia et al., 2022; Yang et al., 2022). The Niutitang Formation is overlain by the Canglangpu, Mingxinsi, Bianmachong, and Palang Formations. The Niutitang Formation's burial depth ranges from 0 to 9900 m while its thickness ranges from 0 to 900 m. The burial depth of the Niutitang Formation increases from east to west in Guizhou Province and does not occur in the southeastern part of Guizhou Province (which includes the Tianzhu, Jianhe, Jingping, Liping, Rongjiang, and Congjiang counties), see Fig. 3a.

The Wufeng-Longmaxi Formation conformably overlies the Baota Formation and is overlain by the Xintan Formation. The formation occurs in the northern parts of Guizhou Province, with a thickness ranging from 0 to 80 m. The Qianbei and Wuling depressions control the distribution and thickness of this formation (Guizhou Geological Survey, 2017). The burial depth of the Wufeng-Longmaxi Formation increases from east to west of North Guizhou, with its maximum burial depth being located in Chishui County (Fig. 3b).

The Dawuba Formation is conformably overlain by the Nandan, Weining, and Shanxi Formations, and it conformably overlies the Tangbagou and Muhua Formations (Fig. 2). This formation occurs only in Southwest Guizhou and not in the other regions in Guizhou Province (Fig. 3c). The maximum thickness of the Dawuba Formation reaches

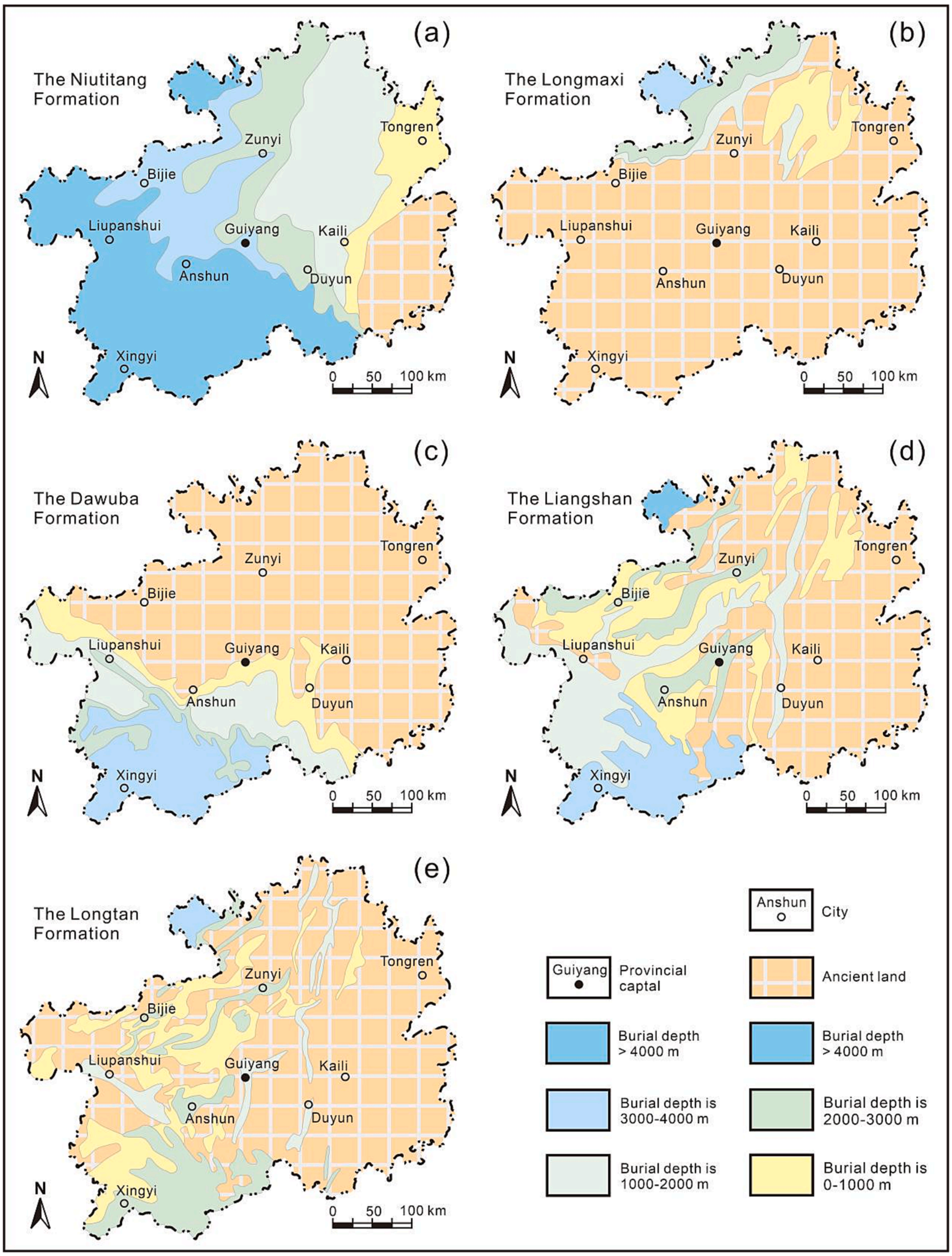

Fig. 3. Burial depth of the shale gas exploration and development target formations (after Zhu et al., 2019). a) The Niutitang Formation, b) the Wufeng-Longmaxi Formation, c) the Dawuba Formation, d) the Liangshan Formation and e) the Longtan Formation.

550 m in the Weining and Luodian counties (Lu et al., 2019). Its burial depth, which ranges from 0 to 3500 m, increases from northeast to southwest in Southwestern Guizhou (Zhu et al., 2019). The maximum burial depth of the Dawuba Formation is located in the core of the Luodian syncline.

The Liangshan Formation unconformably overlies the Pingchuan and Longyin Formations, and it is conformably overlain by the Qixia Formation. The Liangshan Formation occurs in West Guizhou and South Guizhou, with a thickness ranging from 0 to 860 m (Xiao et al., 2021). The maximum thickness of the Liangshan Formation is also located in the Luodian syncline, similar to the Dawuba Formation (Fig. 3d). Its burial depth exceeds 4000 m in the Chishui, Luodian, and Xingyi counties.

The coal-bearing Longtan Formation unconformably overlies the Emeishan basalt Formation and the Maokou Formation (Zhu et al., 2019; Zhao et al., 2021). It mainly occurs in West Guizhou and Northwest Guizhou, with its thickness ranging between 170 and 360 m (Ma, 2017). The burial depth of the Longtan Formation is generally shallower

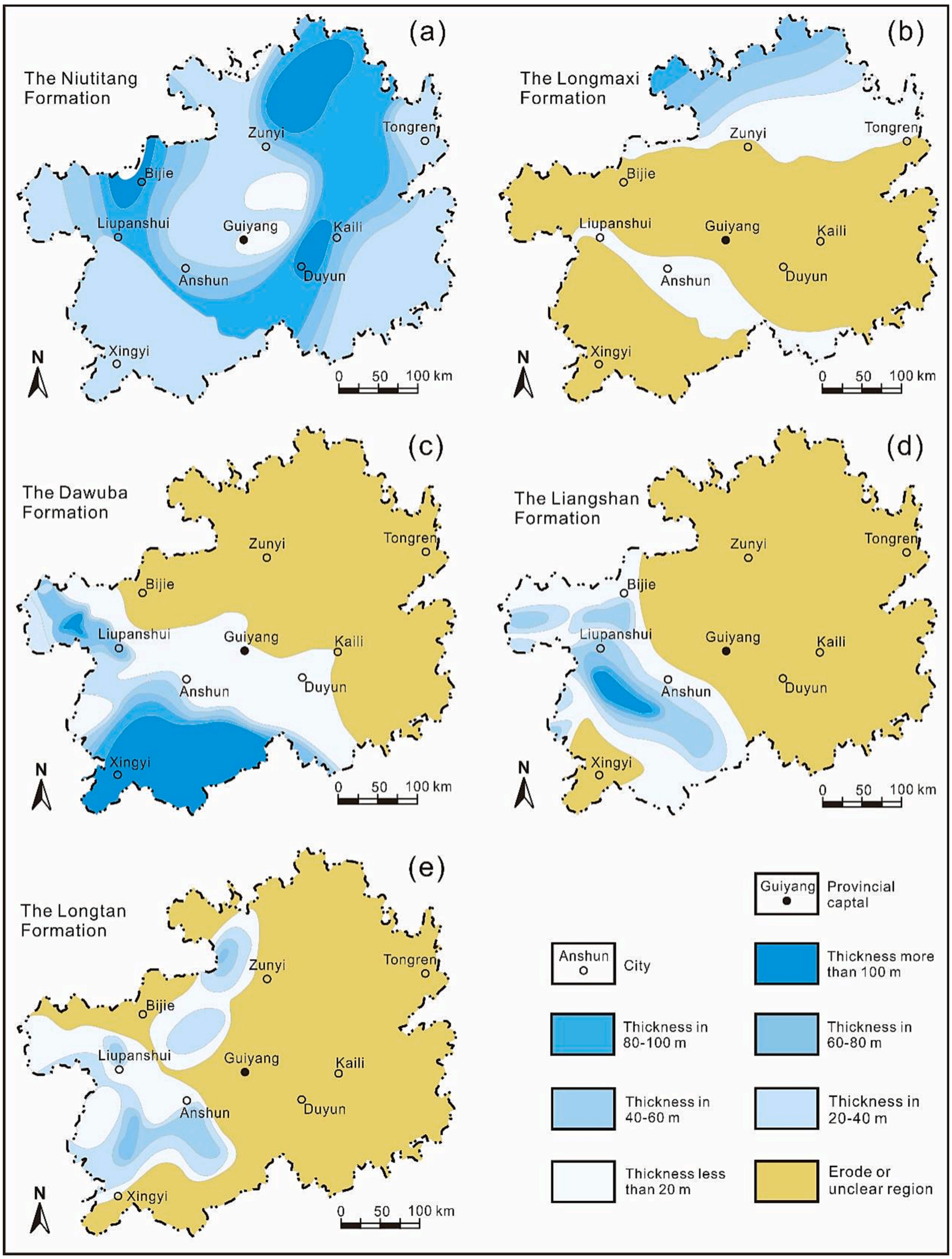

Fig. 4. Distribution of organic-rich shales in Guizhou Province. a) The Niutitang organic-rich shale, b) the Wufeng-Longmaxi organic-rich shale, c) the Dawuba organic-rich shale, d) the Liangshan organic-rich shale and e) the Longtan organic-rich shale.

than 2000 m. In Northeast Guizhou, its burial depth mainly ranges from 0 to 1000 m and ranges from 0 to 2000 m in Southwest Guizhou (Fig. 3e).

3. Distribution of the organic-rich shales

The organic-rich shale of the Niutitang Formation is located in the lower part of the formation (Xia et al., 2018; Xia et al., 2022), with a thickness ranging from 20 to 120 m. This organic-rich shale occurs in the

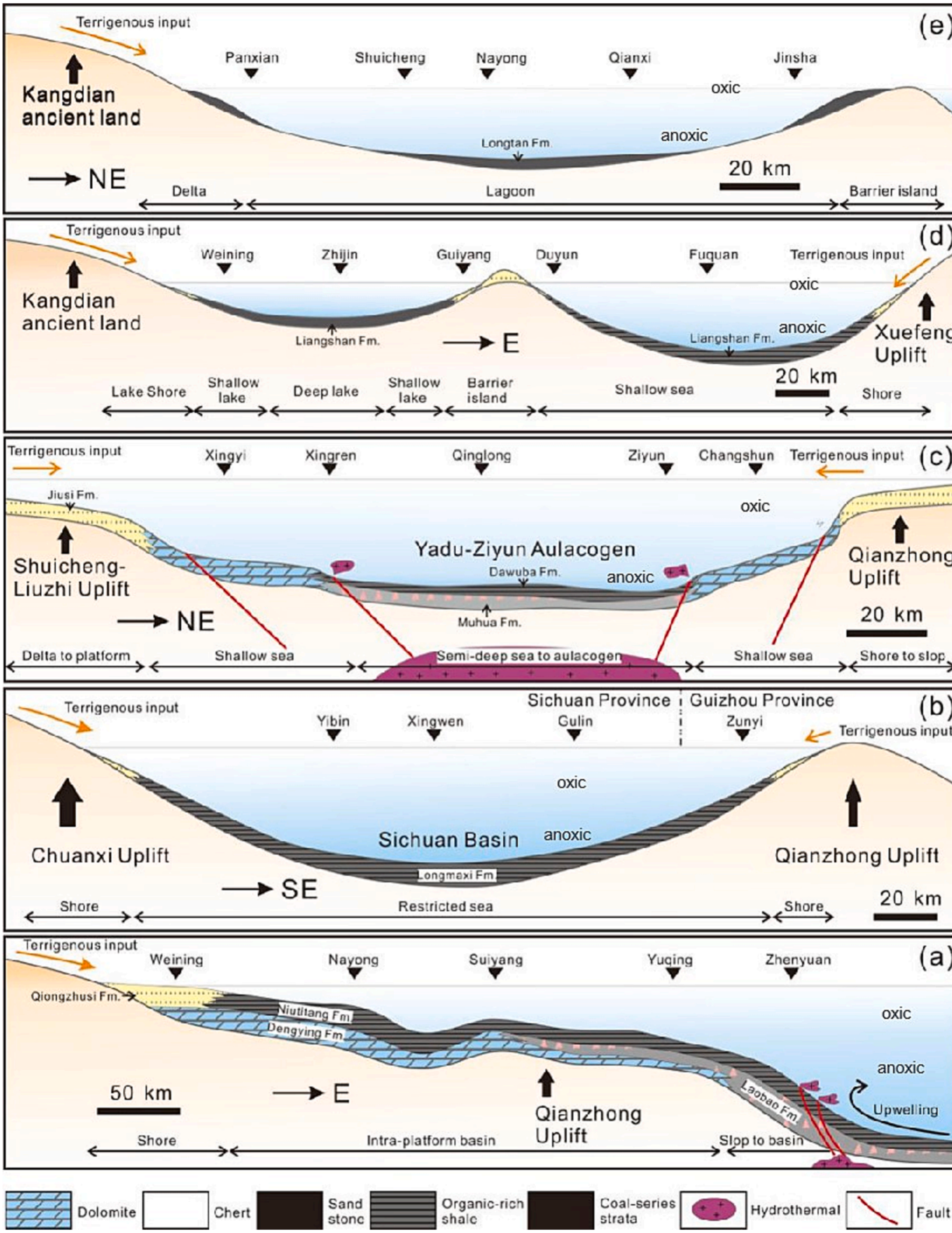

Fig. 5. Schematic sketch illustrating the sedimentary environments of the organic-rich shales in Guizhou Province. a) The Niutitang organic-rich shale, b) the Wufeng-Longmaxi organic-rich shale, c) the Dawuba organic-rich shale, d) the Liangshan organic-rich shale and e) the Longtan organic-rich shale.

whole province except for its southeastern corner and is mainly enriched in the Zunyi, Tongren, Duyun, and Bijie regions (Fig. 4a). The Niutitang and Wufeng-Longmaxi organic-rich shales are some of the most important marine shale gas reservoirs in South China. However, the shale gas resource volume in the Niutitang shale is poor compared to the Wufeng-Longmaxi shale (Zeng and Guo, 2015; Horsfield et al., 2021; Zou et al., 2021).

The organic-rich shale of the Wufeng-Longmaxi Formation is also called graptolite shale. This organic-rich shale is located in the lower part of the Wufeng-Longmaxi Formation with a thickness of less than 80 m (Liang et al., 2017; Lan et al., 2022). The Wufeng-Longmaxi organic-rich shale occurs in North Guizhou, and its thickness gradually decreases from north to south (Fig. 4b). Interestingly, the Wufeng-Longmaxi shale in the center of the Sichuan Basin contributes the most to shale gas production in China at present, with the majority being wells characterized by "high formation pressure and high production". However, shale gas development from this shale has shown less promising results in North Guizhou, characterized by "low formation pressure low production" wells, and occurs on the southeast margin of the Sichuan Basin (Fig. 5b, Dai et al., 2014; Zou et al., 2016, 2021; Xia et al., 2021a). The reason for the considerable difference in shale gas productivity from the margin compared to the central part of the formation may be that the basin margin (such as North Guizhou Province) has much more complicated tectonic movements and cannot preserve the gas resources as well as the central parts of the basin (such as the center of the Sichuan Basin) (Guo and Zeng, 2015; Zhu et al., 2019; Xu et al., 2020; Lan et al., 2022).

The Dawuba organic-rich shale occurs in the lower part of the Dawuba Formation (Lu, 2019) and can reach a thickness of 140 m, but is usually thicker than 40 m (Fig. 4c, Su, 2018; Lu et al., 2021). The Dawuba organic-rich shale is, in addition to the Niutitang and Wufeng-Longmaxi organic-rich shales, a significant marine shale gas reservoir (Zhu et al., 2019). Much less basic research has been done on this organic-rich shale in comparison to the Niutitang and Wufeng-Longmaxi organic-rich shales.

The Liangshan organic-rich shale in the Guizhou Province is a marine-continental transitional deposit (Xu, 2017). Unlike the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales, which occur in the lower parts of their respective formations, the Liangshan organic-rich shale can also occur in the middle and upper parts of the Liangshan Formation (Zhang et al., 2016). The thickness of the Liangshan organic-rich shale ranges from 0 to 201 m, while its sedimentary center occurs in Qinglong County (Fig. 4d, Zhu et al., 2019).

The Longtan Formation is the most significant coal-bearing strata in Guizhou Province (Qin et al., 2012; Yang, 2020). It not only contains shale gas reservoirs, but also coalbed methane reservoirs (Wu et al., 2010; Liu et al., 2022). The thickness of the marine-continental transitional organic-rich shale ranges from 20 to 55 m (Fig. 4e). Since this organic-rich shale is usually associated with coal, it is also called the coal-series shale (Zhao et al., 2021). The sedimentary center of this shale occurs in Qinglong and Zhongshan counties, where its thickness exceeds 50 m. Like the Liangshan shale, the Longtan shale can occur anywhere in the Longtan Formation (Zhao et al., 2021; Lou et al., 2022). This geographical occurrence of the Liangshan and Longtan organic-rich shales may be the result of their marine-continental transitional sedimentary environments (Qin et al., 2012; Xu, 2017).

4. Sedimentary environment of organic-rich shales in different strata

4.1. Sedimentary environment of the Niutitang organic-rich shale

The Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales are marine shales, while the Liangshan and Longtan organic-rich shales are marine-continental transitional shales (Fig. 5, Guizhou Geological Survey, 2017; Zhu et al., 2019; Lu et al., 2021; Xia et al., 2021a, 2022; Zou et al., 2021).

There was an open ocean between the Yangtze Block and Cathaysia Blocks during the initial stages of the Early Cambrian, during which an uplift, platform, slop, and deep basin occurred in the study area (Goldberg et al., 2007; Yeasmin et al., 2017; Li et al., 2020). The Niutitang organic-rich shale was deposited in the intra-platform basin, while the slop and the deep basin occurred from west to east (Fig. 5a). This organic-rich shale was deposited under suboxic to anoxic conditions, while a high paleo-productivity generated a large amount of organic matter, especially in the slop and deep basin settings (Fu et al., 2021; Xia et al., 2022). Before the depositional stage of the Niutitang organic-rich shale, upwelling currents and hydrothermal activities brought large volumes of nutrients such as P and Si, which caused bacterial and algal blooms (Usui and Someya, 1997; Wei et al., 2012; Jia et al., 2018; Xia et al., 2020; Tan et al., 2021). This stage is proven by the phosphorite (Fig. 6), phosphorus-rich rock, chert, and silicon-rich rock that are present in the Niutitang organic-rich shale (Han et al., 2021; Valetich et al., 2022; Zhang et al., 2022). The abnormal enrichment in certain trace elements (such as Ni, Mo, Cu, Pb, Zn, Au, Ag, Ru, Rh, Pd, Ir, and Pt) also indicates hydrothermal activities (Chen, 2006; Lehmann et al., 2016). These bacteria and algae enhanced the primary productivity of the ocean, while their decomposition consumed the oxygen in the seawater. These organisms, therefore, caused an organic matter-rich and oxygen-deficient environment (Fig. 7a), which controlled the enrichment and preservation of organic matter in the Niutitang organic-rich shale.

4.2. Sedimentary environment of the Wufeng-Longmaxi organic-rich shale

During the initial stages of the Early Silurian, a restricted sea occurred between the Chuanxi and Qianzhong Uplifts (Fig. 5b). The Sichuan Basin was an intraplate basin located in the Yangtze Block between the Chuanxi and Qianzhong Uplifts (Liu et al., 2021; Zou et al., 2021). The seawater in the restricted Sichuan basin was anoxic (Fig. 7), which allowed for the preservation of large volumes of organic matter in the Wufeng-Longmaxi organic-rich shale of this basin. The sedimentary centers of the Sichuan Basin were located in the Mianyang-Chengdu and Yibin-Luzhou areas during the deposition of the Wufeng-Longmaxi organic-rich shale (Jin et al., 2009). Most of the Guizhou regions experienced paleo uplift during this stage, so the sedimentary strata were lost in these regions (Fig. 2). Only a part of North Guizhou Province was included in the Sichuan Basin, and today occurs on the margin of the Sichuan basin (Fig. 5b). The Wufeng-Longmaxi organic-rich shale therefore only occurs in North Guizhou Province (Fig. 4b). The thickness of this organic-rich shale in Northern Guizhou Province is however much thinner than that in central parts of the Sichuan Basin (Zou et al., 2021).

In contrast to the Niutitang shale, the development of the Wufeng-Longmaxi shale was not controlled by hydrothermal activities and upwelling currents. This is proven by the high concentration of rare earth element contents (REEs) and the high ratios of light REEs to heavy REEs ($\sum$LREE/$\sum$HREE) in the Wufeng-Longmaxi shale (Fig. 8).

4.3. Sedimentary environment of the Dawuba organic-rich shale

Based on the sedimentary structure, sedimentary environment, and stratigraphic framework of the Dawuba Formation, its sedimentary facies can be divided into the following depositional zones: Two marginal slope facies on both sides of the aulacogen, a shallow semi-deep marine facies transiting to the aulacogen, a trough basin facies in the aulacogen, an uplift shallow marine facies in the Shuicheng area, and a tidal flat lagoon facies in the Weining area (He, 2019; Lu et al., 2021). Of these depositional zones, the most favorable environments for the development of the organic-rich shales were the semi-deep sea and the aulacogen depositional zones (Fig. 5c, Su, 2018). The relatively stable

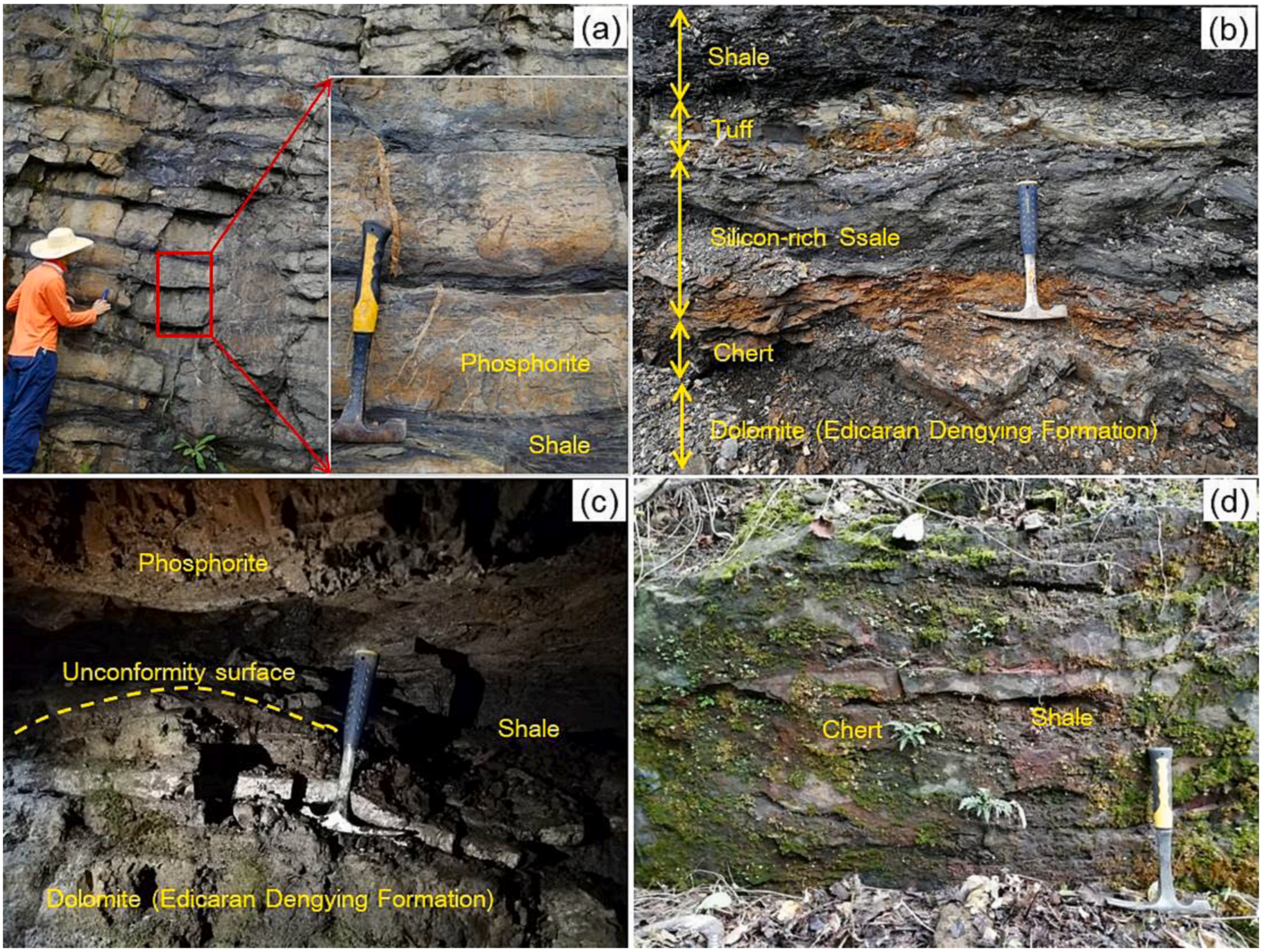

Fig. 6. Field photos of the Niutitang Formation. a) Phosphorite in shale, Zhijin, b) the Niutitang Formation section in Songlin, c) the unconformity surface between the Ediacaran Dengying Formation and the Cambrian Niutitang Formation, Zhijin, and d) Chert in shale, Sansui.

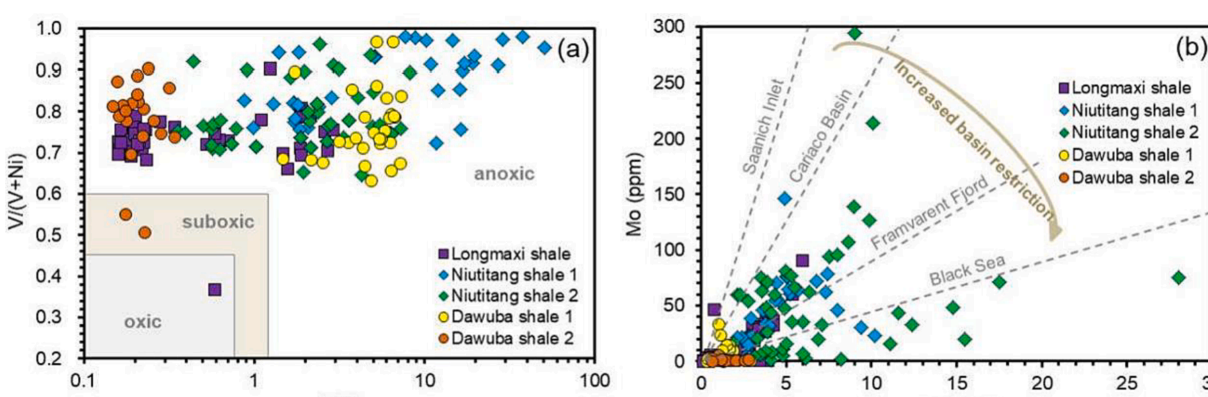

Fig. 7. Paleo environmental proxies of marine shales (Su, 2018; He, 2019, Zhu et al., 2019; Xia et al., 2020, 2022). a) U/Th versus V/(V + Ni) and b) TOC versus Mo.

sedimentary environment of the detained shallow sea to semi-deep sea facies was entered from the slope facies to the aulacogen. The influence of the terrigenous debris is gradually weakened, which enhanced the reduction environment (Fig. 7). This environment allowed the enrichment of the black shale deposits, the reduction of carbonate minerals, the enrichment of pyrite, and the development of spicules. Basin facies sediments occur at the core of the aulacogen of the detention trough, where the fossils of plankton such as spicules and algae are developed. The influence of terrigenous detritus on the organic matter was weaker in the aulacogen, which promoted the enrichment of black shale deposits. The aulacogen was therefore the most significant environment for the deposition of the Dawuba organic-rich shale.

The Shuicheng-Ziyun fault zone mainly controlled the sedimentary facies of West Guizhou. The facies changed from the shore, through the shallow sea, to the semi-deep sea and aulacogen because of the effect of this fault zone (Fig. 5c and Fig. 9). The large fault zone served as a migration pathway for the deep hydrothermal fluid, and we can therefore deduce that the Dawuba organic-rich shale was affected by

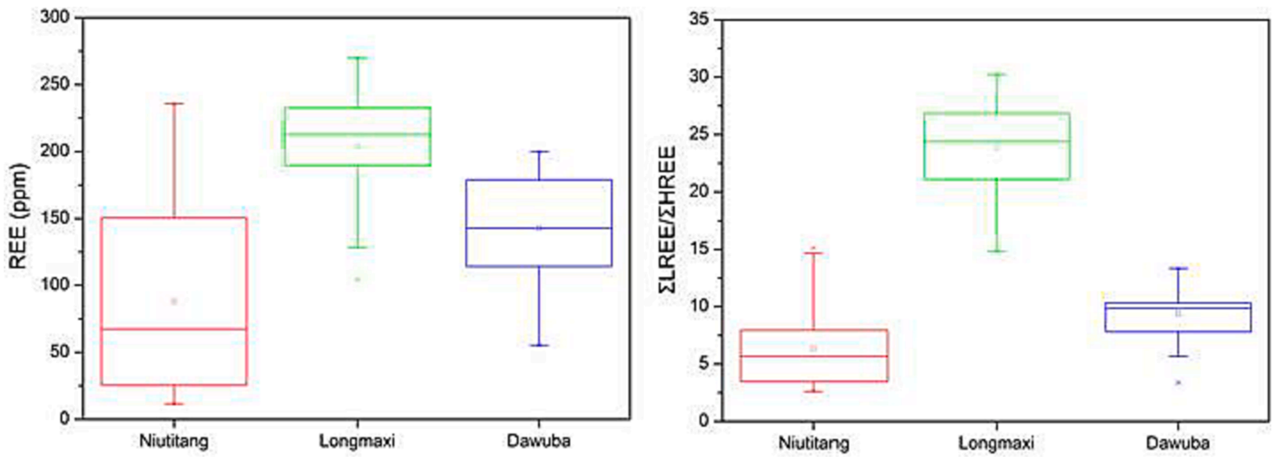

Fig. 8. Rare earth elements content of marine shales. a) REE and b) ∑LREE/∑HREE.

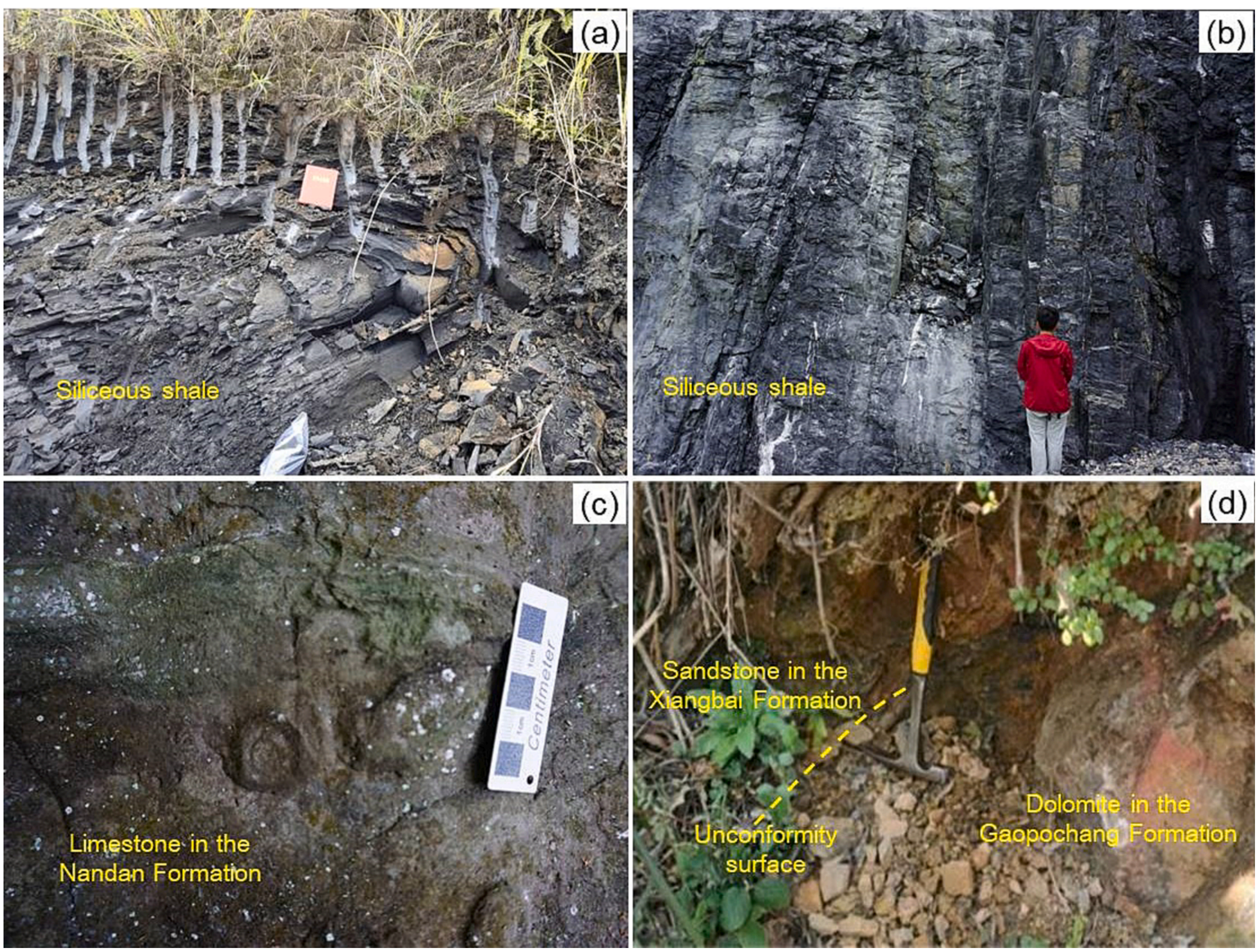

Fig. 9. Field photos of the Lower Carboniferous Formation. a) The siliceous shale in the Dawuba Formation, Huishui, b) the siliceous shale in the Dawuba Formation, Luodian, c) the limestone in the Nandan Formation, Changshun, and d) the sandstone in the Xiangbai Formation, Wudang. The Dawuba, Nandan, and Xiangbai Formations are heterotopic deposits as shown in Fig. 2.

hydrothermal activities. This deduction is supported by the low ratios of ∑LREE/∑HREE (Fig. 8) and the abnormally high thermal maturity of the organic matter in this organic-rich shale (Fig. 10).

4.4. Sedimentary environment of the Liangshan organic-rich shale

Large areas of the Guizhou Province were uplifted into the land under the effects of the Qiangui movement at the end of the Late Carboniferous (Guizhou Geological Survey, 2017). East Guizhou was therefore land, and the Xuefeng and Qianbei Uplifts were located in Northeast and Southeast Guizhou, respectively (Fig. 5d). West Guizhou had a relatively lower altitude compared to East Guizhou, and mainly developed a marine-continental transitional facies group, which included a lagoon, a barrier island, a coast, and a shallow water shelf

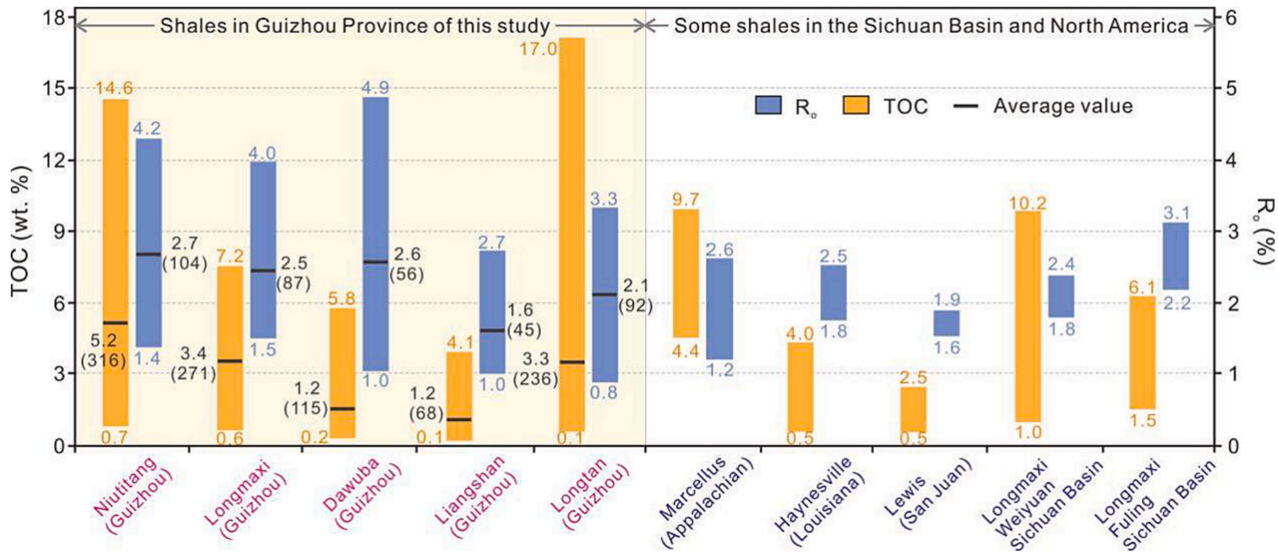

Fig. 10. TOC content and R_o values of the different organic-rich shales (the value in brackets is the sample number of each organic-rich shale).

(Zhong et al., 2020; Liu et al., 2022). The Liangshan Formation was generally deposited in West Guizhou (Fig. 3d), where it unconformably overlies either the Pingchuan Formation or Longyin Formation (Fig. 2) because of the Qiangui upliftment (Zhang et al., 2014).

The organic-rich shale in the Liangshan Formation was generally deposited in the lagoon and shallow water shelf environments (Fig. 5d). Geochemical proxies, including V/Cr, Ni/Co, and V/(V + Ni), indicate that this organic-rich shale was deposited under oxic to dysoxic conditions, see Fig. 11 (Zhang et al., 2016; Zhu et al., 2019). This depositional environment was a much more oxygen-rich environment compared with the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales. In addition to the organic-rich shale, the Liangshan Formation mainly contains quartz sandstone and quartz siltstone, while the general lithological association for the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales are carbonate rocks and mudstone (Zhang et al., 2012). This means that the Liangshan organic-rich shale was more obviously affected by terrigenous input compared to the other three organic-rich marine shales, and the terrigenous influx was generally from the Kangdian ancient land and the Xuefeng ancient land (Guizhou Geological Survey, 2017; Zhu et al., 2019) (Fig. 5d).

4.5. Sedimentary environment of the Longtan organic-rich shale

The Guizhou province contained continental, marine-continental transitional, and marine facies groups during the Late Permian, and the water depth increased from West Guizhou to East Guizhou. The Longtan Formation was deposited in West Guizhou mainly in the Bijie and Liupanshui regions under these conditions (Fig. 3e), while carbonate-rich strata (such as the Wujiaping Formation, Fig. 2) was deposited in East Guizhou during the same stage (Guizhou Geological Survey, 2017; Zhao et al., 2022). The Longtan Formation mainly contains coal, mudstone, sandstone, and limestone (Fig. 12), which means that West Guizhou experienced multiphase seawater intrusions and that the Kangdian ancient land provided large volumes of terrigenous debris during the sedimentary stage of this formation (Wang et al., 2020a; Shao et al., 2021; Li et al., 2022).

The organic-rich shale in the Longtan Formation was deposited in a delta and a lagoon (Fig. 5e). Similar to the Liangshan shale, the Longtan shale was mainly deposited under oxic to dysoxic conditions (Fig. 11, Sun, 2014). The organic-rich shale can still exist in the context of an oxic sedimentary environment (Wang et al., 2022a). This means that the enrichment mechanism of the organic matter is controlled by primary productivity and terrigenous debris influx.

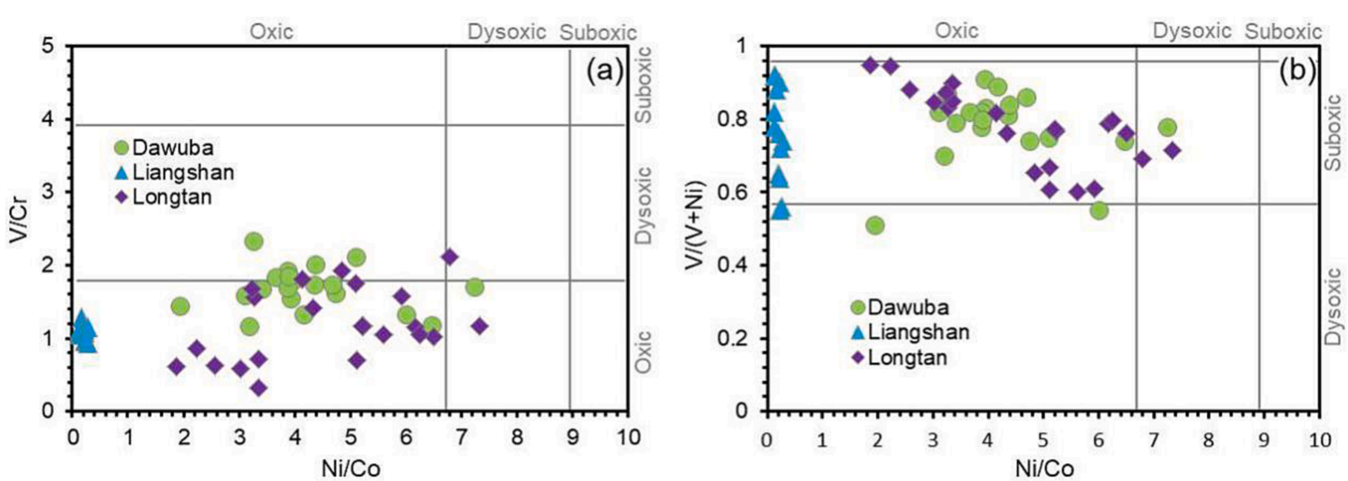

Fig. 11. Paleo environmental proxies of the marine-continental transitional shales and the Dawuba organic-rich shale (Zhang et al., 2016; Su, 2018; Ding et al., 2021). a) Ni/Co versus V/Cr and b) Ni/Co versus V/(V + Ni).

Fig. 12. Drilling core photos of the Longtan Formation from well DHC-1 in the Zhongshan County. a) Organic-rich shale and limestone, b) Coal, organic-rich shale, mudstone, and limestone, c) Plant fossils, and d) Organic-rich shale and limestone.

The sedimentary environments of the five organic-rich shales differ from each other (Fig. 5). We can deduce that the marine organic-rich shales (including the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales) were generally deposited under anoxic conditions. The marine-continental transitional organic-rich shales (including the Liangshan and Longtan organic-rich shales) were most likely deposited under oxic to dysoxic conditions. Upwelling currents and thermal activities caused the anoxic conditions of the Niutitang organic-rich shale, while that of the Wufeng-Longmaxi organic-rich shale was caused by the restricted ocean conditions. The Longtan organic-rich shale has a higher total organic carbon (TOC) content than the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales because of the abundant terrestrial plants that were present during Late Permian, even though it was deposited under oxic conditions.

5. Composition of the different shales

5.1. Geochemical characteristics of the organic-rich shales

5.1.1. Organic matter abundance

The organic geochemical characteristics of the organic-rich shale are described by the abundance, type, and thermal maturity of the organic matter (Hao et al., 2013). The TOC content is the most effective index to indicate organic matter abundance in shales. To serve as an effective source rock for hydrocarbon generation, the TOC content of the source rock must be no less than 0.5 %, while the "sweet spot" of the shale gas resource is usually at a TOC content above 2.0 % (Jarvie et al., 2007; Lu et al., 2019). Interestingly, the Lewis shale in the San Juan Basin has great shale gas productivity even though its TOC content is relatively low at 0.5 %–2.5 %, see Fig. 10. This is mainly because the effective thickness of this shale ranges from 60 to 90 m, which is much thicker than most shales in the USA with a higher TOC content (Li et al., 2012; Gentzis, 2013). The TOC content should therefore be combined with the effective thickness of shale to identify possible "sweet spots" for shale gas development (Zhu et al., 2019).

The TOC content in the Niutitang organic-rich shale ranges from 0.7 % to 14.6 %, with an average of 5.2 % (Fig. 10). About 69.1 % of 316 samples reported by our previous studies have a TOC content higher than 4.0 %, while 12.7 % of these range from 3.0 % to 4.0 % (Zhu et al., 2019; Ning et al., 2021; Xia et al., 2022). There are two high-value TOC areas (where the TOC content is greater than 8 %) in Guizhou Province, one which is located in the Tongren area of the East Guizhou region, and one in the Yuqing-Shibing area of the Southeast Guizhou region, (Fig. 13a). These two high-value areas developed due to the normal shelf slope sedimentation and the sedimentary center that formed under the influence of the Qianzhong Uplift (Fig. 5a). The TOC content decreases from the east to the west of Guizhou Province. The TOC content is, however, still greater than 3.0 % in the West Guizhou region, and still has relatively good hydrocarbon prospectivity.

In the Wufeng-Longmaxi organic-rich shale in Guizhou Province, the TOC content is 0.6 %–7.2 %, with an average of 3.4 %. This shale has a lower TOC content compared to the Niutitang organic-rich shale in Guizhou Province and has a similar TOC content to the Wufeng-Longmaxi shale in the Sichuan Basin (Fig. 10). The Wufeng-Longmaxi organic-rich shale mainly occurs in the North Guizhou region because of the Qianzhong Uplift (Fig. 4b and 5b). In the Daozhen, Tongzi, and

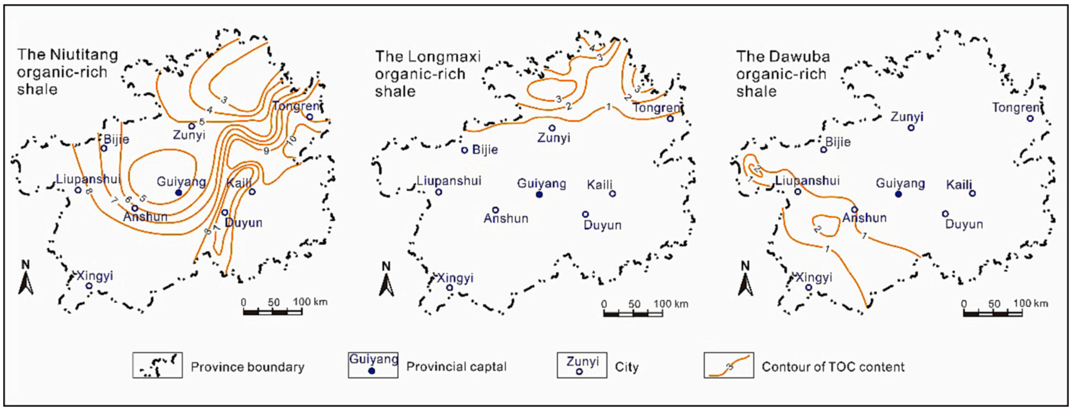

Fig. 13. Distribution of the TOC content of the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales (Zhu et al., 2019; Lu et al., 2021; Ning et al., 2021).

Yanhe areas, which occur in the northern part of this region, the TOC content of the Wufeng-Longmaxi organic-rich shale exceeds 3.0 % (Fig. 13b), which could be the case because these areas are close to the sedimentary center of the Sichuan Basin. The TOC content in the Wufeng-Longmaxi organic-rich shale gradually decreases from north to south.

The TOC conten of the Dawuba organic-rich shale ranges from 0.2 % to 5.8 %, with an average of 1.2 % (Fig. 10). The organic matter is mainly enriched in the Yadu-Ziyun aulacogen (Fig. 5c), while the TOC content in this aulacogen is generally greater than 1.5 % (Fig. 13c). The TOC content gradually decreased from the center of the aulacogen to its sides.

The Liangshan organic-rich shale has a TOC content of 0.1–4.1 %, with an average of 1.2 % (Fig. 10). This organic-rich shale has the lowest TOC of all of the five organic-rich shales. The high TOC content in the Liangshan organic-rich shale mainly occurs in the Yadu-Ziyun aulacogen, similar to the Dawuba organic-rich shale.

The Longtan organic-rich shale is the most significant source rock and reservoir for the marine-continental transitional shale gas facies (Ma, 2017; Wang et al., 2022b). The TOC content in this organic-rich shale ranges from 0.1 % to 17.0 %, with an average of 3.3 % (Fig. 10). Approximately 60.01 % of the 236 samples reported by previous studies (Zhu et al., 2019; Zhao et al., 2021; Lou et al., 2022), have a TOC content higher than 4.0 %, and about 35.0 % have a TOC content less than 3.0 %. The organic matter in this organic-rich shale is mainly enriched in the Shuicheng, Panxian, Xingren, and Liuzhi areas, which are also the main coal-producing areas in Guizhou Province.

5.1.2. *Organic matter type*

The type of organic matter is a significant index that controls the hydrocarbon generation and preservation conditions of shale gas (Zou et al., 2021). Maceral compositions and $\delta^{13}C_{org}$ in shale can be used to identify the organic matter type (Lu et al., 2019). The organic macerals compositions can be used to calculate the type index (TI) according to the following formula:

$$TI = (100.a + 50.b - 75.c - 100.d) / 100.$$

where a, b, c, and d are the sapropelinite, liptilite, vitrinite, and inertinite content, respectively. TI values above 80 indicate type I organic matter; TI values ranging from 40 to 80 indicate type II_1 organic matter; TI values ranging from 0 to 40 indicate type II_2 organic matter, and TI values less than 0 indicate type III organic matter.

In addition to the TI index, the $\delta^{13}C_{org}$ is another significant parameter used to identify the organic matter type. Generally, when $\delta^{13}C_{org} <$ -29 ‰ it indicates type I organic matter; when −29 ‰ $< \delta^{13}C_{org} <$ -27.6 ‰ it indicates type II_1 organic matter; when −27.6 ‰ $< \delta^{13}C_{org} <$ -26 ‰ it indicates type II_2 organic matter, and a $\delta^{13}C_{org}$ above −26 ‰ indicates type III organic matter.

The results of the calculations can be seen in Figs. 14 and 15. The TI index and $\delta^{13}C_{org}$ value of the Niutitang organic-rich shale range from 87.75 to 100.00 and −39.2 ‰–-30.7 ‰ (Zhu et al., 2019; Xia et al., 2020). Both these values indicate that the organic matter in this organic-rich shale can be classified as type I organic matter.

In comparison to the Niutitang organic-rich shale, the Wufeng-Longmaxi organic-rich shale contains both type I and type II_1 organic matter (Fig. 15). The TI index of this organic-rich shale ranges between 44.75 and 95.50, with a $\delta^{13}C_{org}$ value of −30.98 ‰–-28.22 ‰ (Lin et al., 2014; Wang et al., 2022b).

The TI index and $\delta^{13}C_{org}$ value of the Dawuba organic-rich shale range from −21.00 to 29.25, and from −26.87 ‰ to −24.19 ‰, respectively (Fig. 15, Niu et al., 2021; Zheng et al., 2022). Both these values indicate that the organic matter in the Dawuba organic-rich shale belongs to the type II_2 and type III organic matter classes.

The TI index of the Liangshan organic-rich shale ranges from −42.00 to 65.00 (Fig. 14), implying that there is a rich source of organic matter during the sedimentation stage of this shale (Jiang and Cha, 2006; Huang and Gao, 2017). According to the TI index, the Liangshan organic-rich shale contains the type II_1, type II_2, and type III organic matter. The reported $\delta^{13}C_{org}$ value of this organic-rich shale is very limited, with only four values being collected. They range from −26.90 ‰—23.00 ‰, indicating type II_2 and type III organic matter (Fig. 15, Li,

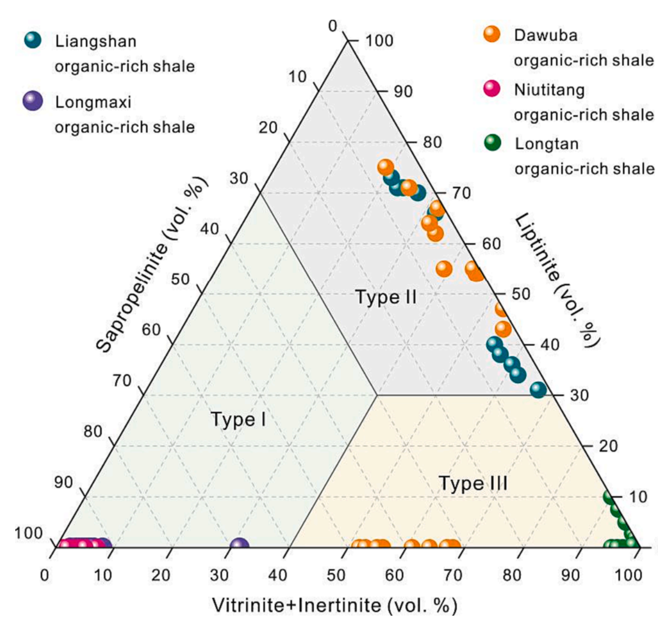

Fig. 14. Ternary diagram showing the different organic matter types.

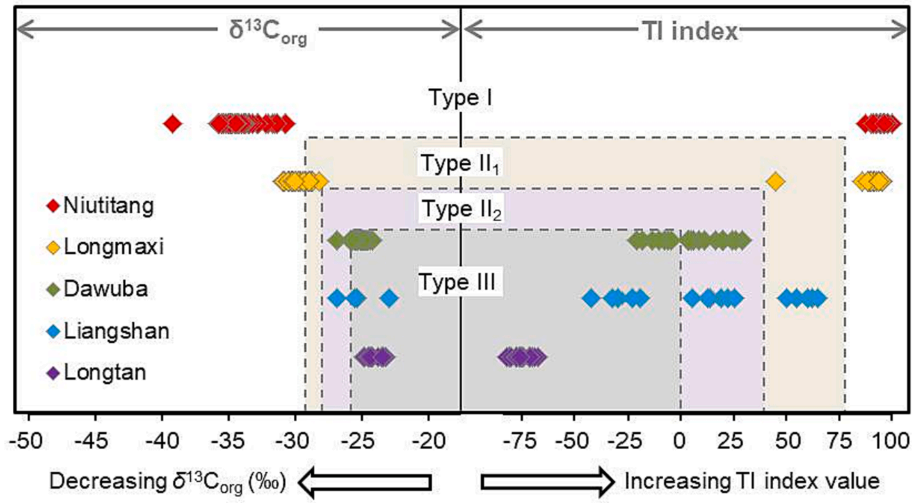

Fig. 15. Organic matter type identification based on the data of the kerogen carbon isotope and the TI index ($\delta^{13}C_{org}$ values is from Lin et al., 2014; Li, 2019; Zhu et al., 2019; Xia et al., 2020; Ma, 2017; Niu et al., 2021; Wang et al., 2022a; Zheng et al., 2022).

2019).

Both the TI index (-82.00–-67.25) and the $\delta^{13}C_{org}$ value (-24.90 ‰—23.20 ‰) indicate that the organic matter in the Longtan organic-rich shale can be classified as type III (Fig. 15, Ma, 2017). The organic matter in the Longtan organic-rich shale therefore mainly derives from terrestrial higher plants. In contrast to the Longtan organic-rich shale, the organic matter in the Niutitang and Wufeng-Longmaxi organic-rich shales came from lower organisms, such as algae and bacteria, while the organic matter in the Dawuba and Liangshan organic-rich shales are from both higher and lower organisms.

5.1.3. Organic matter maturity

Vitrinite reflectance (R_o) is an effective index that indicates the thermal maturity of organic matter (Lu et al., 2019; Huang and Gao, 2017). The R_o values of the Niutitang, Wufeng-Longmaxi, Dawuba, Liangshan, and Longtan organic-rich shales range from 1.4 % to 4.2 % (averaging 2.7 %), 1.5 %–4.0 % (averaging 2.5 %), 1.0 %–4.9 % (averaging 2.6 %), 1.0 %–2.7 % (averaging 1.6 %), and 0.8 %–3.3 % (averaging 2.1 %), respectively (Fig. 10).

Approximately 92.59 % of the 104 R_o values reported by Zhu et al. (2019), Ning et al., (2021), and Xia et al., (2022), have a R_o value higher than 2.0 %, indicating that the Niutitang organic-rich shale is over-mature (Jiang and Cha, 2006). Ninety percent of the 87 of the Wufeng-Longmaxi organic-rich shale that was recently reported (Cao et al., 2020; Sun et al., 2021a; Cao et al., 2022; Shi et al., 2022) have R_o values higher than 2.0 %, therefore the Wufeng-Longmaxi organic-rich shale can also be classified as an over-mature shale. In contrast to the Niutitang and Wufeng-Longmaxi organic-rich shales, the Dawuba, Liangsha, and Longtan organic-rich shales contain more high-maturity samples. The high-maturity shale samples are 28.57 % (56 samples in total), 35.29 % (45 samples in total), and 29.05 % (92 samples in total) in the Dawuba, Liangshan, and Longtan organic-rich shales, respectively.

Of the organic-rich shales in Guizhou Province, the Niutitang and Wufeng-Longmaxi organic-rich shales are classified as over-mature shales, and the Dawuba, Liangshan, and Longtan organic-rich shales are classified as high-mature to over-mature shales. During the high maturity to over-mature stages, the liquid hydrocarbons generated during the thermal evolution of organic matter are cracked into methane at high temperatures (Tilley et al., 2011; Cavelan et al., 2019), which explains why Guizhou Province is oil-poor.

5.2. Shale lithofacies

5.2.1. Mineralogical characteristics

In organic-rich shales, the main minerals include quartz, feldspar (includes K-feldspar and plagioclase), calcite, dolomite, pyrite, and clay minerals (such as smectite, illite, chlorite, and kaolinite) (Fan et al., 2004).

Quartz is the most significant mineral in the Niutitang organic-rich shale and accounts for 30 %–90 % of the mineral composition. Clay is another mineral that is enriched in this organic-rich shale. The clay mainly contains an illite and illite–smectite mixed layer. The clay in the Niutitang organic-rich shale can reach 68 % (Ning et al. (021). The mineral proportions of feldspar, calcite, and dolomite are generally lower than 30 %. Apart from these minerals, pyrite is another significant mineral in the Niutitang organic-rich shale, which is also helpful to analyze the paleo-environment (Xia et al., 2022).

In the Wufeng-Longmaxi shale, the quartz and clay contents are nearly equivalent, with average proportions for both the quartz and clay at about 40 %. Feldspar, calcite, and dolomite are common minerals, with percentages usually lower than 20 %. Pyrite is also common, but its content is generally lower than 5 %. The main clay minerals in this organic-rich shale are illite and illite–smectite mixed layers.

Clay has displaced quartz as the most enriched mineral in the Dawuba, Liangshan, and Longtan organic-rich shales. The proportions of clay minerals in the Dawuba, Liangshan, and Longtan organic-rich shales can reach up to 76.00 %, 73.00 %, and 83.00 %, respectively. The Liangshan and Longtan organic-rich shales have significantly lower contents of carbonate minerals and pyrite in contrast to the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales. This may be because the sedimentary environment of the Liangshan and Longtan organic-rich shale was a marine-continental transitional facies, such as a lagoon-tidal flat, which differs from the marine sedimentary environment of the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales (Guizhou Geological Survey, 2017; Zhu et al., 2019).

5.2.2. Lithofacies classification and features

The methods reported by Wang et al. (2016), Feng et al. (2020), and Ning et al. (2021), which take felsic minerals (quartz and feldspar), carbonate minerals (calcite and dolomite), and clay minerals as three end elements to carry out the shale naming division, were used to divide the shales into a total of 4 shale groups and 12 shale types. The 4 different groups are the Siliceous shale group (I), the Argillaceous shale group (II), the Calcareous shale group (III), and the Mixed shale group

(IV). The 12 shale types include the siliceous shale (I-1), the carbonate-rich siliceous shale (I-2), the argillaceous-rich siliceous shale (I-3), the argillaceous shale (II-1), the silica-rich argillaceous shale (II-2), the carbonate-rich argillaceous shale (II-3), the calcareous shale (III-1), the silica-rich calcareous shale (III-2), the argillaceous-rich calcareous shale (III-3), the argillaceous/siliceous mixed shale (IV-1), the calcareous/argillaceous mixed shale (IV-2), and the siliceous/calcareous mixed shale (IV-3), see Table 1.

Based on the mineral composition, the Niutitang organic-rich mainly includes siliceous shale and argillaceous-rich siliceous shale (Fig. 16). The Wufeng-Longmaxi organic-rich shale is a mixture of an argillaceous-rich siliceous shale, an argillaceous/siliceous mixed shale, and a silica-rich argillaceous shale. Apart from also containing argillaceous-rich siliceous shale, argillaceous/siliceous mixed shale, and silica-rich argillaceous shale, the Dawuba organic-rich shale has large amounts of argillaceous shale, calcareous/argillaceous mixed shale, and siliceous/calcareous mixed shale. The Liangshan organic-rich shale includes a mixture of siliceous shale, argillaceous-rich siliceous shale, silica-rich calcareous shale, argillaceous/siliceous mixed shale, calcareous/argillaceous mixed shale, and siliceous/calcareous mixed shale. Lastly, the Longtan organic-rich shale mainly contains argillaceous shale, silica-rich argillaceous shale, argillaceous/siliceous mixed shale, and argillaceous-rich siliceous shale.

5.3. Pore characteristics

5.3.1. Porosity and permeability

The porosity of the Niutitang, Wufeng-Longmaxi, Dawuba, Liangshan, and Longtan organic-rich shales range from 1.3 to 10.6 % (with an average of 6.96 %), 0.77–9.8 % (with an average of 6.77 %), 0.24–16.37 % (with an average of 10.50 %), 6.64–22.22 % (with an average of 13.34 %), and 0.13–22.00 % (with an average of 12.00 %), respectively

Table 1
Shale classification scheme of the marine shale (after Ning et al., 2021).

Shale groups	Shale types	Code	Minerals composition (%)		
			Felsic minerals	Carbonate minerals	Clay minerals
Siliceous shale group (I)	Siliceous shale	I-1	> 50	< 25	< 25
	Carbonate-rich siliceous shale	I-2	> 50	25–50	< 25
	Argillaceous-rich siliceous shale	I-3	> 50	< 25	25–50
Argillaceous shale group (II)	Argillaceous shale	II-1	< 25	< 25	> 50
	Silica-rich argillaceous shale	II-2	25–50	< 25	> 50
	Carbonate-rich argillaceous shale	II-3	< 25	25–50	> 50
Calcareous shale group (III)	Calcareous shale	III-1	< 25	> 50	< 25
	Silica-rich calcareous shale lithofacies	III-2	25–50	> 50	< 25
	Argillaceous-rich calcareous shale	III-3	< 25	> 50	25–50
Mixed shale group (IV)	Argillaceous/siliceous mixed shale	IV-1	25–50	< 30	25–50
	Calcareous/argillaceous mixed shale	IV-2	< 30	25–50	25–50
	Siliceous/calcareous mixed shale	IV-3	25–50	25–50	< 30

(Lu et al., 2019, Zhu et al., 2019, Ma, 2017, Han et al., 2021, Xia et al., 2021a; Xia et al., 2021b; Zou et al., 2021; Zou et al., 2022). The permeability values of these five organic-rich shales range from 0.0022 $\times$ 10^{-3}–0.0172 $\times$ 10^{-3} μm^2 (with an average of 0.0083 $\times$ 10^{-3} μm^2), 0.0014 $\times$ 10^{-3}–0.0667 $\times$ 10^{-3} μm^2 (with an average of 0.0161 $\times$ 10^{-3} μm^2), 0.0011 $\times$ 10^{-3}–4.7100 $\times$ 10^{-3} μm^2 (with an average of 0.5600 $\times$ 10^{-3} μm^2), 0.0056 $\times$ 10^{-3}–2.6500 $\times$ 10^{-3} μm^2 (with an average of 0.1300 $\times$ 10^{-3} μm^2), 0.0008 $\times$ 10^{-3}–2.9100 $\times$ 10^{-3} μm^2 (with an average of 0.2600 $\times$ 10^{-3} μm^2), respectively. Based on these results, the Dawuba, Liangshan, and Longtan organic-rich shales are much more heterogeneous, which may have been caused by their sedimentary environment.

5.3.2. Pore types

Based on the SEM images reflect, the pore types of the Niutitang shale samples mainly include organic matter pore, interparticle pore, intraparticle pore, intergranular pore, and dissolved pore (Xia et al., 2021b). The organic matter pore is a special kind of interparticle pore that develops within organic matter. These four kinds of pores have been observed in all five organic-rich shales (Fig. 17). Even though the Niutitang and Longtan shales are richer in organic matter than the Wufeng-Longmaxi shale (Fig. 10), the Wufeng-Longmaxi organic-rich shale has a much higher proportion of organic pores in contrast to the other four shales (Zhu et al. 2019, Fig. 18). In the Sichuan Basin, the relatively lower thermal maturity of the Wufeng-Longmaxi organic-rich shale (2.0 % < R_o < 2.8 %) compared to the Niutitang organic-rich shale (3.0 % < R_o < 4.2 %), is the main reason for the difference of organic pores between these two shales (Wang et al., 2020b). In Guizhou Province, the thermal maturity values of the Niutitang and Wufeng-Longmaxi organic-rich shales are however close to each other (Fig. 10). The reason for the differences in the organic pore between the Niutitang and Wufeng-Longmaxi organic-rich shales in the Guizhou Province is still controversial (Wang et al., 2017; Yu et al., 2022). The Liangshan and Longtan organic-rich shales have favorable thermal maturity for developing organic pores, but they have significantly lower organic pore proportions compared to the Wufeng-Longmaxi shale (Fig. 10). The most likely reason is that the organic matter type in the Liangshan and Wufeng-Longmaxi organic-rich shales is type III organic matter, which has fewer pores than type I and type II organic matter (Loucks et al., 2012; Zhang et al., 2020).

The Dawuba, Liangshan, and Longtan shales have higher intraparticle pore proportions compared with the Niutitang and Wufeng-Longmaxi shales. A possible reason for this is their high clay and carbonate minerals content (Fig. 16).

It is important to note that (1) The organic matter in the Wufeng-Longmaxi organic-rich shale is much more porous than in the Niutitang organic-rich shale, even though they have nearly the same type (Figs. 14 and 15) and (2) Based on the thermal maturity (Figs. 10 and 15) the sedimentary environment of the shales gradually changed from marine to continental from the Niutitang shale, through the Wufeng-Longmaxi, Dawuba, and Liangshan shales, to the Longtan shale. At the same time, the organic matter gradually changed from type I to type III, resulting in different organic pores characteristics between these organic-rich shales.

5.3.3. Pore structure

The pore structures of the five sets of potential shale series are very similar (Fig. 19a). Based on the adsorption/desorption curves of the potential shale, the Longtan, Liangshan, and Dawuba shales with high clay mineral content are mainly characterized by parallel plates and sharp cleats (Zhu et al., 2019; Ma, 2017). The Niutitang and Wufeng-Longmaxi shales, in contrast, have a high content of brittle minerals with open pore structures, such as tubular pores with open ends, slit pores with parallel walls, and wedge pores with open sides (Zhu et al., 2019; Xia et al., 2021b). Based on the specific surface area and pore volume diagrams (Fig. 19b), the Wufeng-Longmaxi, Dawuba, and Longtan shales have high values, while the Niutitang shale has low

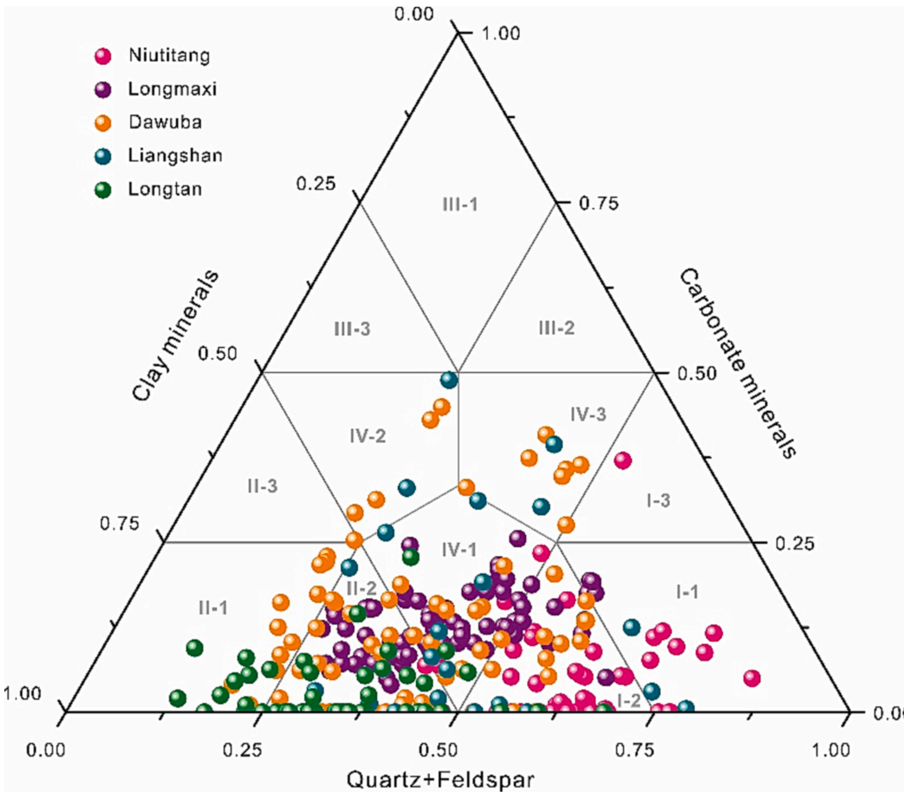

Fig. 16. Ternary diagram showing the lithofacies of the organic-rich shales in Guizhou Province. I-1 is the siliceous shale lithofacies; I-2 is the carbonate-rich siliceous shale lithofacies; I-3 is the argillaceous-rich siliceous shale lithofacies; II-1 is the argillaceous shale lithofacies; II-2 is the silica-rich argillaceous shale lithofacies; II-3 is the carbonate-rich argillaceous shale lithofacies; III-1 is the calcareous shale lithofacies; III-2 is the silica-rich calcareous shale lithofacies; III-3 is the argillaceous-rich calcareous shale lithofacies; IV-1 is the argillaceous/siliceous mixed shale lithofacies; IV-2 is the calcareous/argillaceous mixed shale lithofacies, and IV-3 is the siliceous/calcareous mixed shale lithofacies.

values. The mesopore pore structures account for an absolute proportion of more than 50 % in all five of the potential shale targets in Guizhou Province (Fig. 19a). A possible reason is that most intercrystalline pores of clay minerals and organic pores are mesopores (Xia et al., 2023; Zhao et al., 2023).

6. Prospect of shale gas in Guizhou Province

6.1. Gas resources and origin

Zhu et al. (2019) evaluated the gas resources of the organic-rich shales in Guizhou Province using the volumetric method under conditional probability. The Niutitang organic-rich shale was found to be the most abundant shale gas-enriched reservoir of the five organic-rich shales. The geological resources and recoverable resources in the Niutitang organic-rich shale are 3.55×10^{12} m^3 and 0.64×10^{12} m^3, respectively. The Longtan organic-rich shale is next in line, in which the geological resources and recoverable resources are 1.73×10^{12} m^3 and 0.31×10^{12} m^3, respectively. The Wufeng-Longmaxi and Dawuba also have significant shale gas resources. Their geological resources are 1.48×10^{12} m^3 and 1.44×10^{12} m^3, with recoverable resources at 0.27×10^{12} m^3 and 0.26×10^{12} m^3, respectively. The shale gas in Guizhou Province does however have an abnormally high proportion of nitrogen gas (Xia et al., 2018; Zhu et al., 2019; Han et al., 2021). The geological conditions in Guizhou Province were complicated, as indicated by the distribution of folds and faults (Guizhou Geological Survey, 2017). Faults, folds, and erosion control the preservation and distribution of the shale gas reservoir (Fig. 20, Xia et al., 2021a). Air, carried by surface water, moved into shale gas reservoirs and displaced the shale gas in the pores (Fig. 21, Xia et al., 2018; Zhong et al., 2021). The proportion of nitrogen in the shale gas is therefore higher than the gas. This phenomenon had a significant influence, especially in the Niutitang organic-rich shale, because of an unconformity between it and the Late Ediacaran Dengying dolomite (Fig. 5). This unconformity served as a migration pathway for the surface water causing exchanges between the atmosphere and shale gas in most of the shale deposits of North Guizhou (Fig. 21, Xia et al., 2018).

Fig. 22 shows the $C_1/(C_2 + C_3)$ and $\delta^{13}C$ of methane ($\delta^{13}C_1$) which indicates the hydrocarbon gas origin. The hydrocarbon gas in the Niutitang and Wufeng-Longmaxi organic-rich shales mainly comes from associated gas and from cracking gas of crude oil (Xia et al., 2018; Zhong et al., 2021; Shi et al., 2022). The hydrocarbon gas in the Dawuba and Longtan organic-rich shales is from coal-derived gas (Zhu et al., 2019). These results agree with the sedimentary environment and organic matter type of the organic-rich shales. The sedimentary environment changed from marine to marine-continental transitional conditions from the Niutitang and Wufeng-Longmaxi, through the Dawuba, to the Liangshan and Longtan organic-rich shales, while the shale gas origin changed from crude oil to coal.

6.2. Brittle index and compressibility

The brittle index evaluates the compressibility of shale gas reservoirs. The compressibility can be calculated by the methods of mineral compositions and mechanical parameters, following the Chinese Petroleum Natural Gas Profession Standard (NB/T 10248–2019). The mineral compositions (Fig. 16), were used to calculate the brittle index of each organic-rich shale. The brittle indexes (BI) of the Niutitang, Wufeng-Longmaxi, Dawuba, Liangshan, and Longtan organic-rich shales range from 59 to 96 (with an average of 80), 38–77 (with an average of 56), 24–89 (with an average of 58), 28–80 (with an average of 54), and 15–69 (with an average of 35), respectively. Based on the NB/T

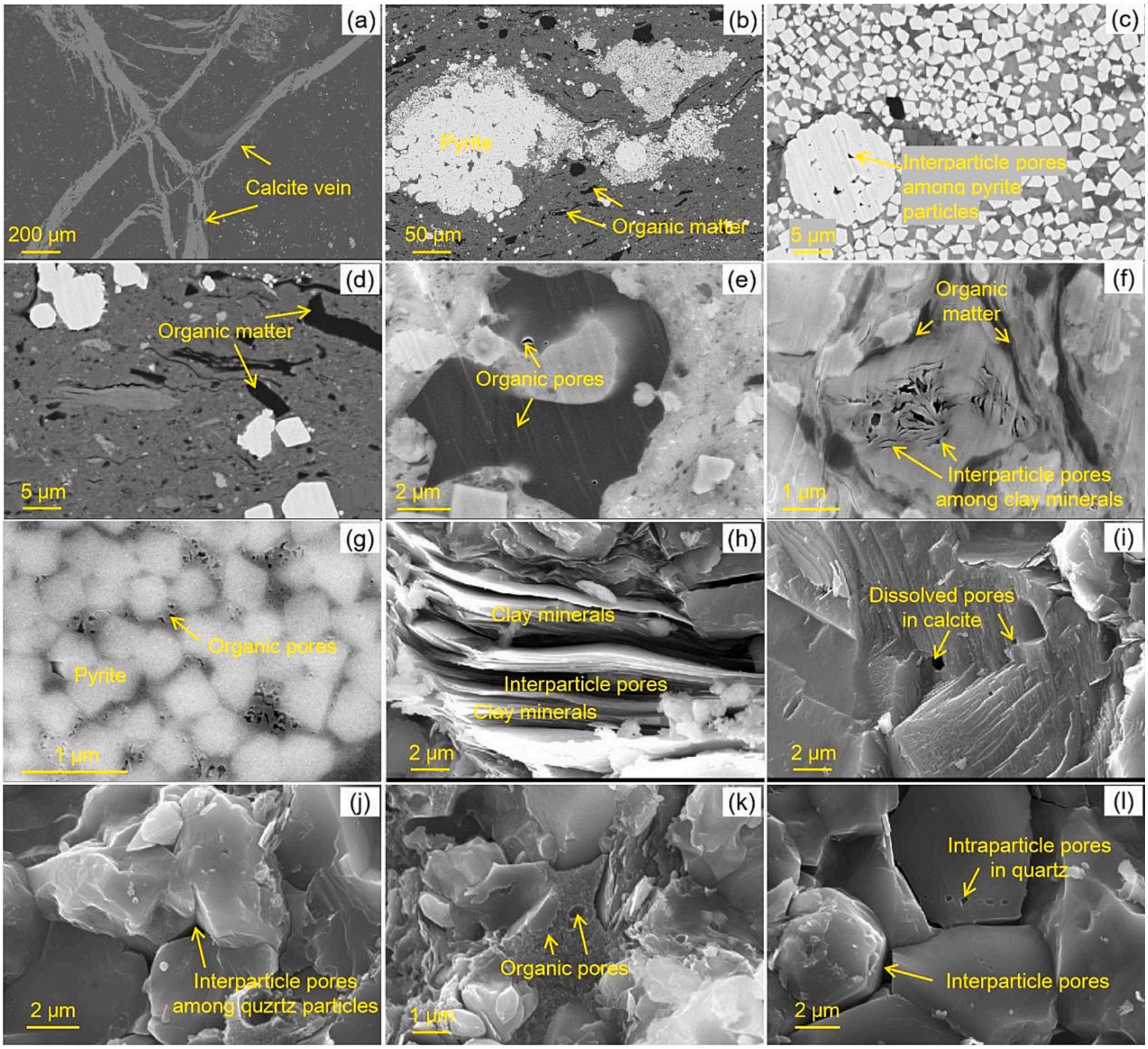

Fig. 17. SEM images of pores in the organic-rich shales. (a)-(f) show the Longtan organic-rich shale. (g)-(i) show the Niutitang organic-rich shale (g is from Ning et al., 2023). (j)-(l) show the Wufeng-Longmaxi organic-rich shale.

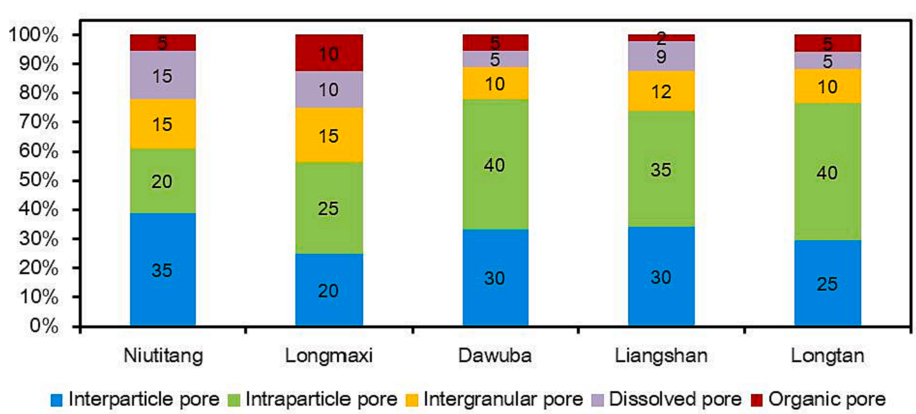

Fig. 18. Pore types of the different organic-rich shales in Guizhou Province (data from Zhu et al., 2019; Xia et al., 2021b).

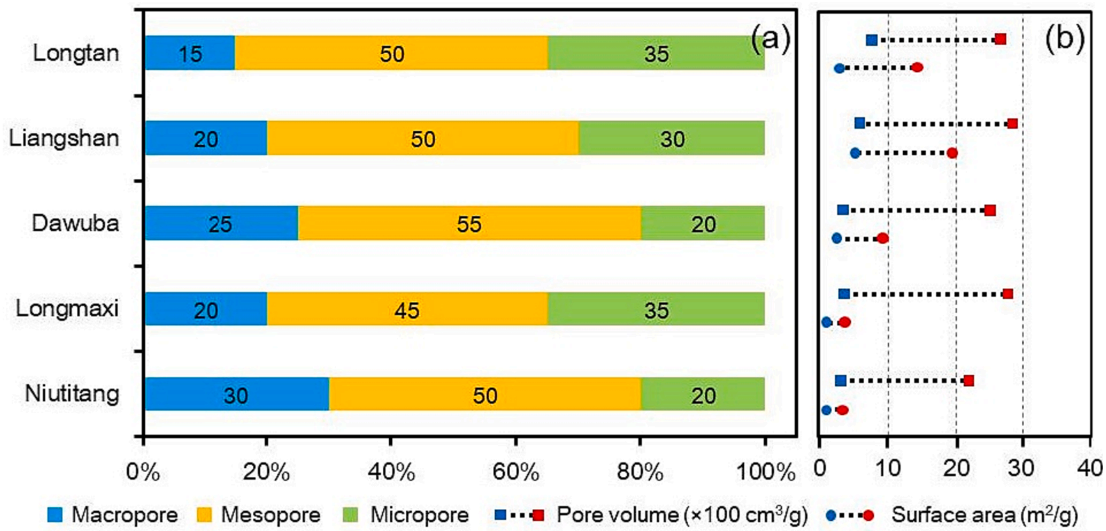

Fig. 19. Pore structure characteristics of organic-rich shales (data from Zhu et al., 2019; Xia et al., 2021b). a) Proportion of pores with different sizes and b) Pore volume and specific surface area.

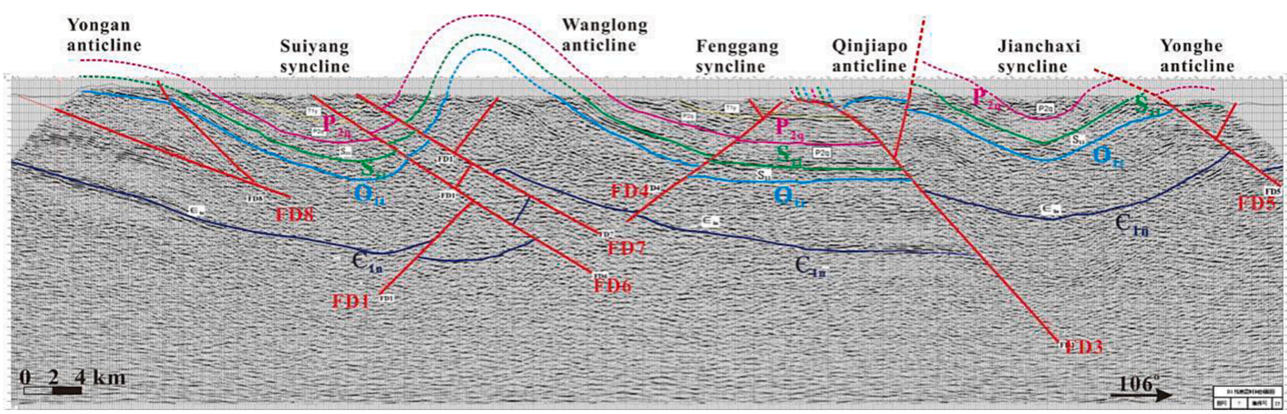

Fig. 20. The Seismic survey shows the structural characteristics of the Niutitang and the Wufeng-Longmaxi organic-rich shales (after Xia et al., 2021a).

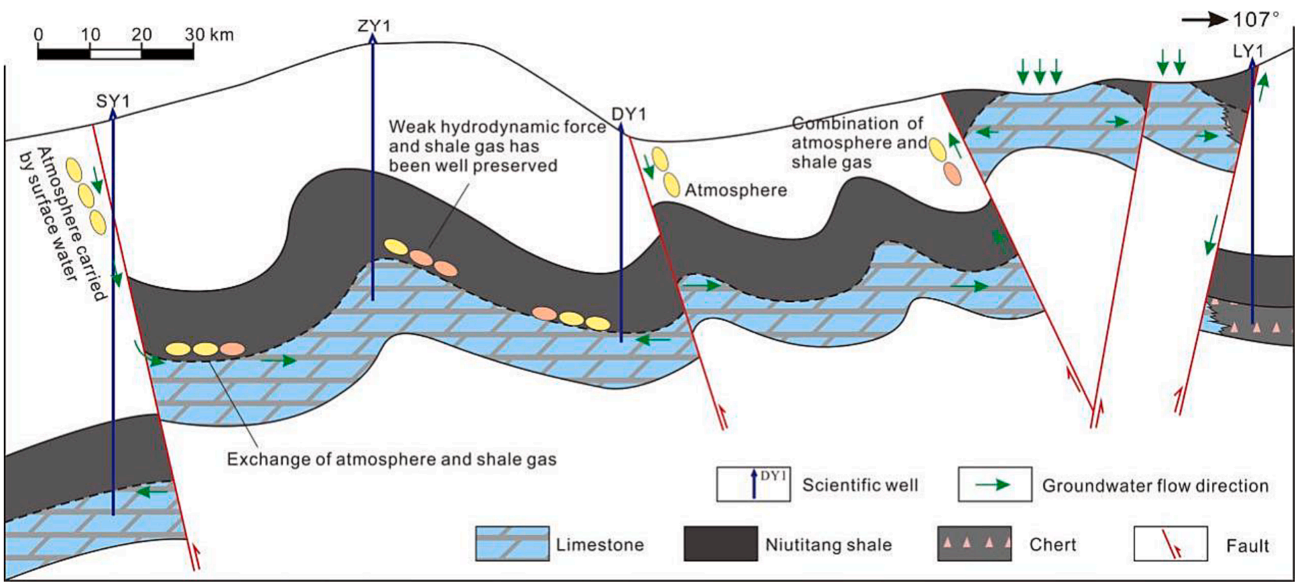

Fig. 21. Relational model of the circular geothermal system of the Niutitang shale gas reservoir in Guizhou Province.

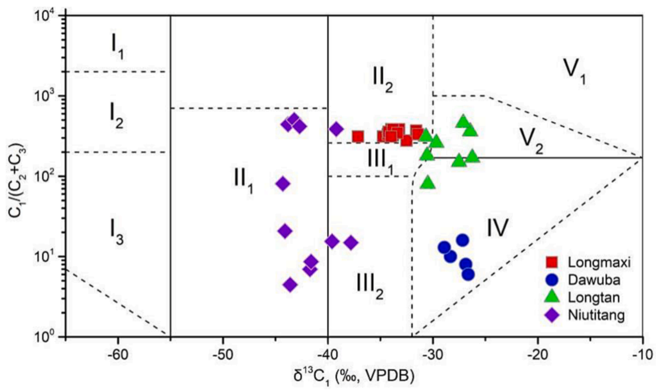

Fig. 22. Diagram of $C_1/(C_2 + C_3)$ versus $\delta^{13}C_1$ showing the hydrocarbon gas origin (data from Xia et al., 2018; Zhu et al., 2019; Zhong et al., 2021; Shi et al., 2022). I_1 is biogas; I_2 is biogenic gas and sub-biogenic gas; I_3 is sub-biogenic gas; II_1 is associated gas of crude oil; II_2 is oil-type cracking gas; III_1 is oil-type cracking gas and coal-formed gas; III_2 is associated gas of condensate and coalbed methane; IV is coal derived gas; V_1 is inorganic gas; V_2 is inorganic gas and coal-derived gas.

10248–2019 grading standard, $70 < BI$ is perfect, $60 \leq BI < 70$ is good, $40 \leq BI < 60$ is medium, and $BI < 40$ is weak. The Niutitang organic-rich shale is very brittle and is favorable for hydraulic fracturing. The Longtan organic-rich shale is not very brittle and is unfavorable for hydraulic fracturing. Methods to improve the permeability of the Longtan organic-rich shale must be developed.

6.3. *Prospect for exploration and development*

The Niutitang, Wufeng-Longmaxi, Dawuba, Liangshan, and Longtan organic-rich shales are the main shale gas reservoirs in Guizhou Province (Xu et al., 2017; Zhu et al., 2019; Han et al., 2021; Lu et al., 2021; Ma, 2017; Xia et al., 2021a; Lan et al., 2022). These shale gas reservoirs have different sedimentary environments, reservoir properties, and shale gas resources (Guizhou Geological Survey, 2017; Zhu et al., 2019; Xia et al., 2020). Both the Niutitang and Wufeng-Longmaxi organic-rich shales are over-mature marine shales. However, the Niutitang organic-rich shale has a higher organic matter content but cannot preserve shale gas very well, in contrast to the Wufeng-Longmaxi organic-rich shale (Xia et al., 2018; Cao et al., 2022; Lan et al., 2022). The Dawuba organic-rich shale is also deposited in a marine system, but it is controlled by deep fault zones (such as the Yadu-Ziyun fault zone, Fig. 5c), and has a higher thermal maturity and a lower TOC content compared with the Niutitang and Wufeng-Longmaxi organic-rich shales (Fig. 10).

In comparison to the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales, the Liangshan and Longtan organic-rich shales have been deposited in marine-continental transitional environments, and are also called coal-series shales (Zhang et al., 2016; Xu et al., 2017; Zhao et al., 2021; Lou et al., 2022). Exploration and development of the Liangshan organic-rich shale are limited, and more fundamental geological research is needed in the future. The Longtan shale is rich in shale gas resources and has a high organic matter content. However, it is the least brittle of the five organic-rich shales, which complicates hydraulic fracturing. The Longtan organic-rich shale is associated with the coal seams of the Longtan Formation, which is the most significant coal-containing strata in Guizhou Province. The shale gas and coalbed methane in the Longtan Formation must therefore be explored and developed concurrently.

The relationship between the environment, the lithofacies, and the reservoir properties are close and would provide additional information for shale gas exploration and development (Ning et al., 2021; Yu et al., 2022). Fig. 23 shows the information on the sedimentary environment, the lithofacies, and some reservoir properties of a typical marine shale (the Niutitang organic-rich shale) and a typical marine-continental transitional shale (the Longtan organic-rich shale). There are significant differences between the sedimentary environment, the lithofacies, the organic matter type, and the reservoir properties of these two shales. The marine shale corresponds to anoxic conditions and is a siliceous-rich lithofacies that contains type I organic matter. In contrast to the marine shale, the marine-continental transitional shale generally corresponds to dysoxic to oxic conditions and is an argillaceous-rich lithofacies that contains type III organic matter. Therefore, the reservoir properties, such as the brittleness and the pore structure, differ between the marine and the marine-continental transitional shale. The marine shale is enriched in quartz because of the large amount of biogenic silicon it contains (Dong et al., 2021; Xia et al., 2022). The quartz content correlates positively with the TOC content (Fig. 24a). However, there is no notable positive or negative correlation between the quartz and the TOC

Fig. 23. Comparisons of the sedimentary environment, the lithofacies, and the reservoir properties between a typical marine shale and a typical marine-continental transitional shale. Here, SS is siliceous shale lithofacies; A-SS is argillaceous-rich siliceous shale lithofacies; AS is argillaceous shale lithofacies; S-AS is silica-rich argillaceous shale lithofacies, and AS-MS is argillaceous/siliceous mixed shale lithofacies.

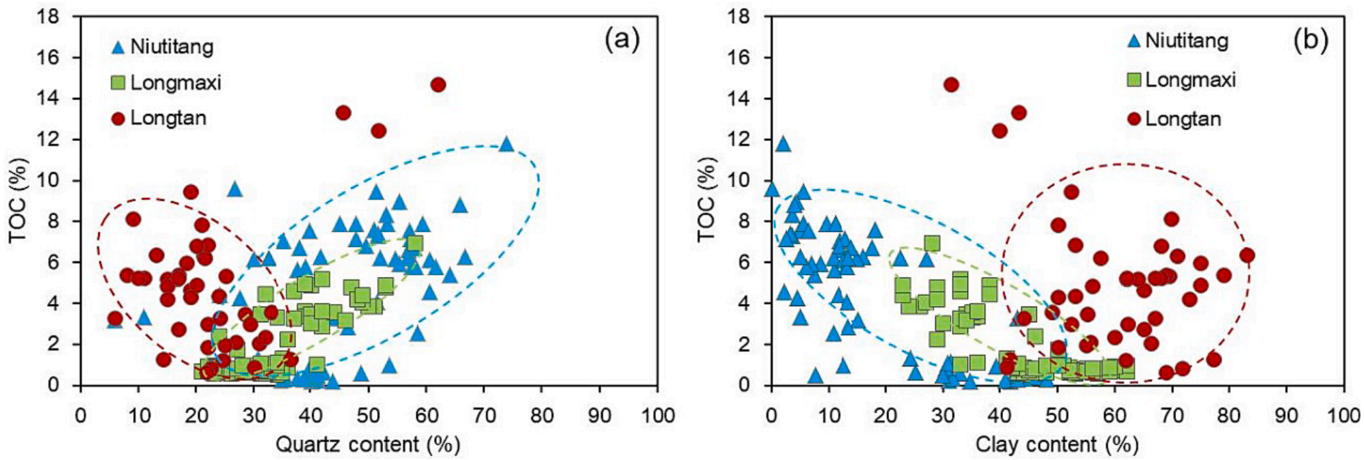

Fig. 24. Relationships between the minerals and the TOC content. a) Quartz content versus TOC content and b) clay content versus TOC content.

content in the marine-continental transitional shale. This may be because of its terrigenous input, which brought in clay and plant residue. Samples with higher clay mineral content usually have a higher TOC content (Fig. 24b). These results imply that the relationships between the sedimentary environment, the lithofacies, and the reservoir properties are significant and can guide shale gas exploration and development. More research on these relationships is needed in the future.

6.4. "Sweet spot" of shale gas

Based on the geochemical characteristics of shale gas reservoir discussed in this study, the enrichment of shale gas in the Niutitang organic-rich shale is controlled by its floor conditions. The spots with the floor of the Dengying Formation dolomite are characterized by low gas content and high nitrogen proportion, and those spots with the floor of the Laobao Formation siliceous rock usually has high gas content and low nitrogen proportion (Xia et al., 2018). Therefore, the the spots with siliceous rock floor on the western edge of the Xuefeng uplift is a favorable area for future exploration of shale gas in the Niutitang organic-rich shale.

Although the Wufeng-Longmaxi organic-rich shale has achieved significant breakthroughs in North Guizhou, the thickness of this shale has become thinner from north to south because of the changes of sedimentary facies (Zhu et al., 2019; Xia et al., 2021a). This organic-rich shale with a thickness greater than 20 m is only distributed in several synclines and Chishui terrestrial basins (Cao et al., 2022). The burial depth of this organic-rich shale in the Chishui terrestrial basin is greater than 4000 m (Fig. 4b), which can be selected as a "sweet spot" for deep to ultra deep shale gas exploration and development.

The Dawuba Formation has achieved breakthroughs in industrial airflow. Its organic-rich shale is mainly developed in the center of the aulacogen (Fig. 5c). Several wells in the center of the aulacogen have achieved good gas display (Lu et al., 2021), and thus this area is a favorable area for the shale gas exploration of the Dawuba Formation.

The exploration level of the Longtan and Liangshan formations is relatively low, and more basic geological research work is needed to select favorable areas.

7. Conclusions

Prospective shale gas reservoirs in Guizhou Province include marine shales and marine-continental transitional shales. The main marine shales are the Niutitang, Wufeng-Longmaxi, and Dawuba organic-rich shales, while the main marine-continental transitional shales include the Liangshan and Longtan organic-rich shales. These marine organic-rich shales were generally deposited under anoxic conditions, and are characterized as siliceous-rich lithofacies (including siliceous shale lithofacies and argillaceous-rich siliceous shale lithofacies), and are type I organic matter dominated with strong brittleness. In contrast to the marine organic-rich shales, the marine-continental transitional organic-rich shales were most likely deposited under dysoxic to oxic conditions, and they are generally characterized as argillaceous-rich lithofacies (including argillaceous shale lithofacies, silica-rich argillaceous shale lithofacies, and argillaceous/siliceous mixed shale lithofacies), and is type III organic matter dominated with weak brittleness. Of the five organic-rich shales, the Niutitang and Wufeng-Longmaxi organic-rich shales are classified as over-mature shales, and the Dawuba, Liangshan, and Longtan organic-rich shales are classified as highly mature to over-mature shales. The relationships between the sedimentary environment, the lithofacies, and the reservoir properties are significant and can guide shale gas exploration and development. However, more research on these relationships is needed in the future.

The spots with siliceous rock floor on the western edge of the Xuefeng uplift is a favorable area for future exploration of shale gas in the Niutitang organic-rich shale. The Chishui terrestrial basin is faverable area for shale gas expolation and development of the Wufeng-Longmaxi organic-rich shale. The center of the aulacogen is a favorable area for the shale gas exploration of the Dawuba Formation. More basic geological research work is needed to select favorable areas for the Liangshan and Longtan organic-rich shales.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the National Natural Science Foundation Project of China (Nos. 42002166, 42162016, 42063009), Guizhou Provincial Fund Project (No. ZK[2020]YIBAN106, (2022)ZD005, [2020]4Y037), and Geological Exploration Fund Project of Guizhou Province (No. 52000021MGQSE7S7K6PRP).

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