Chemical characteristics of Middle Permian formation water and hydrocarbon preservation conditions in Northwest Sichuan

C L Yang¹², Z Y Xie¹²*, S Q Pei³, J Y Guo¹²*, L Zhang¹², C Y Dong¹, A S Hao¹², C X Yang³, and Z X Liu⁴

¹ Petrochina Research Institute of Petroleum Exploration and Development, Beijing, 100083, China.
² Key Laboratory of Gas Reservoir Formation and Development, CNPC, Langfang, 065007, China.
³ Geological Institute of Northwest Sichuan Southwest Oil and Gas Field Branch, PetroChina, Jiangyou, Sichuan 643000, China
⁴ CNPC Economics & Technology Research Institute, Beijing 100724, China.

*Corresponding author’s e-mail address: gijy_17711224@petrochina.com.cn, xiezengye69@petrochina.com.cn

Abstract: The analysis of the chemical characteristics of the Middle Permian formation water in 10 wells in the northwest of Sichuan Basin indicates that: the TDS of the Middle Permian formation water in Northwest Sichuan increases longitudinally with the burial depth of the formation, and the formation water is mainly of CaCl₂ type (Surin classification), Cl-Na-Ca type and Cl-Ca-Na type (Shukarev classification). The rNa⁺/rCl⁻ and rSO₄²⁻*100/rCl⁻ of the formation water are 0.05-0.95 and 0-5 respectively, reflecting strong water-rock interaction and strong sealing conditions. The analysis of the chemical characteristics of formation water and the preservation conditions of oil and gas shows that the overall preservation conditions of the Middle Permian in Northwest Sichuan are good, most of which is located in the “preservation zone”; longitudinally, the preservation conditions of Qixia Formation are better than those of Maokou Formation; areally, the preservation conditions of Shuangyushi and Jiulongshan regions are good; the sealing property of the strata in Hewanchang region is poor.

1. Introduction
Oil, gas, and water have a close relationship and strong interaction during the development of geological history. Lots of hydrogeological research results of oil and gas fields indicate that formation water directly participates in and records the evolution process of geological bodies during the process of the generation, migration and accumulation of oil and gas as well as late transformation and destruction, and the geochemical characteristics of formation water are direct record results[1]. The chemical characteristics of formation water in carbonate reservoirs are particularly important. The dissolution of carbonate rocks by formation water plays a vital role in the formation of reservoirs and the preservation of gas reservoirs[2-3]. Therefore, the preservation conditions of oil and gas can be discussed through the study of the geochemical properties of formation water.
There are more than 20 pay zones from Sinian to Jurassic in Sichuan Basin longitudinally\cite{4}. The exploration of the Middle Permian in Sichuan Basin began in the 1950s. The Middle Permian gas reservoirs discovered in early exploration are mainly concentrated in South Sichuan, and are dominated by fractured gas reservoirs and fracture-vug type limestone gas reservoirs\cite{5}. Since 2014, many wells including well ST1, well ST3, etc. in Qixia Formation in Northwest Sichuan have been tested in the Middle Permian and have obtained high production gas flows, showing the good exploration prospects of the Middle Permian in Northwest Sichuan. At present, there are few studies of natural gas preservation conditions in the Middle Permian in Northwest Sichuan from the perspective of the chemical properties of formation water. The author has discussed the vertical and transverse distribution characteristics of formation water using the type, TDS, rNa+/rCl-, and rSO4^2-*100/rCl of formation water as evaluation parameters, and has analyzed their relationships with oil and gas preservation on the basis of the formation water test analysis of more than 10 Middle Permian wells in Northwest Sichuan.

2. Regional geology overview
The research area, located in the northwest of Sichuan Basin (Figure 1), is surrounded by several structural belts, where faults are developed\cite{6, 7}. The research area mainly includes the north section of Longmenshan thrust nappe structure belt, the north section of the foreland thrust detachment structure belt, and the north section of the foreland fold belt. Longmenshan thrust belt in Northwest Sichuan has experienced multistage foreland basin formation—extinction processes during the geological history, and is now a well-known thrust nappe belt with a huge topographic height difference\cite{8}. During the Middle Permian, Sichuan Basin experienced 2-3 transgressions and slow regressions, and was in a platform or gentle slope environment as a whole\cite{9}. Northwest Sichuan is affected by multi-phase tectonic movements, and plentiful developed faults lead to a close relationship between the development of Middle Permian carbonate reservoirs and the geochemical properties of formation water, which is an important basis for the study of oil and gas preservation conditions.

![Figure 1. Distribution of Middle Permian gas reservoirs and sampling wells in Northwest Sichuan](image)

3. Chemical characteristics of formation water
The geological parameters that can be used to evaluate oil and gas preservation conditions mainly include the type, TDS, hydrodynamic conditions, and hydrochemical conditions of formation water.
Hydrogeological conditions and the sealing conditions of strata are judged according to the related parameters of formation water, and then the preservation conditions of oil and gas are judged.

3.1. Water type
The main cations in formation water are Na\(^+\), K\(^+\), Mg\(^{2+}\), and Ca\(^{2+}\), and the main anions are Cl\(^-\), SO\(_4^{2-}\), HCO\(_3^-\), etc. According to the relationship between ion concentrations, the classification of hydrochemical characteristics can be carried out. Typical formation water classification methods include Surin classification and Shukarev classification\(^{[10]}\) (Table 1). By Surin classification, formation water is divided into four types such as NaHCO\(_3\), Na\(_2\)SO\(_4\), MgCl\(_2\), and CaCl\(_2\). The characteristic changes of "NaHCO\(_3\)→Na\(_2\)SO\(_4\)→MgCl\(_2\)→CaCl\(_2\)" in Surin classification reflect the process of the preservation environment from opening to transition to closure of strata. Shukarev classification is relatively more stable in the sense of phase. Shukarev classification is mainly aimed at CaCl\(_2\) type in Surin classification, and formation water is further divided according to the concentration of ions such as Cl\(^-\), Na\(^+\) and Ca\(^{2+}\). The characteristic changes of “Cl\(^-\)-Na→Cl\(^-\)-Na→Cl\(^-\)-Ca→Cl\(^-\)-Ca-Na” in Shukarev classification reflect that the degree of metamorphism of formation water is further enhanced\(^{[1,10]}\).

| Closing degree | Opening type | Transition type | Closed type |
|----------------|--------------|----------------|-------------|
| Surin type     | NaHCO\(_3\)→Na\(_2\)SO\(_4\)→MgCl\(_2\)→CaCl\(_2\) | CaCl\(_2\) | CaCl\(_2\), part of Na\(_2\)SO\(_4\) |
| Shukarev type  | Cl-Na→Cl-Na-Ca→Cl-Ca-Na | Cl-Ca-Na | Cl-Ca-Na |
| Preservation conditions | Poor | Relatively poor | Relatively good |

| Strata                  | Qixia Fm. | Maokou Fm. |
|-------------------------|-----------|------------|
| TDS/(g/L\(^{-1}\))      | 142.3     | 68.3       |
| [Cl\(^-\)]/(g/L\(^{-1}\)) | 28.4     | 16.4       |
| [HCO\(_3^-\)]/(g/L\(^{-1}\)) | 0.8     | 0.5        |
| [SO\(_4^{2-}\)]/(g/L\(^{-1}\)) | 0.084   | 0.4        |
| [Ca\(^{2+}\)]/(g/L\(^{-1}\)) | 7.3     | 1.9        |
| [Mg\(^{2+}\)]/(g/L\(^{-1}\)) | 1.6     | 0.2        |
| [K\(^+\)+Na\(^+\)]/(g/L\(^{-1}\)) | 2.7     | 3.8        |
| PH                      | 6.48     | 6.27       |
| Formation water type    | CaCl\(_2\)| CaCl\(_2\), part of Na\(_2\)SO\(_4\) |

According to the analysis result from 10 wells in the research area(Table 2), the formation water type is mainly CaCl\(_2\) type (Cl-Na-Ca type and Cl-Ca-Na type by Shukarev classification) by Surin classification; in addition, there is a small quantity of Na\(_2\)SO\(_4\) type formation water. The type of formation water in Qixia Formation in Shuangyushi, Longgang, etc. is CaCl\(_2\) type, and the type of formation water in Maokou Formation in Hewanchang region is mainly Na\(_2\)SO\(_4\) type. By Shukarev
classification, Cl-Na-Ca type and Cl-Ca-Na type predominate, and there is a small quantity of Cl-Na type formation water. Comprehensively considering the two classification methods, closed formation water in the Middle Permian in Northwest Sichuan accounts for an extremely high proportion; except for Maokou Formation in Hewanchang region, the sealing property is good, and the overall opening degree of strata is relatively low.

3.2. TDS
TDS (Total dissolved Solid) refers to the content of inorganic minerals per unit volume of formation water, in the case of good preservation conditions of formation water, the TDS is generally high; on the contrary, the TDS is low\textsuperscript{[11]}. The TDS of the Middle Permian formation water in Northwest Sichuan is generally 13-150g/L, and in few cases, the TDS of formation water is less than 10g/L or higher than 150g/L. The TDS of overall formation water tends to increase with the increasing depth (Figure 2). However, during the tectonic evolution of Sichuan Basin, the phenomenon of formation water desalination will occur in local regions due to the cutting of strata by faults or the uplifting and denudation of strata. For example, the TDS of formation water in Maokou Formation is obviously low. This is because at the end of the Middle Permian, Maokou Formation was exposed on the surface due to structural uplifting caused by tectonic movements, and the exposure time was up to 1-3 Ma\textsuperscript{[12]}, resulting in a certain degree of desalination of formation water.

\textbf{Figure 2.} Trend chart of the change of the Middle Permian formation water TDS with depth in Northwest Sichuan

3.3. Hydrodynamic conditions (open/closed environment)
Hydrodynamic conditions mainly refer to the sealing strength of strata. The degree of water-rock reaction is usually characterized by the content and relative proportion of ions in formation water. The rNa\textsuperscript{+/}\textasciitilde Cl\textsuperscript{−} can characterize the degree of groundwater metamorphism and the intensity of hydrodynamic alternation. The larger the rNa\textsuperscript{+/}\textasciitilde Cl\textsuperscript{−}, the higher the degree of groundwater metamorphism and the more obvious the influence of infiltration water\textsuperscript{[13]}. The rNa\textsuperscript{+/}\textasciitilde Cl\textsuperscript{−} value of modern seawater is about 0.85. After alternate cation adsorption and strong water-rock interaction, the rNa\textsuperscript{+/}\textasciitilde Cl\textsuperscript{−} value of sedimentary water becomes small, and is basically less than 0.85. The rNa\textsuperscript{+/}\textasciitilde Cl\textsuperscript{−} value of groundwater affected by atmospheric precipitation leaching is greater than 1.0. Therefore, if the metamorphism coefficient of the formation water is less than 0.85, it indicates that the formation water has undergone condensation and metamorphism, which corresponds to good preservation conditions; on the contrary, it corresponds to poor preservation conditions. The metamorphic coefficient of the Middle Permian formation water in Northwest Sichuan is 0.05-0.95, and in few cases, it is greater than 1, indicating that the Middle Permian
formation water in Northwest Sichuan has mainly experienced alternate cation adsorption and strong water-rock interaction and the concentration and metamorphism of the formation water are strong. The metamorphic coefficient of only a small part of formation water samples distributed in Hewanchang region is more than 0.85, and the formation water belongs to typical infiltration water and may have been subjected to atmospheric precipitation leaching. From the perspective of longitudinal changes, the samples with metamorphic coefficient more than 0.85 are mainly from Maokou Formation, the overall average metamorphic coefficient of the formation water in Qixia Formation and Maokou Formation is 0.21 and 0.34 respectively, and the metamorphic coefficient tends to decrease with the increasing burial depth.

3.4. Hydrochemical conditions (oxidizing/reducing environment)

The hydrochemical conditions of formation water mainly refer to an oxidizing/reducing environment, which mainly depends on the recharge conditions of oxidizing agents or reducing agent in strata. The oxidizing agents in shallow formation water are mainly dissolved oxygen in the water; except for shallow layers, the main oxidizing agent is SO$_4^{2-}$. Organic matter is the most common and strongest reducing agent in strata. The dynamic balance relationship between the quantity of oxidizing agents and that of reducing agents determines the hydrochemical conditions of formation water. The $r$SO$_4^{2-}$×100/rCl characterizes the intensity of de-sulfate action and is an important indicator reflecting the oxidizing/reducing environment of formation water. When the action is complete, the coefficient is 0, indicating a good degree of sealing and strong water-rock interaction. The $r$SO$_4^{2-}$×100/rCl of the Middle Permian formation water in Northwest Sichuan is mostly 0-5, and in few cases, it is more than 3, indicating that the formation water is mostly in a reducing ~ weak reducing environment; that is, the strata have good preservation conditions and strong sealing ability. The $r$SO$_4^{2-}$×100/rCl of only the formation water samples distributed in Hewanchang region is mostly larger than 5, belonging to a weak oxidizing ~ oxidizing environment and showing poor preservation conditions. Longitudinally, the samples with de-sulfate coefficient more than 1 are mainly from Maokou Formation, the overall average de-sulfate coefficient of the formation water in Qixia Formation and Maokou Formation is 0.33 and 1.73 respectively, and the de-sulfate coefficient tends to increase with the increasing burial depth.

Based on the above analysis of the type, TDS, metamorphic coefficient, de-sulfate coefficient, etc. of formation water, as the burial depth increases, the overall metamorphic degree of the formation water in Northwest Sichuan increases and the sealing property of the strata gets better. Except that the local regions such as Hewanchang etc. are unfavorable for the preservation of oil and gas due to being affected by atmospheric leaching water, most of the remaining regions are favorable for the preservation of oil and gas.

4. Relationship between chemical properties of formation water and oil and gas preservation

Formation water has experienced various actions such as dissolution, alternate cation adsorption, diffusion, concentration, etc. during the evolution of geological history. The combination of multiple actions determines the geochemical characteristics of formation water. According to the research on the chemical characteristics of the Middle Permian formation water in Northwest Sichuan, the chemical characteristics of the Middle Permian formation water in Northwest Sichuan are controlled mainly by the opening or closing state of the geological environment, and indirectly by the intensity of tectonic activities. Maokou Formation in Northwest Sichuan is in the Hercynian extensional cycle and close to a large unconformity surface, and is obviously affected by shallow water infiltration. The formation water in Maokou Formation is different from that in Qixia Formation to some extent in terms of TDS, metamorphic coefficient reflecting hydrodynamic alternating intensity and de-sulfate coefficient reflecting the oxidizing-reducing conditions of water medium. The relationship between the chemical characteristics of formation water and oil and gas preservation conditions is judged by the metamorphic coefficient and de-sulfate coefficient of formation water (Figure 3), which can more intuitively reflect the oil and gas preservation environment of the Permian strata in the research area. This judgment method divides oil and gas preservation conditions into four types such as preservation zone, transition
zone, weak preservation zone and non-preservation zone, which can be used as important indexes for the evaluation of oil and gas preservation conditions.

![Figure 3](image)

**Figure 3.** Judgment chart of Middle Permian formation water-oil and gas preservation conditions in Northwest Sichuan (Discriminant criteria according to Ref\(^\text{[1]}\).

The preservation conditions of the Middle Permian Qixia Formation in Northwest Sichuan are good; the projection points of metamorphic coefficient-de-sulfate coefficient are all in the preservation zone, mostly belonging to Shuangyushi region; Maokou Formation has certain differences areally; the preservation conditions of Jiulongshan and Shuangyushi regions are good; Hewanchang region is mostly in the weak preservation zone and non-preservation zone.

5. **Conclusions**

1. The TDS of the Middle Permian formation water in Northwest Sichuan is 13-150g/L. By Surin classification, the formation water type is mainly CaCl\(_2\) type (Cl-Na-Ca type and Cl-Ca-Na type by Shukarev classification), and the type of formation water in Hewanchang region is Na\(_2\)SO\(_4\) type. As the burial depth increases longitudinally, the TDS of formation water increases, the degree of metamorphism of formation water is enhanced, and the sealing property of strata gets better.

2. The \(r\text{Na}^+/r\text{Cl}^-\) of the Middle Permian formation water in Northwest Sichuan is 0.05-0.95, and in few cases, it is greater than 1, indicating that the formation water has experienced strong alternate cation adsorption and strong water-rock interaction. The \(r\text{SO}_4^{2-}×100/r\text{Cl}^-\) is mostly 0-5, and in few cases, it is more than 3, indicating that the Middle Permian strata are mostly in a reducing-weak reducing environment and have strong sealing ability.

3. According to the comprehensive judgment of the conditions of oil and gas preservation by formation water, it is deemed that areally the preservation conditions of Shuangyushi and Jiulongshan regions are good, and the formation water type is CaCl\(_2\) type; the strata in Hewanchang region have poor sealing property, and the reservoirs is mainly composed of Na\(_2\)SO\(_4\) type formation water in an open and transitional environment.

**Acknowledgements**

This study is funded by the National Science & Technology Major Project (No. 2016ZX05007-003), the Science and technology project of CNPC (No. 2019B-0605), the Science and technology project of CNPC (No. 2019B-0604).
References
[1] Deng D P. 2015 Marine Origin Petroleum Geology. 20(01)62-70.
[2] Yang C L, Xie Z Y, Dong C Y, et al. 2018 China Offshore Oil and Gas. 30(005)55-62.
[3] Chen P Y, Duan X M, Guo L N, et al. 2017 China Offshore Oil and Gas. 29(2)46-52.
[4] Yang G, Li G H, Li N, et al. 2016 Natural Gas Industry. 36(11)1-11.
[5] Ma X H, Yang Y, Wen L, et al. 2019 Petroleum Exploration and Development. 46(1)1-13.
[6] Jia D, Chen Z X, Jia C Z, et al. 2003 Geological Journal of China Universities. 9(3)402-410.
[7] Deng K L, Yu F L. 2005 Oil & Gas Geology. 26(2)214-219.
[8] Hu S Q, Guo W P, Tong C G. 2001 Journal of Southwest Petroleum University. 23(2) 5-8.
[9] Shen H, Wang H, Wen L, et al. 2016 Natural Gas Industry. 36(8)11-21.
[10] Hanor J S. 1994 Geological Society London Special Publications. 78(1)151-174.
[11] Shen L L, Li X, Wei Y T. 2006 Guangdong Trace Elements Science. 13(9)56-60.
[12] Tang D H, Xiao D, Tan X C, et al. 2016 Petroleum Exploration and Development. 43(5): 689-695.
[13] Jia H P, Xu S H. 2005 Journal of Chongqing University of science and technology. 7(2)12-15.