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Geochemical characteristics and origin of the formation water of the Saline Lake Basin: a case study of the Quaternary Qigequan Formation in the Sanhu Depression, Qaidam Basin

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Abstract

Clarifying the geochemical characteristics of formation water and its origin is conducive to clarifying the gas migration path, elaborating the law of gas migration and accumulation, and further predicting the favourable area of gas accumulation. Taking Quaternary formation water from the Tainan-Sebei area of the Sanhu Depression as the research object, the chemical characteristics and origin of the region are clarified using anion analysis, cation analysis, hydrogen isotope analysis, oxygen isotope analysis and so on. The results are as follows. (1) The formation water in the study area has a high total dissolved solids (TDS) content and is mainly type IV and V of $CaCl_2$. (2) Low $r(Na^+)/r(Cl^-)$, low desulfurization coefficient, high $r(Ca^{2+})/r(Mg^{2+})$ and high indices of base exchange indicate that the Qigequan Formation is in a stagnant zone, which is beneficial for the accumulation and preservation of biogenic gas. (3) Due to albitization and water–rock reactions, the formation water is rich in Ca^{2+}, poor in Na^+ and poor in Mg^{2+}. (4) The formation water in the study area originates from the glacial meltwater of the Kunlun Mountains, which converts into groundwater and seeps into the formation along the piedmont slope zone. In the process of groundwater infiltration and convergence, many salt substances in the formation are dissolved, resulting in a gradual increase in TDS. Then, the formation water with a high TDS migrates to the anticline in the northern part of the depression and is finally trapped in the formation.

Keywords Formation water characteristics, Formation water origin, Sanhu Depression, Saline Lake Basin, Quaternary

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Introduction

Formation water refers to the comprehensive reflection of hydrogeology, fluid-rock interactions, fluid flow and mixing in the burial stage of the whole basin (Land and Macpherson 1989; Sun and Liu 2001; Fisher and Boles 1990; Hanor 1994; Hou et al. 2002; Li et al. 2003a, 2003b). The Sanhu Depression is the largest Quaternary biogenic gas field in China, and the Sebei 1, Sebei 2 and Tainan gas fields have been discovered in it (Cheng et al. 2009). The chemical migration and exchange of elements between the formation water and the oil and gas in the basin have been ongoing for a long time. However, the unclear geochemical characteristics of the formation water, unclear formation water origin and serious outflow of gas wells restrict the further exploration and development of biogenic gas in this area. Therefore, clarifying the geochemical characteristics and genesis of the formation water is conducive to clarifying the migration path of gas, elaborating the law of gas migration and accumulation, and further predicting favourable target areas. Therefore, it is highly important to study the geochemical characteristics and genesis of formation water to guide the exploration and development of gas fields.

Research on the chemical characteristics of formation water has focused on two main aspects: the classification of formation water and the distribution characteristics of formation water. Many previous studies have been carried out on the classification of formation water. Palmer grouped anions and cations and then obtained Palmer characteristic values according to the order of chemical affinity of the anions and cations. Finally, the oil field water was classified according to its characteristic values (Palmer 1911). Sulin proposed a division scheme for formation water based on the genesis, in which formation water was divided into four types according to the equivalent concentration ratio of each ion (HCO^{3-}, SO_4^{2-}, Cl^-, Ca^{2+}, Na^+ and Mg^{2+}) in the formation water (Sulin 1935; Ostroff 1967). Schoeller classified formation water into 6 major water types, 4 water groups and 3 water classes based on the dissolved chloride content (Schoeller 1956; Yang 1993; Saka et al. 2013). Based on Sulin's classification, Bojarsk divided $CaCl_2$ formation water into I, II, III, IV and V by Na^+/Cl^- (Bojarski 1970). Liu Jimin divided formation water into two water types and six water classes based on the ionic chemical index of field water, combined with the structure and reservoir characteristics (Liu 1982). Liu Chongxi and Sun Boxiong proposed a classification method for the formation water according to the characteristics of the water in various oil fields. The chemical composition of the formation water in China was divided into 6 types and 3 groups according to soluble gaseous hydrocarbons, main ions, salts and total dissolved solids (TDS) in the water (Liu and Sun 1988). Gao Xixing proposed a multivariate stepwise discriminant analysis method to further supplement and modify Sulin's classification (Gao 1994). As there are many factors to consider in the classification of formation water, there is currently no unified classification standard. Although domestic scholars have proposed several subsequent classification methods according to the characteristics of the formation water in China, Sulin's classification is the most widely used because it reflects both the ion concentration and origin. Research on the distribution characteristics of formation water has focused mainly on vertical distribution characteristics. Sulin proposed the vertical zonation method for formation water, which can be divided into the active exchange zone, delayed exchange zone, and stagnant zone from top to bottom according to the strength of the connection between the formation water and surface water (Sulin 1935, 1946). In the shallowest active exchange zone, the formation water and surface water are basically in free contact, and the water type of the formation water is dominated by the $NaSO_4$ type. In this zone, it is poorly preserved, and gas reservoirs are vulnerable to damage. In the deepest stagnant zone, surface water and formation water basically cannot be connected, and the water type of the formation water is dominated by the $CaCl_2$ type. In this zone, the gas preservation conditions are good. The delayed exchange zone is between the above two zones, the upper part of which is dominated by the $NaSO_4$ type, and the lower part is dominated by the $CaCl_2$ and $MgCl_2$ types. Based on Sulin's formation water zone, the vertical zonation of formation water chemistry was studied by combining the distribution characteristics of the chemical parameters of the formation water and the genetic mechanism of the formation water (Collins 1980; Zeng et al. 2008; Lou et al. 2009). Therefore, the vertical zonation of formation water not only reflects the vertical characteristics of formation water but also reflects the concentration and desalination at different burial depths during the evolution of formation water.

The Sanhu Depression of the Qaidam Basin is an important area where biogenic gas is produced in China. Since the discovery of the Yanhu gas field, the first biogenic gas field in 1958, three major biogenic gas fields with great resource potential (Sebei 1 (1964), Sebei 2 (1975) and Tainan (1987)) have been successively discovered in the Quaternary Qigequan Formation. In recent years, a large number of drillings have been carried out around gas fields, but no breakthroughs have been made; thus, biogenic gas exploration has encountered a bottleneck. In terms of biogenic origin, early studies suggested that biogenic gas was generated by diagenesis through biochemical action and was pooled with free phases in the near-vertical direction (Dang et al. 2008), which has been verified in terms of sedimentology and isotopes (Pang et al. 2005; Dang et al. 2008). However, through comparative analysis of the hydrogeological conditions of gas fields, it was found that biogenic gas in the Sanhu Depression first migrated horizontally in the form of water-soluble gas for a long distance and then migrated vertically in a favourable position as a free phase to form reservoirs (Li et al. 2003a). This accumulation pattern also occurred on the southern margin of the Alberta Basin, Michigan Basin, and other large biogenic gas fields (Littke et al. 1999; Shurr and Ridgley 2002). Other researchers believe that the Quaternary biogenic gas in the Sanhu Depression migrated horizontally into the gas reservoir after formation and that vertical migration did not occur (Zhang et al. 2003). Therefore, the origin of biogenic gas in the Sanhu Depression is still controversial. Additionally, the hydrogeological conditions in the Sanhu Depression are complicated, and the generation, migration and accumulation of biogenic gas are closely related to the formation water. However, there are few special studies on the formation water of the three gas fields, especially on the hydrogeochemical origin of the formation water. Therefore, clarifying the hydrochemical composition of the formation water and identifying its origin and evolution using isotopic hydrology help understanding the genesis of biogenic gas in saline lake basins and scientifically support the exploration of biogenic gas in the Sanhu Depression.

Geological settings

Sedimentary and stratum characteristics

According to the stratigraphic sequence revealed by drilling and earthquakes, the Neogene Shizigou Formation and the Quaternary were deposited from bottom to top in the Sanhu Depression (Fig. 1). According to the regional geological drilling data and well logging analysis, most wells in the Sanhu Depression encountered only the Quaternary Qigequan Formation, and a small number of wells encountered the Shizigou Formation.

The Neogene Shizigou Formation is mainly composed of gray and yellowish-gray conglomerate at the edge of the basin and a set of grayish-brown and yellowish-gray argillaceous rock deposits rich in gypsum and carbonaceous mudstone at the center of the basin. During the late Himalayan movement and neotectonic movement after the deposition of the Shizigou Formation, the western Qaidam Basin experienced strong tectonic activity (Ao et al. 2022; Hao et al. 2022; Wu et al. 2023). The residual thicknesses of the western and northern margins of the Qaidam Basin are small due to uplift and denudation. The formation of parts close to the piedmont and the structural high parts are missing. The distribution area is approximately 20,000 km^2, and the maximum sedimentary thickness is 1400 m.

The Quaternary strata of the Sanhu Depression start from the Jianshishan and Jianshan structures in the west and extend to North Huoxun Lake in the east, the Lingjian Fault in the north, and the front of the Kunlun Mountains in the south, covering an area of approximately 41,800 km^2. Due to the influence of late Himalayan movement and neotectonic movement, the southern and northern margins of the basin were uplifted, and the Qigequan Formation in the northern and western parts of the basin experienced denudation thinning or loss of thickness to varying degrees (Dang et al. 2008; Cheng et al. 2021). According to the drilling data, the lithology is mainly light brown-gray, light gray, gray mudstone and sandy mudstone, mixed with the same color siltstone and argillaceous siltstone, and a certain amount of carbonaceous mudstone. At present, this formation is the most important gas-producing and developing interval in the basin, with a cumulative thickness of 1500–2500 m. Based on the electrical characteristics, this interval can be further divided into 11 standard layers (K0-K13) (Fig. 1).

Tectonic characteristics

The Sanhu Depression is located in the southeastern Qaidam Basin. Due to the late Himalayan movement, the depositional center of this basin moved continuously from west to east and migrated to the Sanhu Depression during the Quaternary. The whole exploration area, bounded by the Chuanxingqiu structure, northern and southern Huobuxun Lake, the Beiling Mound and the Kunlun Mountains, is approximately 37,000 km^2. It can be further divided into 3 s-order structural units (the north slope, central sag and south slope) (Fig. 2), and all the gas fields are distributed on the north slope (Pang et al. 2005; Shuai et al. 2013; Chen et al. 2015).

Methods and materials

Samples

One hundred and forty-two formation water samples from 127 wells in the Tainan-Sebei area of the Sanhu Depression were taken (well locations are shown in Fig. 2). Anion analysis, cation analysis, hydrogen and oxygen isotope analysis and other experiments were carried out.

Analysis of Anions and Cations

Anion and cation analyses were completed at the China University of Petroleum (Beijing). The water samples were filtered through a 0.45 μm filter membrane. Anion analysis was performed using the 930T ion

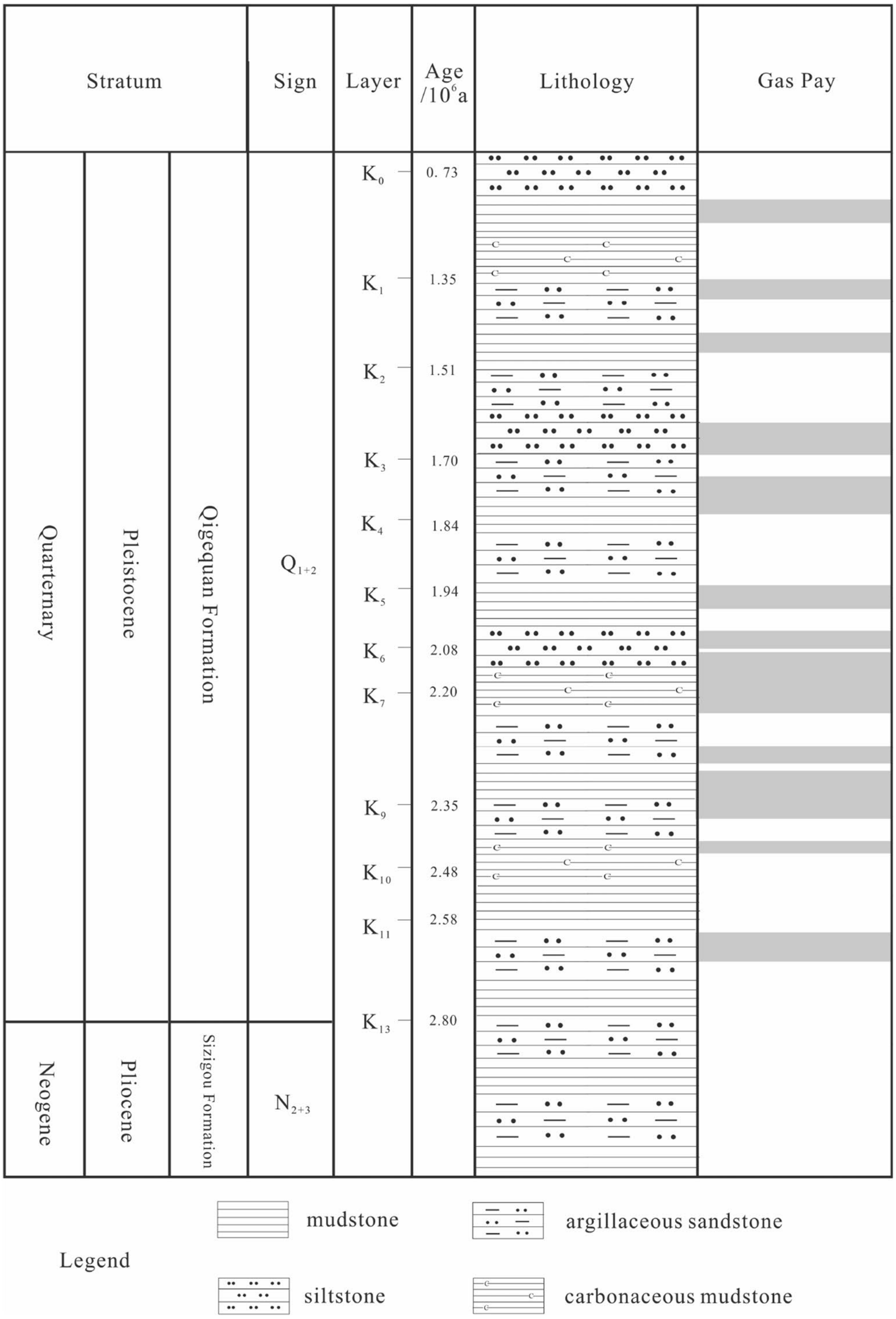

Fig. 1 Stratigraphy and lithology profile of the Sanhu Depression

chromatograph. HCO_3^- and CO_3^{2-} were tested using a T90 potentiometric titrator. Cation analysis was performed by iCAP7400 inductively coupled plasma optical emission spectroscopy (ICP–OES). The collected signals were processed by Qtegra Intelligent Scientific Data Solution (ISDS) software to obtain the content of each anion.

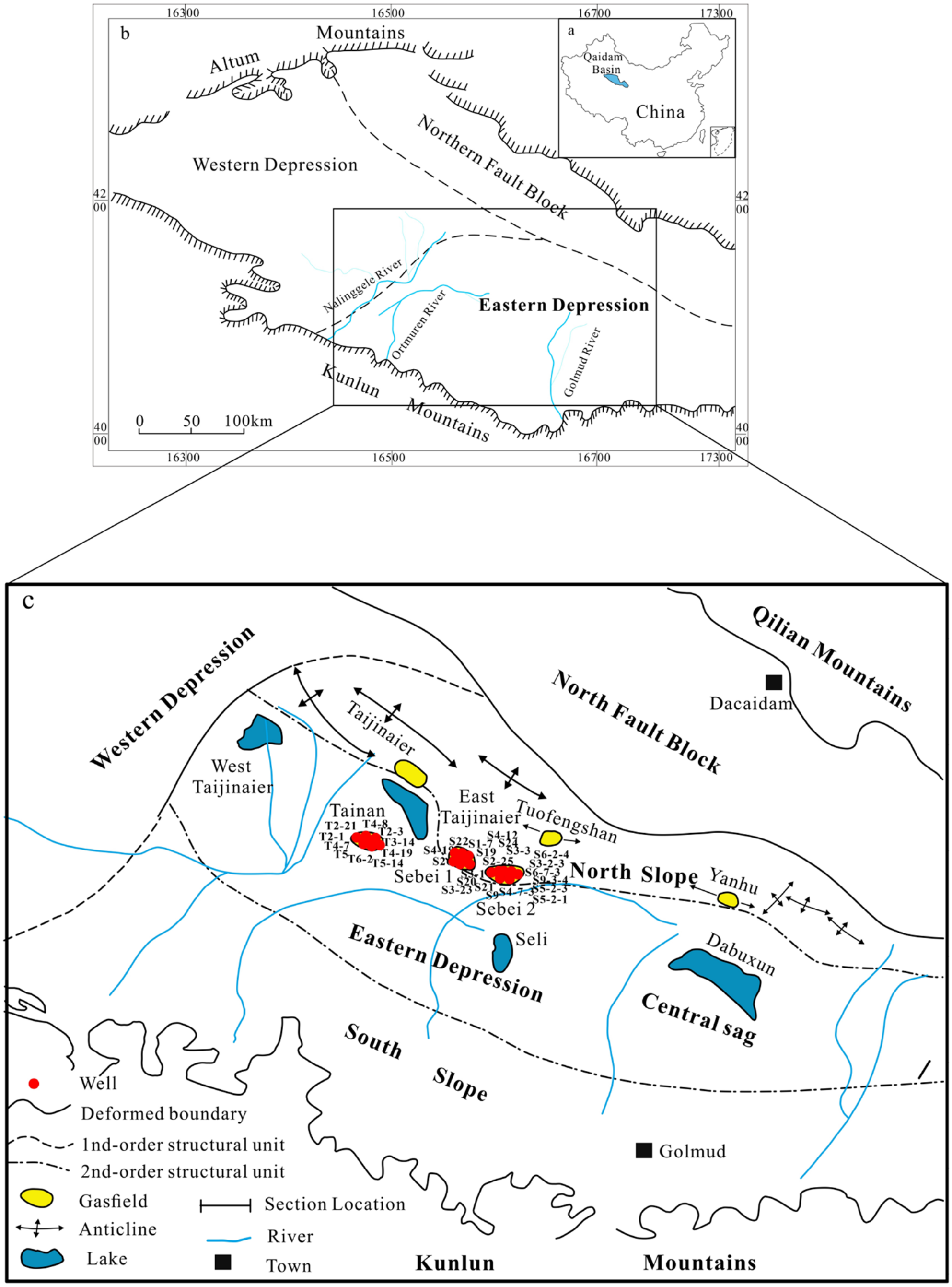

Fig. 2 Regional structure map of the Sanhu Depression in the Qaidam Basin (**a** the location of the Qaidam Basin in China; **b** the location of the study area in the Qaidam Basin; **c** the structural map of the Sanhu Depression.)

Hydrogen and oxygen isotope analysis

Hydrogen and oxygen isotopes are very sensitive to evapotranspiration and can be compared to trace water back to its source. Hydrogen and oxygen isotope analysis was performed at the China University of Petroleum (Beijing) using a MAT-253 isotope mass spectrometer with V-SMOW as the reference material.

δD was determined by the zinc reduction method (Coleman et al. 1982). The water samples were passed under vacuum through a reactor containing zinc pellets and silica heated to 400 °C. The hydrogen produced was collected with activated carbon under liquid nitrogen freezing and analyzed by mass spectrometry isotope analysis.

$\delta^{18}O$ was determined by the carbon dioxide-water equilibrium method (Horibe et al. 1973). The water samples were brought to achieve oxygen isotope exchange equilibrium with CO_2 of known isotopic composition at 25 °C. After dehydration by the refrigerant, the equilibrated CO_2 was collected by liquid nitrogen. Then, the oxygen isotopic composition was determined by mass spectrometry, and the $\delta^{18}O$ in the water samples was calculated.

Mineral composition

Fifty powdered samples were taken to measure the mineral composition. The mineral composition was determined at the China University of Petroleum (Beijing) using the Ultima IV X-ray diffractometer with Ni-filtered Cu Kα radiation operated at 40 kV and 30 mA. The scan step was 0.02, and the scanning range was 10–90°. Detectors and goniometers detect the intensity and position of diffraction lines and convert them into electrical signals using a computer to automatically record, analyze and process the data to obtain the contents of different minerals.

Geochemical characteristic parameters

The combined characteristics of various chemical parameters of the formation water reflect some characteristics of gas accumulation and preservation. Na^+, Cl^- and other ions are widely distributed in the formation water. Cl^- is stable, and Na^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} are sensitive to environmental changes, so their combination can be commonly used to reflect formation water characteristics. Common parameters of formation water include total dissolved solids (TDS), $r(Na^+)/r(Cl^-)$, desulfurization coefficient ($100\times r(SO_4^{2-})/r(Cl^-)$), $r(Ca^+)/r(Mg^{2+})$ and indices of base exchange (IBE).

Total dissolved solids (TDS)

TDS refer to the total amount of dissolved solid substances in water, including both inorganic and organic substances. TDS is often measured in parts per million (ppm). The dissolved solid substances in water include bicarbonate, chloride, sulfate, calcium, magnesium, sodium, and potassium (Xu and Mei 2006; Gong et al. 2010).

$r(Na^+)/r(Cl^-)$

The degree of metamorphism of the formation water can be reflected by $r(Na^+)/r(Cl^-)$. The higher the $r(Na^+)/r(Cl^-)$ is, the lower the metamorphism degree. In other words, the infiltration water affects the formation water more easily and further increases the difficulty of preserving the gas. In contrast, the smaller the value is, the greater the metamorphism degree, and the weaker the formation water is affected by infiltration water. Therefore, it is more favourable for the preservation of hydrocarbons (Wang et al. 2010, 2012).

According to $r(Na^+)/r(Cl^-)$, $CaCl_2$ water types can be further divided into 5 types (Table 1) (Lou et al. 2006; Jia et al. 2019; Wang et al. 2019).

Desulfurization coefficient ($100\times r(SO_4^{2-})/r(Cl.^-)$)

The desulfurization coefficient ($100\times r(SO_4^{2-})/r(Cl^-)$) can reflect the desulfurization intensity and the redox environment of the formation water. In a reducing environment, when organic matter is present, desulfurization bacteria can reduce SO_4^{2-} to H_2S, resulting in a decrease or disappearance of SO_4^{2-} in the formation water. Therefore, the smaller the coefficient is, the stronger the desulfurization effect of the formation water, and the stronger the environmental reducibility is, the better it is for gas preservation (Dou et al. 2010; Liang et al. 2013).

$r(Ca^+)/r(Mg.^{2+})$

$r(Ca^+)/r(Mg^{2+})$ can reflect the metamorphism degree of the formation water. The larger the value is, the greater the degree of metamorphism and the better the sealing of the formation (Liang et al. 2013).

Table 1 Classification of $CaCl_2$ water types and their significance (Bojarski 1970; Lou et al. 2006; Jia et al. 2019)

Type	$r(Na^+)/r(Cl^-)$	Petroleum geological significance
I	> 0.85	The water velocity is large and the hydrodynamics is active. Gas preservation conditions are poor. There are almost no gas reservoirs
II	0.75–0.85	The transition zone between the hydrodynamic zone of the sedimentary basin and the relatively stable static zone. The ability to preserve gas is poor
III	0.65–0.75	Gentle hydrodynamic conditions are conducive to the preservation of gas. Favourable environment for preservation of hydrocarbons
IV	0.50–0.65	The sealing condition is good for hydrocarbon accumulation. Favourable zone for hydrocarbon preservation
V	< 0.50	Slow or still, sealed remnants of ancient sea water. The most promising area for hydrocarbon accumulation

Indices of base exchange (IBE)

The IBE ($[Cl^- - (Na^+ + K^+)]/Cl^-$) is used to reflect the source of formation water and the degree of cation exchange between water and rocks (Johnson 1979; Rezaei et al. 2019). The larger the value is, the fewer cations in the water and the cations on the rock surface that are exchanged with each other, indicating better hydrocarbon preservation conditions.

Method of studying the evolution characteristics of formation water

To study the evolution characteristics of the formation water, the relationships between the concentrations of different ions in the formation water in the study area were analyzed. The sedimentary environment of the Tainan-Sebei area is mainly a river–lake environment, and the sedimentary facies are mainly delta and littoral-lacustrine. On this basis, the evolution process of the formation water is studied by combining the sea-river mixing line and evaporation line.

Results and discussion

Geochemical characteristics of the formation water

Total dissolved solids (TDS)

By counting 142 water samples, the TDS of the formation water is 3.41–231.78 g/L, with an average of 103.95 g/L and a median of 107.21 g/L. Most of the data are 35–140 g/L (Fig. 3). Additionally, 91.55% of the samples have TDS higher than 35 g/L (TDS of seawater) (Hitchon and Friedman 1969; Al-Malhy and Hodgkiess 2003; Scanlon et al. 2020), indicating that the formation has better gas preservation conditions. This is consistent with the conclusions (the TDS of the formation water has a positive correlation with the sealing property of the formation) obtained by previous studies (Liu 1982; Zeng et al. 2008; Lou et al. 2011).

Type of formation water

The formation water in the Tainan-Sebei area is mainly the $CaCl_2$ type (82.39%), followed by the $MgCl_2$ type (14.79%) and $NaSO_4$ type (2.82%) (Fig. 4). This suggests that the formation water is mainly located in the stagnant zone. In this zone, surface water and formation water are unable to interact (Sulin 1946; Krause et al. 2007; Wu et al. 2012; Jia et al. 2019; Wang et al. 2019), so the preservation conditions of gas are good.

The $CaCl_2$-type formation water in the Tainan-Sebei area is mainly type IV (83.80%) and type V (13.38%) (Fig. 5). This indicates that the Qigequan Formation in the study area has strong sealing ability and is in a

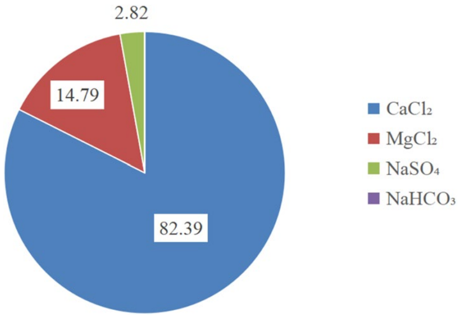

Fig. 4 Formation water type distribution in the Tainan-Sebei area. The formation water in the Tainan-Sebei area is mainly the $CaCl_2$ type, $MgCl_2$ type and $NaSO_4$ type

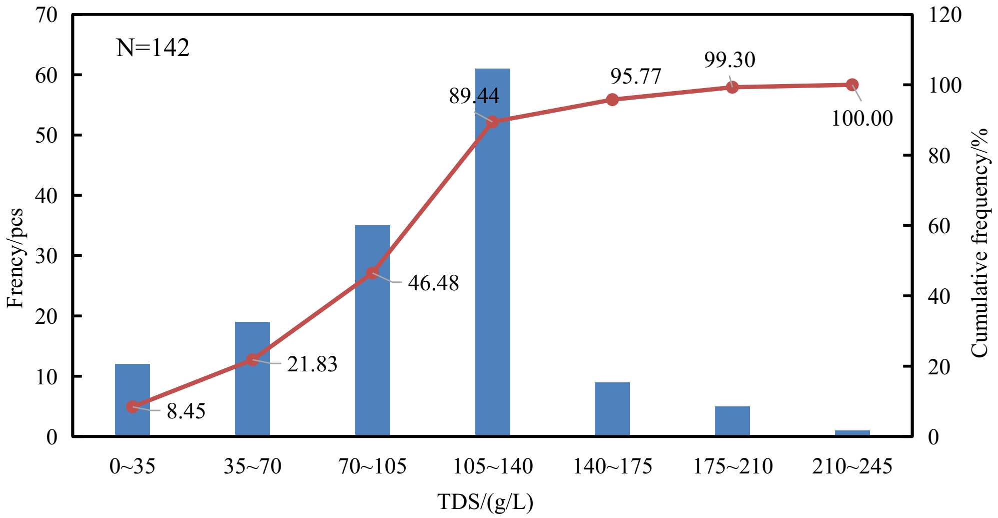

Fig. 3 Distribution of TDS in the Tainan-Sebei area. Most TDS values are 35–140 g/L, and 91.55% of the samples have TDS values higher than 35 g/L (TDS of seawater)

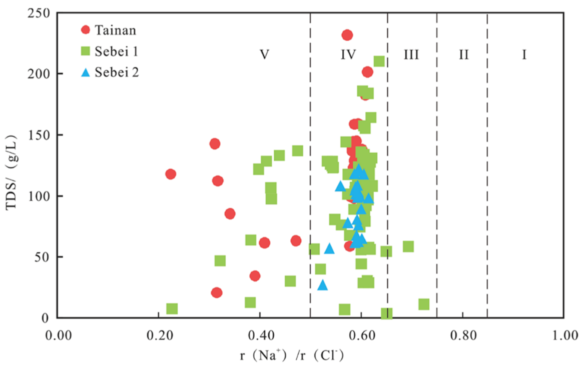

Fig. 5 Relationship between salinity and r(Na^+)/r(Cl^-) of formation water in the Qigequan Formation in the Sanhu Depression. The $CaCl_2$-type formation water of the Qigequan Formation in the Tainan-Sebei area is mainly type IV and type V

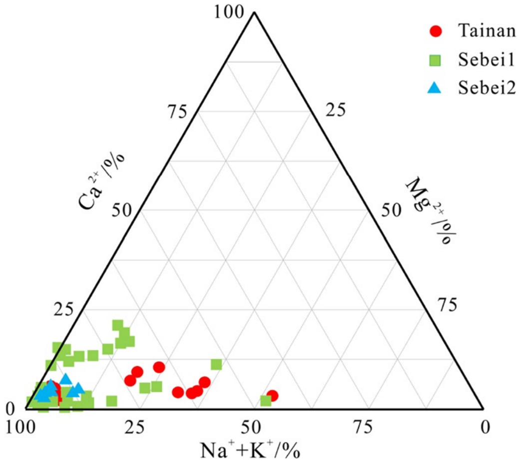

Fig. 7 Triangulation of formation water cation mass fraction in the study area

stagnant zone with good gas retention conditions that are conducive to hydrocarbon accumulation and biogenic gas generation and preservation (Additional file 1).

Ion composition

From high to low, the ion concentrations of the water are Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and HCO_3^-. The anions are mainly Cl^- (73.44%–99.83%), followed by SO_4^{2-} and very low amounts of HCO_3^- (0.09%–16.31%). This is because the bacteria reduce sulfate to sulfide in a confined environment, reducing the SO_4^{2-} and HCO_3^- contents in the formation water. The cations are mainly $Na^+ + K^+$ (most are 52.64–97.35%, and only two points are less than 50%), and Ca^{2+} and the amount of Mg^{2+} are relatively low (Figs. 6, 7).

In addition, the TDS of the formation water has a good correlation with the Cl^- and Na^+ concentrations (Fig. 8). This indicates that the TDS of the formation water is closely related to the concentration of evaporation or the dissolution of saline minerals (Zeng et al. 2008; Lou et al. 2011). The small difference in the ion content indicates that the late transformation effect and the interaction between the formation water and surrounding rocks are weak.

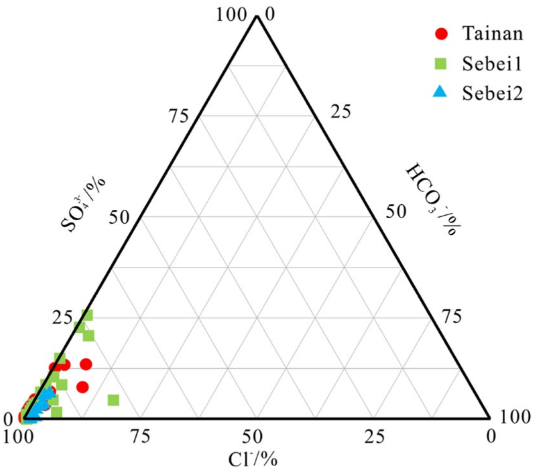

Fig. 6 Triangulation of formation water anion mass fraction in the study area

Geochemical characteristic parameters

The r(Na^+)/r(Cl^-) of the formation water is 0.22–0.72 (Fig. 9a), with an average value of 0.56 and a median of 0.59. All of the values are lower than 0.85 (r(Na^+)/r(Cl^-) of modern seawater). This indicates that the Quaternary Qigequan Formation in the Tainan-Sebei area of the Sanhu Depression is strongly metamorphosed, which is conducive to the preservation of biogenic gas.

The desulfurization coefficient of the formation water is 0.06–34.77 (Fig. 9b), with an average value of 2.91 and a median of 1.11. In addition, 84.51% of the data are 0–5. This indicates that the formation water of the Qigequan Formation of the Quaternary in the Tainan-Sebei Area of the Sanhu Depression has a strong desulfurization effect and is in a reducing environment, which is conducive to the preservation of biogenic gas.

The r(Ca^+)/r(Mg^{2+}) of the formation water is 0.04–4.40 (Fig. 9c), with an average value of 1.51 and a median of 1.63. This indicates that the formation water of the Qigequan Formation is highly metamorphosed and that the formation has good sealing properties.

The IBE of the formation water is 0.28–0.78 (Fig. 9d), with an average value of 0.44 and a median of 0.41. This indicates that the formation water in the study area has a small degree of cation exchange and is in a stagnant zone, which is favourable for biogenic gas preservation.

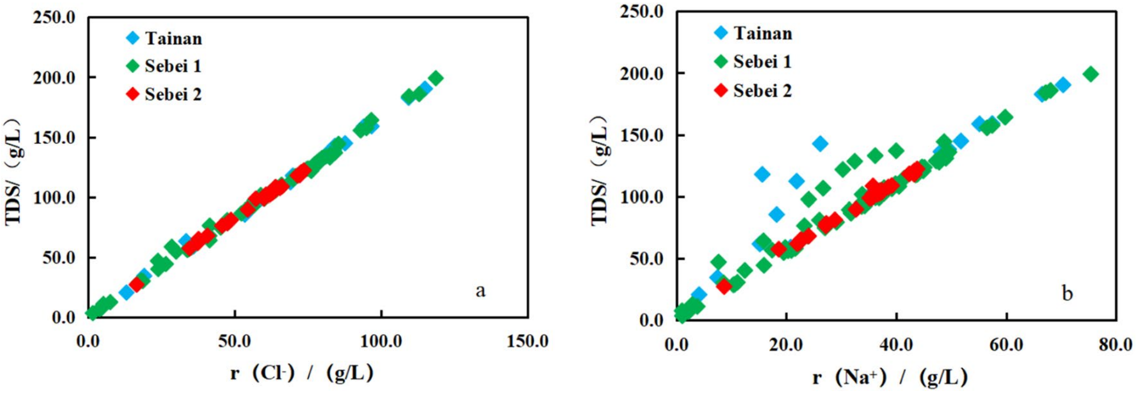

Fig. 8 Relationships between TDS and r(Cl^-) and between TDS and r(Na^+) of formation water in the Tainan-Sebei area of the Sanhu Depression (**a** the graph showing that TDS increases with r(Cl^-); **b** the graph showing that TDS increases with r(Na^+))

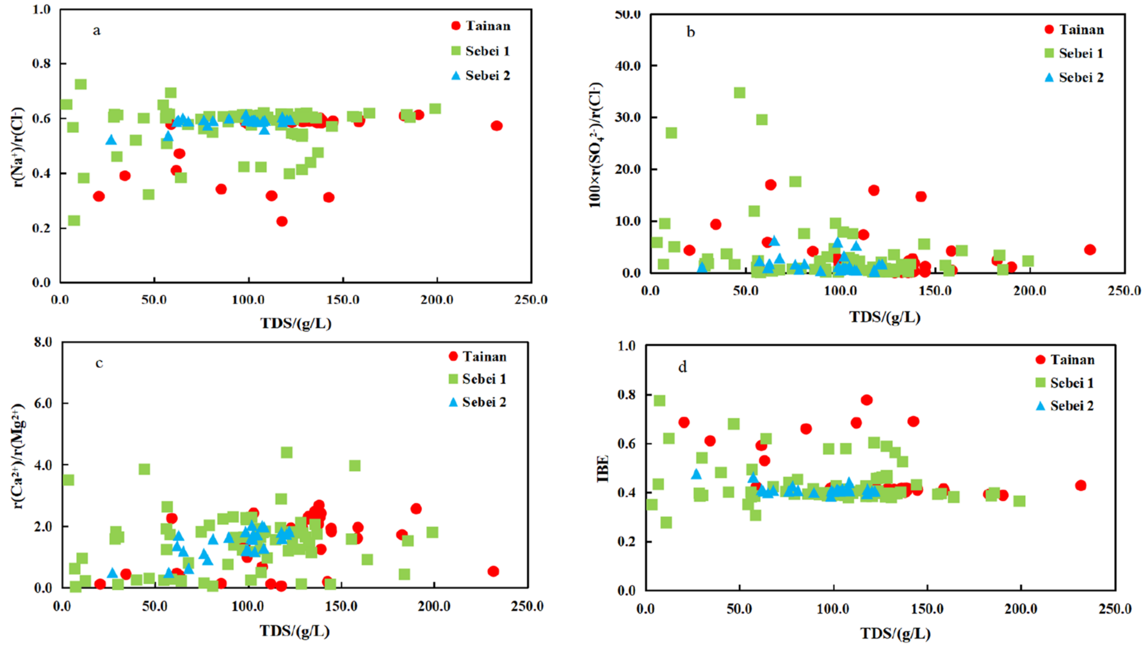

Fig. 9 Relationship between ionic chemical parameters and salinity of Quaternary formation water in Sanhu Tainan-Sebei Area. (**a** Relationship of r(Na^+)/r(Cl^-) and TDS; **b** Relationship of 100 × r(SO_4^{2-})/r(Cl^-) and TDS; **c** Relationship of r(Ca^{2+})/r(Mg^{2+}) and TDS; **d** Relationship of IBE and TDS)

The formation water has a low r(Na^+)/r(Cl^-), low desulfurization coefficient, high r(Ca^+)/r(Mg^{2+}) and high IBE. This shows that the formation is well sealed and dominated by residual water and ancient sedimentary water with high metamorphism, which is conducive to the accumulation and preservation of biogenic gas.

Origin and source of formation water

Characteristics of ionic relationships

Cl^- is chemically stable and does not undergo rock-forming reactions with other minerals, so it is used to explore the origin of the formation water (Zhou and Li 1995; Xu 2021). The lg[r(Cl^-)]-lg[r(Ca^{2+})], lg[r(Cl^-)]-lg[r(Na^+)] and lg[r(Cl^-)]-lg[r(Mg^{2+})] relationships were analyzed. (Fig. 10), and the following characteristic is found (lg[r(X)] is the logarithm of the X content).

(1) In the lg[r(Cl^-)]-lg[r(Ca^{2+})] diagram, the points are mainly distributed on the line and its right side, indicating the enrichment of Ca^{2+}.
(2) In the lg[r(Cl^-)]-lg[r(Na^+)] diagram, the points are mainly distributed on the left side of the line, indicating a deficit in Na^+.

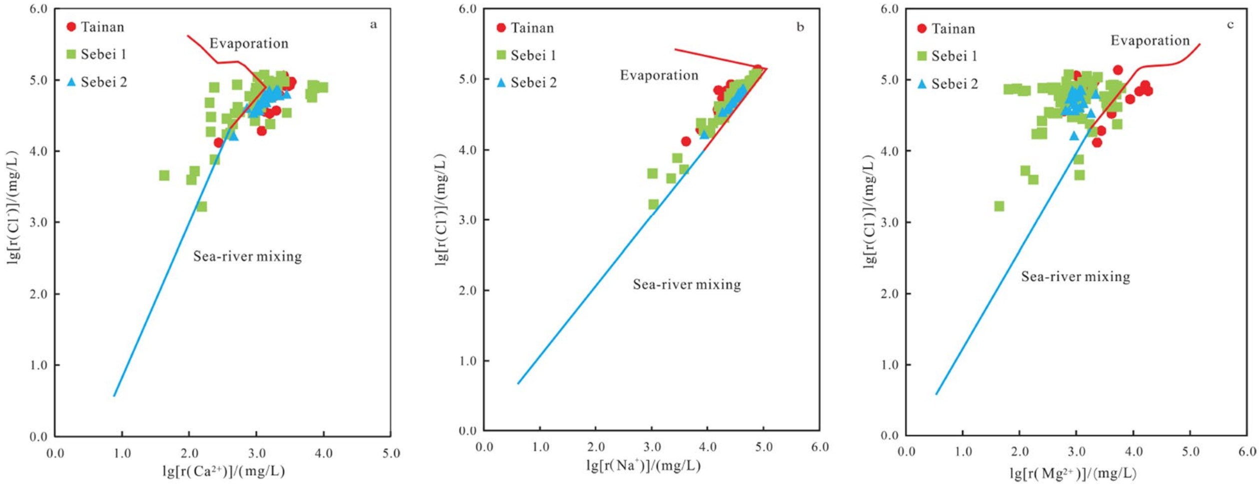

Fig. 10 Relationship between Cl^- and various ion concentrations of formation water(lg[r(X)] is logarithm of content of X. **a** the graph showing the enrichment of Ca^{2+}; **b** the graph showing the deficit of Na^+, **c** the graph showing the deficit of Mg^{2+}) (evaporation line and sea-river mixing line are from Zhou and Li 1995; Xu 2021)

(3) In the lg[r(Cl^-)]-lg[r(Mg^{2+})] diagram, the sample points are mainly distributed on the left side of the binding line, indicating a deficit in Mg^{2+}.

Causes of Ca^{2+} enrichment and Na^+ deficit

The X-ray diffraction (XRD) and thin sections of the Qigequan Formation in the study area show that the feldspar content (composed mainly of cline feldspar with a low potassium feldspar content) is high in the Qigequan Formation (the cline feldspar content is 7.5%–22.2%, potassium feldspar content is 0–6.5%). The formation water of the Qigequan Formation in the Tainan-Sebei area is characterized by an enrichment in Ca^{2+} and a deficit in Na^+, indicating albitization (2 Na^+ exchange 1 Ca^{2+}) (Davission and Criss 1996). In conclusion, the deficit in Na^+ in the Qigequan Formation is mainly controlled by albitization.

The change in Ca^{2+} concentration is mainly controlled by water–rock reactions, and the degree of Ca^{2+} enrichment is closely related to the dissolution of calcium-bearing minerals. The analysis reveals that Ca^{2+} enrichment is related to albitization, and Ca^{2+} enrichment occurs at the same time as a Na^+ deficit. In addition, the sandstone and mudstone in the study area are in the early stage of diagenesis, so cementation is very weak or even absent. No calcite or dolomite fills the reservoir interstitium, and the carbonate mineral content is low (2.6%–19.7%). Ca^{2+} is consumed in the precipitation of cement, so a large amount of Ca^{2+} can be preserved due to weak diagenesis.

The cause of Mg^{2+} deficit

The strength of the water–rock reaction directly affects the content of cations in the formation water. The contents of magnesite-rich minerals (such as dolomite) are low, so few dolomite cements are observed. Therefore, it is believed that the relative deficit of Mg^{2+} in the formation water is due to the lack of magnesite-rich minerals such as dolomite (the content of dolomite is 0–9.5%, with an average of 4.04%).

Hydrogen and oxygen isotope characteristics

The hydrogen and oxygen isotopes in water become heavier during evaporation. However, the δD and $\delta^{18}O$ values range from − 65.23‰ to − 49.58‰ and from − 7.01‰ to − 3.21‰, respectively. This amount is much lower than that of the lake water in the basin, indicating that the water is less affected by evaporation. In section "4.1.3 Ion Composition", it is inferred from the relationship between the TDS and the concentrations of Cl^- and Na^+ that the TDS of formation water are closely related to the concentration of evaporated or dissolved salt minerals. Therefore, nearly all salts are derived from the dissolution process of the formation elements. During carbonate dissolution in water, $\delta^{18}O$ exchange generally occurs; therefore, a high $\delta^{18}O$ value often leads to an increase in the $\delta^{18}O$ value in water. A comparison of the $\delta^{18}O$ values with those of glacial meltwater reveals that the $\delta^{18}O$ values in the formation water of the Tainan-Sebei area exhibit a positive drift of 2.00‰–7.88‰ (average 2.63‰) (Fig. 11). This further indicates that the development of formation water in the study area dissolves the salts of the formation.

The evolution line of the formation water in the study area intersects with the global atmospheric precipitation line at δD = − 9.40‰ and $\delta^{18}O$ = − 67.75‰. The intersection is located between the snow water of the Kunlun

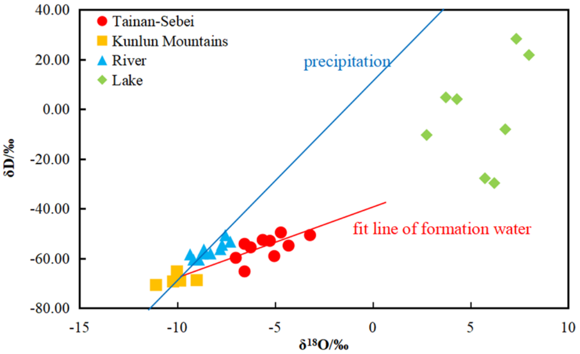

Fig. 11 Distribution of hydrogen and oxygen isotopes in the formation water and surrounding water. (Some of the hydrogen and oxygen isotope data are from Xu 2015; Li et al. 2019; Li et al. 2021)

Mountains and the river (Fig. 11), indicating that the formation water of the Tainan-Sebei area originates from meltwater from the Kunlun Mountains and groundwater in front of the mountains. On the northern margin of the Kunlun Mountains, there is a large deep fault, and part of the meltwater from ice and snow can penetrate down to the deep strata thousands of meters along the fault, participating in the groundwater cycle. Since the area from the Kunlun Mountains to the piedmont slope and then to the Sanhu Depression is high in the south and low in the north, the deep groundwater forms a hydraulic gradient under the significant height potential difference and is further displaced along the piedmont slope belt to the Sanhu Depression and reaches the water stagnation area where it is trapped in the formation.

In conclusion, the formation water of the Tainan-Sebei area originates from the glacier snow water of the Kunlun Mountains, which is converted into groundwater and seeps into the strata of the Sanhu Depression along the piedmont slope. During the process of groundwater infiltration and convergence, a large number of salt substances in the strata dissolve. This gradually increases the TDS of the water and migrates to the anticlinal belt of the northern depression. Eventually, formation water with higher salinity is formed (Fig. 12).

Implications of formation water characteristics and origin for biogenic gas generation and exploration

The organic matter abundance of the Quaternary gas source rocks in the Sanhu Depression is low (TOC is 0.3% on average). The amount of biogenic gas generated in situ obviously cannot meet the requirements for reservoir formation and the formation of such large-scale gas fields. Theoretically, a higher salinity of the formation water greatly inhibits the growth of methanogens and gas production. Therefore, the southern slope, which has a low TDS, is a favourable area for biogenic gas generation, but almost no gas reservoir is found in it. Instead, biogenic gas is found in the low-amplitude tectonic anticline of the northern slope. From the origin of the formation water, it is hypothesized that large quantities of biogenic gas are generated on the southern slope in front of the Kunlun Mountains. However, the gas preservation conditions in the southern slope are poor, which makes it difficult to preserve gas. At the same time, the underground hydrodynamic conditions in the basin from south to north cause large quantities of biogenic gas to be transported to the north. When it is transported to the anticline of the north slope, the solubility of the biogenic gas is reduced due to pressure release and a large increase in

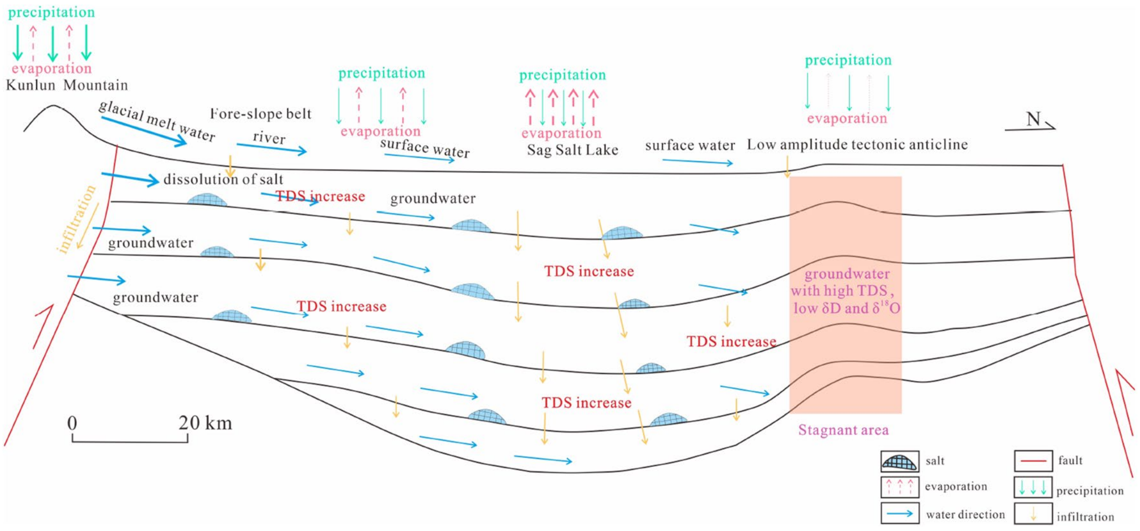

Fig. 12 Formation water model of the Quaternary Qigequan Formation in the Sanhu Depression, Qaidam Basin

water salinity, and the water-soluble gas precipitates in large quantities and mixes with the in situ generated gas in the strata to accumulate dynamically. The evolution of the formation water indicates that the biogenic gas in this region exhibits lateral transport and dynamic accumulation. This unique transport and accumulation law suggests that in the process of biogenic gas exploration in the Sanhu Depression, in addition to the source rocks and preservation conditions, the study of the formation water flow system and the hydrogeological process should receive considerable attention.

Conclusion

In this paper, the geochemical characteristics of the formation water from the Qigequan Formation of the Quaternary in the Sanhu Depression of the Qaidam Basin are studied, and the origin is analyzed via anion analysis, cation analysis, hydrogen and oxygen isotope analysis and other experiments. The chemical characteristics and origin are clarified.

The formation water is high in TDS and mainly contains type IV and type V $CaCl_2$, with ion concentrations ranging from high to low as $r(Cl^-) > r(Na^+ + K^+) > r(Ca^{2+}) > r(Mg^{2+}) > r(SO_4{}^{2-}) > r(HCO_3{}^-)$. All the formation water parameters indicate that the Qigequan Formation is well sealed and stagnant, which is conducive to the accumulation and preservation of biogenic gas.

The formation water of the Qigequan Formation is enriched in Ca^{2+}, deficient in Na^+ and deficient in Mg^{2+}. The enrichment of Ca^{2+} and deficit of Na^+ are mainly due to albitization and water–rock reactions (low content of carbonate minerals and cement), while the deficit of Mg^{2+} is due to water–rock reactions (lack of magnesium-rich minerals such as dolomites).

The formation water in the study area originates from the glacial meltwater of the Kunlun Mountains, which is converted into groundwater and infiltrates into the strata along the piedmont slope zone. In the process of groundwater infiltration and convergence, many salt substances in the strata are dissolved, resulting in an increase in TDS. The formation water with a high TDS finally formed in the anticlinal zone in the northern part of the depression.

The origin and evolution of the formation water indicate that biogenic gas has an enrichment law of lateral transport and dynamic accumulation, and it also proves that the origin, transport and salinization processes of the formation water influence the generation, transport and enrichment of biogenic gas. Therefore, in the process of biogenic gas exploration, in addition to the source rocks and preservation conditions, the study of the formation water flow system and the hydrogeological process should be emphasized.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s40562-024-00332-y.

Additional file 1: Table S1. Geochemical characterization of formation water. **Table S2.** Carbon and hydrogen isotopes of formation water. **Table S3**. XRD results of Qigequan Formation shale in Sanhu Depression

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Author contributions

Conceptualization, X.L.; methodology, X.L. and M.X.; validation, Z.J. and J.Z.; formal analysis, X.L., F. Z., Y. W. and X.T.; data curation, X.L. and Z.J.; writing-original draft preparation, X.L.; project administration, Z.J. and X.T. All authors have read and agreed to the published version of the manuscript.

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Availability of data

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

There are no conflicts of interest with respect to the results of this paper.

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