

Iron speciation and mineral characterization of upper Jurassic reservoir rocks in the Minhe Basin, NW China

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Abstract Six samples from a natural outcrop of reservoir rocks with oil seepage and two control samples from surrounding area in the Minhe Basin, northwestern China were selectively collected and analyzed for mineralogical composition as well as iron speciation using X-ray powder diffraction (XRD) and Mössbauer spectroscopy, respectively. Iron species revealed that: (1) the oil-bearing reservoir rocks were changed by water-rock-oil interactions; (2) even in the same site, there was a different performance between sandstone and mudstone during the oil and gas infusion to the reservoirs; and (3) this was evidence indicating the selective channels of hydrocarbon migration. In addition, these studies showed that the iron speciation by Mössbauer spectroscopy could be useful for the study of oil and gas reservoirs, especially the processes of the water-rock interactions within petroleum reservoirs.

Keywords Iron species · Mössbauer spectroscopy · Water-rock interactions · Redox · Minhe Basin

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2015), Hamburg, Germany, 13–18 September 2015*

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1 Introduction

Oil-gas reservoirs, as a place of hydrocarbon occurrence, are the direct main layers of oil and gas exploration. The quality of reservoir rocks directly controls the production of oil and gas, in which water-rock interactions (WRI) play an important role in the later reservoir reconstruction. The qualification and geochemical evolution of reservoir rocks are largely based on the study of water-rock-hydrocarbon interactions, so as to know the scale of hydrocarbon accumulation process and provide theoretical foundation [1]. Involved in the entire diagenetic evolution of reservoir rocks, WRI is one of the major driving forces to the formation and evolution of secondary pores and fractures and thus significant to the properties of reservoir rocks, especially to one with low or extremely low porosity and permeability. Therefore, WRI is attracting more attentions on the study of oil-gas reservoirs, such as petrology, mineralogy, and organic geochemistry. However, only fewer scientists mentioned the importance of redox condition and reaction to the WRI occurred in the reservoir rocks. Iron is one of redox sensitive elements and implicated in many fields of earth sciences [2]. Mössbauer spectroscopy, as a reliable and valuable technique for iron species measurement, can be used to measure iron species and thus be implicated for the study on reservoir properties based on iron speciation.

The Minhe Basin with the symbiosis of coal, oil, gas and shale has an exploration history of about 70 years by far. Previous studies on the Minhe Basin were mainly concentrated in the characteristics of tectonic evolution and sedimentary environment [3–5], and there were also in-deep researches in distribution and evaluation of hydrocarbon source rocks [6, 7]. Nevertheless, the study of oil and gas reservoir rocks in the Minhe Basin seems to be insufficient, probably due to limited samples of cored reservoir rocks underground and less techniques available. The diagenetic evolution of reservoir rocks under hydrocarbon impregnation conditions is one of the highlights of WRI researches in recent years. In order to investigate the geochemical evolution of oil-gas reservoir in the Minhe Basin, especially the hydrocarbon impregnation effect on oil-gas reservoir rocks, a large sum of samples were collected from the southern bank of Datong River and examined by X-ray powder Diffraction (XRD) and Mössbauer spectroscopy. Based on the previous experiences in related researches, the interactions of oil-gas-water-rocks and their geochemical evolution process are discussed in this paper. The injection of oil-gas and/or water into the reservoir rocks had a distinct effect on the diagenetic evolution, and also resulted in a profound transformation of the mineral composition in the reservoir rocks.

2 Study site and samples

The Minhe Basin, located on the boundary of Gansu Province and Qinghai Province, NW China, is a typical fault-controlled basin that was developed on the central Qilian Mountains uplift zone. The major Jurassic sequences in the basin include the Tandonggou Group (J_{1t}), Daxigou Group (J_{1d}), Yaojie Group (J_{2y}), Xiangtang Group (J_{3x}) and Datonghe Group (J_{3d}), of which the gray siliciclastic rocks are classified as the Datonghe Group [7]. This group of rocks with single lithology and considerable thickness (182 ~ 442 m) is considered as the main reservoir rocks of petroleum in the Minhe Basin. Their porosity and permeability are about 4 ~ 12 % and 0.7 ~ 7.6 mD, respectively [7]. The fine sandstones of reservoir rocks have planar cross bedding, which may indicate a lakeshore environment for sedimentation.

The sampling section is selected on the southern bank of the Datong River at 102° 49'55"N and 36°21'11"E, where there are distinguished outcrops of the reservoir rocks. On

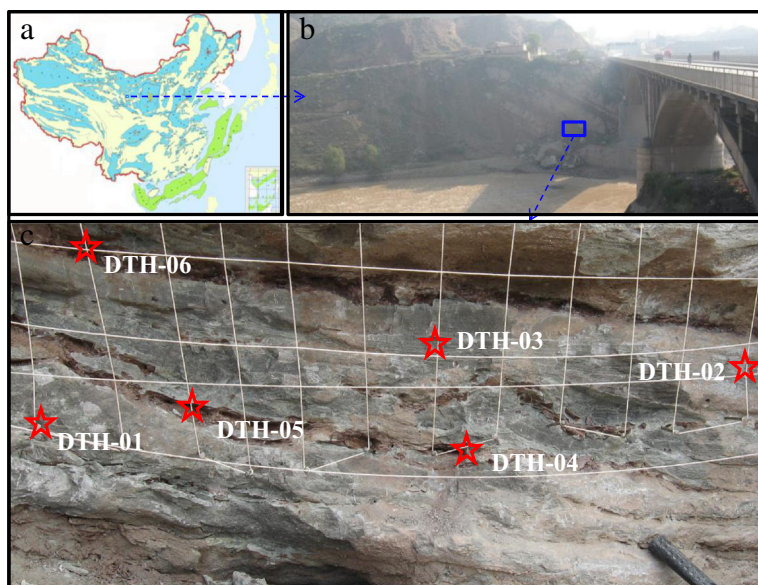


Fig. 1 Sampling scheme. **a** map of China showing study location; **b** photo of the study site, showing the outcrops of Datonghe Group along the southern bank of Datong River in the Minhe Basin; **c** photo of sampling section, showing the samples collection plan

the section, there is a strong gasoline smell and the rocks are interbedded with purple mudstone and gray-green sandstone. Actually the rocks are in various colors once the fresh rock was unearthed in the field, and their colors and chromaticity are clearly different from the rocks without oil contamination in the surrounding area even they are in the same layer of strata, showing typical bleaching effect by oil seeps [3]. The samples with oil dissemination were named as DTH-01 through DTH-06 (Fig. 1). For comparison, two samples without oil contamination named as DTH-07 and DTH-08 (not shown on the map) were also collected from the surrounding sandstone on the same lithological section.

3 Experiments

The samples were crushed into powder after dry using an agate mortar and pestle without any chemical pretreatment. Total organic carbon (TOC) was tested on CS-344 C-S analyzer at the Key Laboratory of Petroleum Resources Research, Chinese Academy of Sciences. Mineral compositions were measured by a routine powder X-ray diffraction. Conventional XRD was conducted on a new D8 advance, Bruker diffractometer equipped with a graphite monochromator and operated at 40 kV and 40 mA using Cu-K α radiation at the University of Tokyo, Japan. A portion of sample was further crushed into fine powder using a small clean mortar and then mounted on a plastic holder (φ 25mm, depth 1mm) for XRD analysis. The samples were scanned over an interval of $2 \sim 60^\circ$ (2θ) at a scanning speed of $2^\circ/\text{min}$ for every 0.03° (2θ) step. Divergence, scattering and receiving slits were 0.5° , 0.5 and 0.10 mm, respectively. The XRD data analysis was performed using software of MDI jade5.

Mössbauer spectra were measured at 293 K with a Bench MB-500 Mössbauer spectrometer using a γ -ray source of 0.93 GBq $^{57}\text{Co}/\text{Rh}$. The measuring procedure and curve

Table 1 Geological description, relative contents of iron species and the carbon contents of the samples from the reservoir rocks in the Minhe Basin

Samples	Description	TC(%)	TOC(%)	Fe ³⁺ (%)	Fe ²⁺ (%)
Site-1 Oil-bearing rock samples					
DTH-01	Sandstone \ Gray-green	1.58	1.03	33.16	66.84
DTH-02	Sandstone \ Gray-green	1.52	1.05	23.84	76.16
DTH-03	Sandstone \ Gray-green	1.43	1.00	25.84	74.16
DTH-04	Mudstone \ Gray	0.20	0.13	63.84	36.16
DTH-05	Mudstone \ Purple	0.15	0.07	64.78	35.22
DTH-06	Mudstone \ Purple	0.18	0.10	50.82	49.18
Site-2 Rock samples without oil contamination					
DTH-07	Sandstone \ Gray	1.09	0.04	73.66	26.34
DTH-08	Sandstone \ Gray	0.90	0.01	100	0

fitting have been described in detail elsewhere [8]. Briefly, measured spectra were fitted to Lorentzian line shapes using standard line shape fitting routines. Isomer shifts were expressed with respect to the centroid of the spectrum of metallic iron foil (Table 1).

4 Results and discussion

4.1 Mineralogy and iron species

The mineral assemblages of rock samples measured by XRD are illustrated in Table 2. It is clearly shown that the mineral assemblages were primarily consisted of quartz, plagioclase, K-feldspar, calcite and clay minerals. The clay minerals were dominated by illite, kaolinite and smectite. These minerals are typical components of sandstone and mudstone in terrestrial sedimentary basins [9]. However, there were distinguishable differences in mineral compositions between the oil-bearing rock samples and the control rocks without oil contamination. For example, the quartz in the oil-bearing sandstone samples was about 69.1 % whereas it was about 60.4 % in the control sandstone samples without oil contamination. Feldspar in oil-bearing sandstone was about 26.9 % whereas it was about 35.5 % in sandstone without oil contamination. Dolomite was not detected in rock samples without oil contamination while it occurred in the oil-bearing sandstone sample. In comparison, calcite was presented in samples of sandstone without oil contamination, and was reduced in the oil-bearing sandstone sample and even disappeared in sample DHT-02. The samples DTH-04-DTH-06 had a relatively low content of quartz because they were collected from the mudstone layer. The relative contents of illite, chlorite, kaolinite and smectite in these three samples are more than 15 times higher than other samples of sandstone, probably indicating that the sandstone and mudstone may have different performance in the progress of oil and gas infusion to the reservoir rocks.

The Mössbauer spectra of eight selected samples at room temperature (RT, constant at 293 K) are shown in Fig. 2, in which several overlapping doublets and sextets are observed.

Table 2 Mineral composition of the samples from the reservoir rocks in the Minhe Basin (XRD)

Samples ID.	Relative content (%)									
	Smectite	Illite	Kaolinite	Chlorite	Quartz	K-feldspar	Plagioclase	Calcite	Dolomite	Hematite
Site-1 Oil-bearing rock samples										
DTH-01	n.d.	1.50	1.20	0.702	67.40	8.40	17.9	2.70	0.198	n.d.
DTH-02	n.d.	0.800	0.600	0.500	69.9	13.6	14.5	n.d.	0.100	n.d.
DTH-03	n.d.	n.d.	0.780	0.799	69.9	9.72	16.7	1.90	0.201	n.d.
DTH-04	3.29	15.8	10.9	5.39	36.5	11.5	13.1	n.d.	1.19	2.33
DTH-05	3.53	16.51	11.7	5.01	31.9	15.2	14.5	n.d.	0.732	0.918
DTH-06	4.82	15.0	12.0	6.08	32.56	12.1	13.5	1.26	0.790	1.89
Site-2 Rock samples without oil contamination										
DTH-07	n.d.	1.00	1.40	0.400	57.2	12.4	22.7	4.70	n.d.	0.200
DTH-08	n.d.	1.60	1.70	0.600	63.6	11.7	24.2	6.20	n.d.	0.400

The curve fitting with iron components was robust, with sufficiently small Chi-squared values. Two doublets with smaller quadruple splitting were ascribed to either paramagnetic high-spin ferric iron (*para*-Fe³⁺). Which probably originated from clay minerals and/or hydrated Fe(III) oxides [10]. The *para*-Fe³⁺ in all samples was mainly due to ferric iron in clay, for example, in smectite, as determined by the Mössbauer parameters (Table 3) and also considered of their XRD patterns. The doublets with greater quadruple splitting were attributable to paramagnetic low-spin and high-spin ferrous irons. According to their Mössbauer parameters, the *para*-Fe²⁺ might be due to the iron in clay minerals [11]. For the sextet, it could be identified as hematite, as determined from their RT Mössbauer parameters. The corresponding iron species for each spectrum are listed in Table 3.

The results showed that samples without oil contamination (samples DHT-07 and DTH-08) were dominated by *para*-Fe³⁺, and it reached 73.66 % and even 100 %, respectively. However, the *para*-Fe³⁺ in oil-bearing rock samples (DHT-01 ~ DTH-06) was much lower than that of samples without oil contamination, from 23.84 % to 64.78 %. Furthermore, in the same section, the content of *para*-Fe³⁺ was strongly depended on the types of rocks. For example, the mudstone with purple color (samples DTH-04 ~ DTH-06) were enriched in *para*-Fe³⁺ with an average value 59.81 % whereas the sandstone with gray-green color (sample DTH-01 ~ DTH-03) were poor in *para*-Fe³⁺ (Fig. 3), showing sharp reduction of ferric iron during oil filling in sandstone.

4.2 Water-rock-hydrocarbon interaction in reservoir

4.2.1 The dissolution of feldspar and the secondary enlargement of quartz

Feldspar in sandstone without oil contamination (DTH-07 and DTH-08) was higher about 5 % and quartz was lower about 5 % than those in oil-bearing rocks except the samples DTH-04 ~ DTH-06 that were collected from mudstone interlayer (Fig. 4). The major cause for this phenomenon could be lied in the change of pH value of the geofluid in

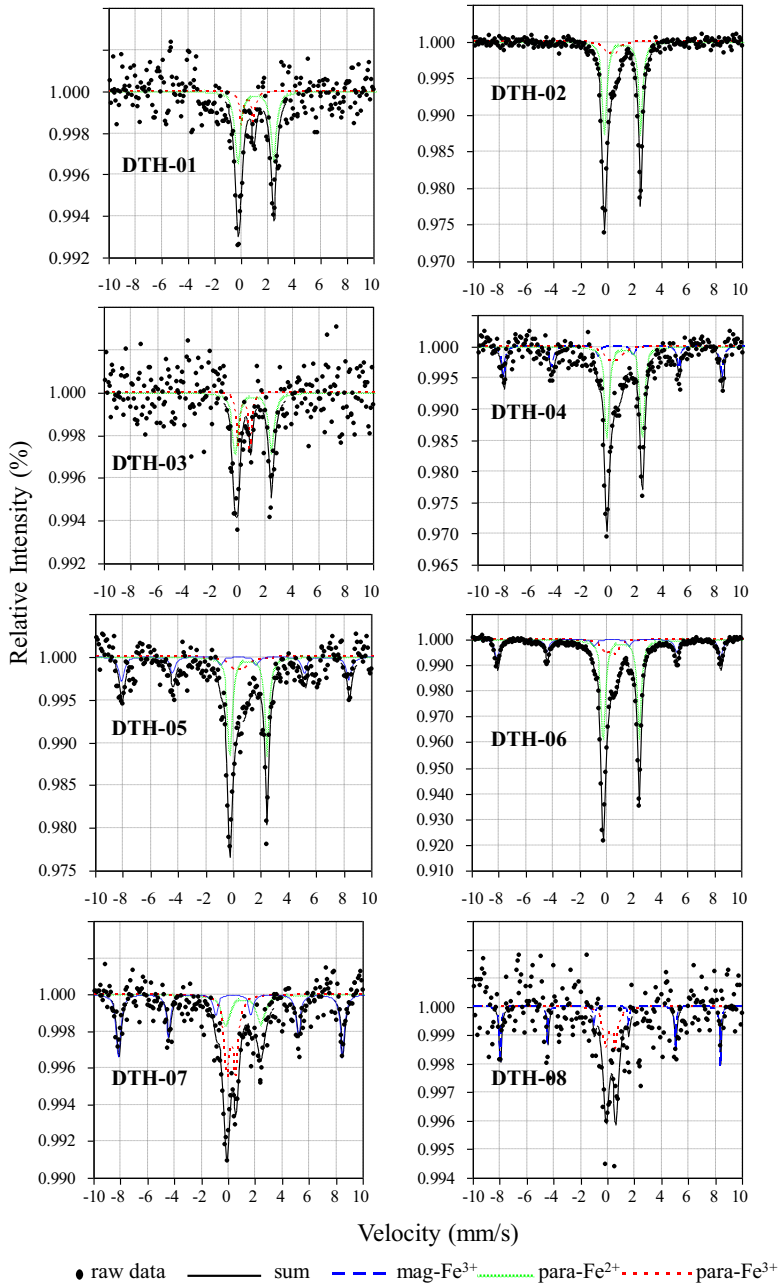


Fig. 2 Mössbauer spectra of eight samples selected from the southern bank of the Datong River measured at room temperature (293 K)

terms of the injection of hydrocarbon with formation water. The injection of hydrocarbon may transfer the diagenetic environment into a relatively acidic condition because of

Table 3 Mössbauer parameters of eight samples from the Minhe Basin (293K)

Sample ID	Iron species	Relative content %	IS/ mm s ⁻¹	QS/ mm s ⁻¹	HW/ mm s ⁻¹	Hi/T
Site-1 Oil-bearing rock samples						
DTH-01	para-Fe ²⁺	79.25	1.073±0.002	2.718±0.004	0.257±0.005	
	para-Fe ³⁺	20.75	0.476±0.006	0.934±0.010	0.001±0.013	
DTH-02	mag-Fe ³⁺	38.81	0.302±0.002	-0.210±0.004	0.171±0.006	51.184±0.022
	para-Fe ³⁺	24.86	0.291±0.005	0.738±0.010	0.487±0.018	
	mag-Fe ³⁺	36.33	1.073±0.001	2.668±0.002	0.197±0.002	
DTH-03	para-Fe ²⁺	35.35	1.070±0.001	2.684±0.002	0.200±0.002	
	para-Fe ³⁺	21.5	0.392±0.001	0.720±0.000	0.489±0.021	
	mag-Fe ³⁺	43.15	0.264±0.003	-0.239±0.005	0.224±0.008	51.045±0.018
DTH-04	para-Fe ²⁺	74.85	1.097±0.001	2.690±0.002	0.194±0.004	
	mag-Fe ³⁺	25.15	0.317±0.011	0.608±0.016	0.340±0.026	
DTH-05	mag-Fe ²⁺	46.92	1.063±0.000	2.673±0.001	0.190±0.001	
	para-Fe ³⁺	21.06	0.301±0.003	0.737±0.005	0.366±0.007	
	mag-Fe ³⁺	32.02	0.286±0.002	-0.211±0.004	0.179±0.008	51.444±0.012
DTH-06	para-Fe ²⁺	77.39	1.069±0.004	2.679±0.007	0.262±0.011	
	para-Fe ³⁺	22.61	0.415±0.005	0.926±0.010	0.150±0.015	
Site-2 Rock samples without oil contamination						
DTH-07	para-Fe ²⁺	25.4	1.099±0.010	2.599±0.018	0.392±0.017	
	para-Fe ³⁺	24.83	0.233±0.006	0.688±0.011	0.253±0.010	
	mag-Fe ³⁺	49.77	0.288±0.003	-0.213±0.006	0.192±0.010	51.591±0.020
DTH-08	para-Fe ³⁺	54.64	0.238±0.004	0.740±0.007	0.246±0.011	
	mag-Fe ³⁺	45.36	0.245±0.003	-0.094±0.005	0.086±0.010	50.779±0.016

Fig. 3 Variation of ferrous iron (*para*-Fe²⁺) and ferric iron (*para*-Fe³⁺) in the studied samples. Samples DTH-01 ~ DTH-06 are mainly dominated by ferrous iron whereas samples DTH-07 ~ DTH-08 are dominated by ferric iron

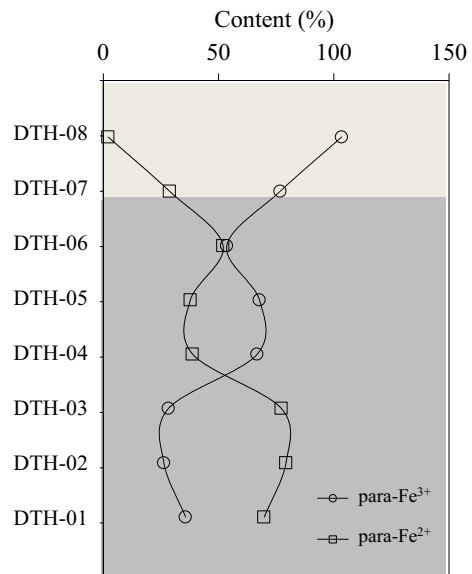
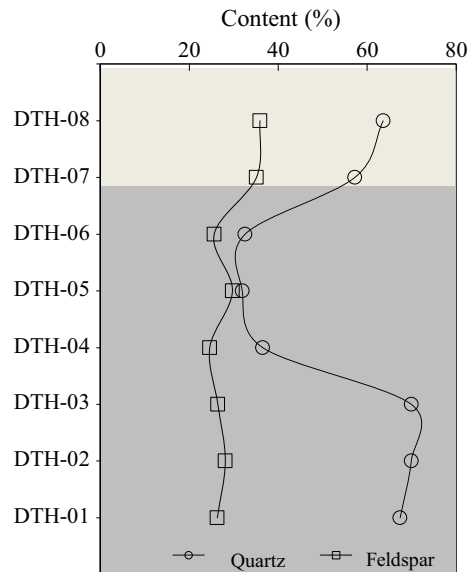
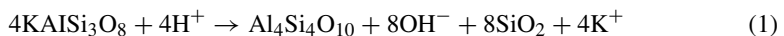


Fig. 4 The distribution quartz and feldspar in the studied samples. There is more quartz in samples DTH-01 ~ 03 than that in samples DTH-07 ~ 08



their oxidation of hydrocarbons and other organic matters to produce carboxylic acids, and then the feldspar would be dissolved easily. This acidic condition can be formed in the follow ways: (1) Kerogen can generate large amounts of water-soluble organic acids, especially various kinds of carboxylic acids; (2) The decomposition of organic matter can form a large amount of humic acids; (3) The chemical reaction between organic matter and the sulfate can further produce organic acids; (4) The oxidation of organic matter can produce carbon dioxide, which can form carbonic acid when it dissolves into the pore fluids; (5) Oil can produce organic acids by biodegradation or thermal catalysis [12, 13]. These acidic substances will control the pH values of pore fluids, thus forming the acid diagenetic environment in reservoirs. The reaction mechanism could be summarized as the followings:

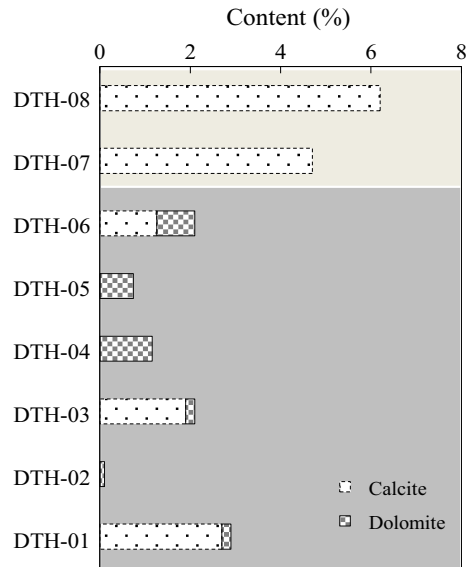


Feldspar dissolved under the acidic conditions and its product of SiO_2 could provide basic material for the secondary enlargement of quartz. Actually, there was a different extent of dissolution in various kinds of feldspar, such as K-feldspar and albite.

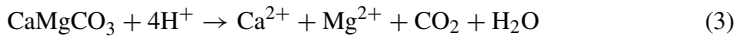
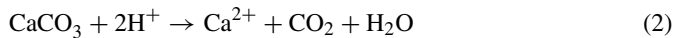
4.2.2 The dissolution of carbonate minerals

The content of carbonate minerals in oil-bearing reservoir rocks was distinctly reduced in comparison with the rock samples without oil contamination (Fig. 5). Carbonate

Fig. 5 The distribution of calcite and dolomite in the studied samples. There is more albite in samples DTH-07 ~ 08 than that in samples DTH-01 ~ 06



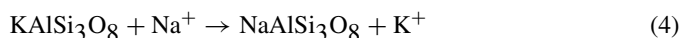
minerals could be easily dissolved under acidic conditions. The reaction equations could be summarized as the followings:



The injections of hydrocarbon may result in an acidic condition, and then contribute to the dissolution of calcite and dolomite, and thus will promote the formation of secondary intergranular pores. The other obvious change was the occurrence of dolomite in the samples of oil-bearing reservoir rocks (Fig. 5), which may indicate that the reservoir rocks had undergone the process of dolomitization. Dolomitization could cause the change of reservoir storage space and also their connection properties, result in alteration of original rock fabric, and improve the dissolution of fluid space.

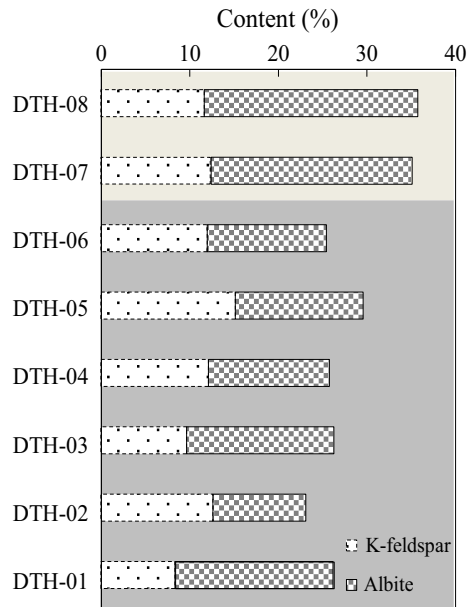
4.2.3 Metasomatism

The albitization of K-feldspar is a common phenomenon in petroleum reservoir. It is a replacement reaction with K^+ and Na^+



The results of XRD in this study showed that the albitization degree of oil-bearing layer was smaller than that of oil-bearing reservoir (Fig. 6).

Fig. 6 The distribution of K-feldspar and albite in the studied samples. There is more albite in samples DTH-07 ~ 08 than that in samples DTH-01 ~ 06

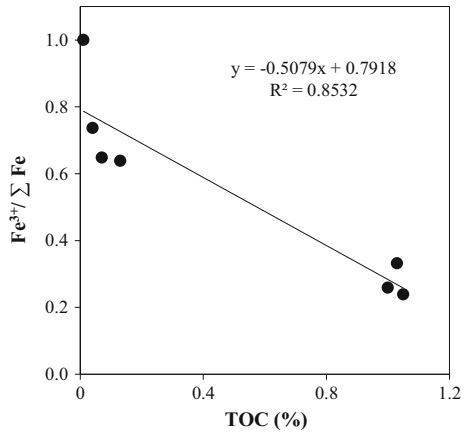


The conversion of calcite partially or wholly into dolomite is normally called dolomitization. As shown in the Fig. 5, the content of dolomite in the oil-bearing sandstone samples was much higher than that of the sandstone samples without oil contamination. This was mainly because the oil and gas penetrated into the reservoir, so that the viscosity of the fluid would be changed. Therefore, the migration of Na^+ (Ca^{2+}) and K^+ (Mg^{2+}) were hindered, and the albitization of K-feldspar and dolomitization of calcite were suppressed. Compared with the rock samples without oil contamination in the same layer nearby, the albitization (dolomitization) degree in the oil-bearing rocks was about 5 ~ 15 % lower as for metasomatism.

4.2.4 Redox reactions involving hydrocarbons

Hydrocarbon invasion into sandstones that contain mineral oxidants and carbonate or sulfate intergranular cements may result in redox reactions and significantly enhanced the rocks porosity [13]. Based on chemical species of iron by Mössbauer spectrum (i.e., the kinds of iron oxides and the occurrence state of iron), redox conditions can be judged. The distribution of various iron species between the oil-bearing rocks and the rocks without oil influence suggested that the reduction of iron was the major geochemical reactions, which was commonly caused by petroleum bleaching [14]. In addition, iron reduction processes appeared to follow certain sequences; the reduction of hematite was probably the earliest target, and then the ferric iron in smectite. By measuring the relative contents of various iron species, it was shown that the relative contents of reduced species (e.g. *para*- Fe^{2+}) got increased in the oil-bearing reservoir rocks in comparison with the rocks without oil contamination (Fig. 2). Even in the oil-bearing rocks, *para*- Fe^{2+} enriched in sandstone than that in mudstone. Thus, the injection of hydrocarbons could cause the reduction of species, and in hence also some

Fig. 7 The relationship between total organic carbon (TOC) and relative content of ferric iron ($\text{Fe}^{3+}/\sum\text{Fe}$). There is a clearly negative correlation between ferric iron and TOC in the studied samples



kinds of minerals such as smectite. There is also a good negative correlation between ferric iron and total organic carbon (TOC) (with $R^2 = 0.85$) for all studied samples (Fig. 7). In this sense, the relative contents of ferric iron could be able to provide useful information about hydrocarbons migration in reservoir rocks [15].

5 Conclusions

Based on all the data and evidences described above, a rather simplified view is presented about iron speciation and mineral composition in the reservoir rocks from the study area, (1) the diagenetic evolution of reservoir rocks was obviously affected by petroleum dissemination, being mainly reflected in the feldspar corrosion, quartz overgrowth and some dolomitization; (2) reduction of iron species was the primary process in oil-bearing reservoir rocks. Large amount of ferric iron species might be reduced into ferrous species such as the iron in illite and chlorite during the hydrocarbon-water-rock interactions. In addition, there was a clearly positive correlation between ferrous iron and TOC in the reservoir rock samples, indicating that organic matters such as hydrocarbons might be able to reduce ferric iron into ferrous iron and this phenomenon could be considered as a useful tracer for hydrocarbons' migration in reservoir rocks.

Acknowledgments We thank for Prof. Yoshio Takahashi guiding XRD test at the University of Tokyo. This study is supported by the National Natural Science Foundation of China (41402129, 41273112, 4151101268) and the "Light of Western China" of Chinese Academy of Sciences (Y508RC1MXX). Profs. Mingjie Zhang and Shouyun Liang from Lanzhou University conducted the field trips and gave many valuable suggestions on the study.

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