# ORIGINAL PAPER



# Characteristics and implication of multilayer dawsonite in heterogeneity reservoir of the Honggang anticline, southern Songliao Basin, NE China

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#### Abstract

Reservoir heterogeneity is one of the key factors regarding the long-term fate of the injected  $CO_2$ . Natural  $CO_2$  reservoir and ancient  $CO_2$ -bearing reservoir is a natural analog to investigate the influence of reservoir heterogeneity on the migration of  $CO_2$ and CO2-rock interaction with geological timescale. Dawsonite cements are detected in both sandstone and mudstone of the Upper Cretaceous Qingshankou reservoir in Honggang anticline of the southern Songliao Basin, China. Here, we present results of a petrographic characterization of this reservoir based on polarizing microscope, X-ray diffraction, and fluid inclusion data. These data were used to identify the vertical distribution characteristic of dawsonite and to identify the migration characteristics for the supercritical  $CO_2$  in heterogeneity reservoir. Our analytical results show that as the "CO<sub>2</sub> trace mineral," dawsonite appears as multilayered zones of cementation that are separated by mudstone interlayers. These multilayered dawsonite could be one of the geological produces for supercritical  $CO<sub>2</sub>$  flooding through the heterogeneous rock, acting as the lateral migration and upward diffusion. Supercritical  $CO<sub>2</sub>$  could move through the thinner mudstone interlayer, with the product of dawsonite developing in the mudstone as its "footprint," although the vertical distance of diffusion in low-permeability caprock is limited. Combined with the truth that most of the present  $CO<sub>2</sub>$  gas reservoirs (in K1q4) are in the deeper layers than the dawsonitebearing sandstone (K1q4-K2y1) (developed in non-CO<sub>2</sub> reservoir), we can deduce that  $CO<sub>2</sub>$  was at some time abundant in the Honggang anticline but had now part of  $CO<sub>2</sub>$  been migrated, with the other part consumed by the reaction with the primary rock and captured as new carbonate minerals. The dawsonite-bearing sandstones also record a sequence of hydrocarbon filling events. Combined with the truth that the injection time of  $CO<sub>2</sub>$  is later than that of hydrocarbon, the early hydrocarbon should be deasphalted by the injection and migration of mantle CO<sub>2</sub>. Therefore, CO<sub>2</sub> could also be stored as long-term carbonate minerals after the termination of a  $CO<sub>2</sub>$ -EOR project.

Keywords Dawsonite  $\cdot$  Multilayer distribution  $\cdot$  Supercritical CO<sub>2</sub>  $\cdot$  CO<sub>2</sub> migration  $\cdot$  Songliao Basin

## Introduction

Monitoring and determination of the underground  $CO<sub>2</sub>$  plume migration is one of the great challenges in carbon capture and storage (CCS) development (IPCC [2005](#page-15-0); Aminu et al. [2017;](#page-15-0) Shin and Son [2018](#page-17-0); Karimi et al. [2018](#page-16-0); Giuliano et al. [2019\)](#page-15-0). Reservoir heterogeneity at various length scales is a wellestablished fact, and the heterogeneity is a key factor influencing the long-term security of  $CO<sub>2</sub>$  geological storage. The longterm fate for the injection  $CO<sub>2</sub>$  in CCS has been predicted by numerical simulations, while the traditional homogeneous geological models are likely to be too simple given the strong heterogeneity of the reservoirs in the case of  $CO<sub>2</sub>$  injection. Nowadays, a series of laboratory experimental (Park et al. [2017\)](#page-16-0) and geological numerical simulations (Al-Khdheeawi et al.  $2018$ ; Qiao et al. [2020\)](#page-17-0) focus on characterizing  $CO<sub>2</sub>$ plume migration in multilayer reservoirs with strong heterogeneity. In fact, natural  $CO<sub>2</sub>$ -bearing reservoirs can also provide a natural analog for  $CO<sub>2</sub>$  migration in heterogeneity reservoir.

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Dawsonite has been identified as a possible carbonate product resulting from the injection of  $CO<sub>2</sub>$  into the sandstone reservoirs, such as in the Permian Supai Formation of Springerville Field, USA (Moore et al. [2005\)](#page-16-0); the BGS basin system, Eastern Australia (Baker et al. [1995;](#page-15-0) Golab et al. [2006\)](#page-15-0); the Lam Formation of Shabwa Basin, Yemen (Worden [2006](#page-17-0)); the Nantun Formation of Hailar Basin, China (Gao et al. [2009\)](#page-15-0); the Qingshankou Formation of south Songliao Basin, China (Liu et al. [2011;](#page-16-0) Yu et al. [2014](#page-17-0)); and the Mingyuefeng Formation of Lishui Sag, China (Zhao et al. [2018\)](#page-17-0). Numerical simulations (Zhang et al. [2004;](#page-17-0) Álvarez-Ayuso and Nugteren [2005](#page-15-0); Hellevang et al. [2005,](#page-15-0) Okuyama et al. [2009;](#page-16-0) Shi et al. [2019](#page-17-0)) and thermodynamic calculations imply that dawsonite grows under elevated  $CO<sub>2</sub>$  pressure conditions (partial pressures of  $CO<sub>2</sub>$  is at least 50 bar) or when abundant  $CO_3^2$ <sup>-</sup> or HCO<sub>3</sub><sup>-</sup> is coupled with aluminosilicate dissolution. However, a debate exists concerning the status of dawsonite and the possibility of precipitating this phase in an artificial CO<sub>2</sub> storage in sandstones. Some researchers hold that dawsonite will become unstable as  $CO<sub>2</sub>$  pressure decreases following injection through equilibrium-based experimental and modeling evaluation (Hellevang et al. [2005,](#page-15-0) [2014](#page-15-0); Bénézeth et al. [2007](#page-15-0); Kaszuba et al. [2011](#page-16-0); Kampman et al. [2014\)](#page-16-0). They argue that the lack of nucleation and growth rate data for dawsonite, the lack of dawsonite growth in laboratory experiment under  $CO<sub>2</sub>$  storage conditions, and the uncertainty in growth conditions for the natural analogues rendered numerical predictions highly uncertain. In any case, precipitation of dawsonite induced by  $CO<sub>2</sub>$  injection is supported by field observations (e.g. Baker et al. [1995;](#page-15-0) Moore et al. [2005;](#page-16-0) Noh et al. [2018;](#page-16-0) Worden [2006](#page-17-0); Zhao et al. [2018](#page-17-0)). In Permo-Triassic sedimentary rocks of the Bowen-Gunnedah-Sydney basin system, eastern Australia, dawsonite is widespread as a cement, replacement, and cavity filling, while the distribution and interpreted origin of dawsonite (magmatic carbon source) imply that magmatic  $CO<sub>2</sub>$  seepage into the Permo-Triassic sequences on a continental scale (Baker et al. [1995\)](#page-15-0).

The Honggang anticline, which is located in the southern Songliao Basin, NE China, is an ideal area for studying the indicators of  $CO<sub>2</sub>$  migration on account of the development of abundant dawsonite cements (Liu et al. [2011\)](#page-16-0) and the presence of a locally developed  $CO<sub>2</sub>$ -bearing gas reservoir within the anticline (Hou et al. [2009\)](#page-15-0). The sandstone reservoir of the Honggang anticline contains oil, gas, and mantle-magmatic  $CO<sub>2</sub>$ . The injection of oil-gas is demonstrated by the existence of oil-gas-bearing inclusions and the intergranular oil staining in the sandstones, while the injection of  $CO<sub>2</sub>$  is recorded by the presence of carbonate minerals that formed during  $CO<sub>2</sub>$ -rock interaction, such as dawsonite (Liu et al. [2011\)](#page-16-0).

Several petrographic studies have been undertaken on the Quantou and Qingshankou Formation in the Honggang area, many of which were contracted by oil companies to assess reservoir quality (Niu et al. [2012\)](#page-16-0). Recent studies of the Honggang area have investigated the interaction of  $CO<sub>2</sub>$  with the minerals in sandstones (Liu et al. [2011](#page-16-0)) and mudstones (Wang [2013](#page-17-0); Ming [2017](#page-16-0)). The mineralogy, diagenetic features, and isotopic compositions of dawsonite-bearing sandstones in the Honggang anticline have been characterized by Liu et al. ([2011](#page-16-0)), who found that the mineral assemblage that formed after  $CO<sub>2</sub>$  flooding comprises dawsonite, microcrystalline quartz II, kaolinite II, calcite II, and ankerite. Some dawsonite cements have been detected in mudstones using X-ray diffraction (Ming [2017](#page-16-0)). These aforementioned studies have described the diagenetic effects caused by  $CO<sub>2</sub>$  injection within a single reservoir interval over geological time.

For the present study, we focus on the Lower Cretaceous Qingshankou Formation, which is producing hydrocarbon reservoir, and aim to discuss the spatial distribution characteristic of dawsonites within dawsonite-bearing sandstones and dawsonite-bearing mudstones of the Honggang anticline. The results of the study contribute to understanding the  $CO<sub>2</sub>$  migration characteristics in the heterogeneity reservoir with geological timescale.

## Geological background

The Songliao Basin is the largest Mesozoic-Cenozoic sedimentary basin in the Cathaysian system and the largest oilproducing province in China (Xu et al. [2000](#page-17-0)). The Qingshankou and Nenjiang mudstones were deposited during two large lake-flooding events in the Songliao Basin and constituted the main hydrocarbon source rocks and major reservoirs in the basin (Zhang and Bao [2009](#page-17-0)). The Honggang anticline is one of the subordinate structural belts of the central depression in Songliao Basin (Fig. [1](#page-2-0)). From the end of deposition of the Nenjiang Formation to the end of deposition of the Mingshui Formation, the whole of the Honggang area was occupied by an anticline with the axis trending NS (Chen, [2003\)](#page-15-0). There are mainly three stages of structure evolution in Songliao Basin, including rift stage, depression stage, and inversion stage. Strong fault activities went through these three stages. Honggang fault, as the basement fault, is cutting through the T5 reflection layer, upward through the T02 reflection layer (Fig. [1](#page-2-0)). This fault was active from Carboniferous and Permian, but the most active period of it was during late K1q-early K2qn and structural inversion stage (Fig. [3](#page-4-0)) (Liu et al. [2018](#page-16-0)).

The burial history in this area during the Late Cretaceous included a punctuated rifting stage into a maximum burial  $($ 2400 m) and maximum temperature  $(\sim 117 \text{ °C})$  in Paleocene, a modest uplift stage, leading to a reduction in the ambient temperature of the sedimentary rocks (Fig. [2\)](#page-3-0) (Zou et al. [2005;](#page-17-0) Yang et al. [2010\)](#page-17-0). The average geothermal gradient and heat flow in the Paleocene was about 4.26  $\degree$ C/m and 95–107 mW/

<span id="page-2-0"></span>

Fig. 1 Map of the S corner of the Songliao Basin showing the research area in Honggang. The locations of the wells containing dawsonitebearing sandstones are marked. (A) Location of Songliao Basin; (B) boundary of major structural units for southern part of Songliao Basin: (a) Honggang Step, (b) Changling Depression, (c) Huazijing Step, and (d) Fuxin Uplift; (C) researching area and distribution of dawsonite-bearing sandstones containing well; (D) cross section for southern part of Songliao Basin according to Liu et al. ([2018](#page-16-0)); I-BF: the basement faults

m<sup>2</sup>, respectively (Ren et al. [2001](#page-16-0)). The present-day reservoirs' temperature and pressure are  $73 \sim 99$  °C and  $12.5 \sim 18.7$  Mpa (Ren et al. [2001\)](#page-16-0).

being continuously active during the syn-rift stage only cutting through the T4 or T5 reflection layer; I-II-BF: the basement faults being continuously active during the period from the syn-rift to post-rift stages cutting through the T4 or T5 reflection layer, upward through the T2 reflection layer; I-II-III-BF: the basement faults being continuously active during the period from the syn-rift stage to structural inversion stage cutting through the T4 or T5 reflection layer, upward through the T02 reflection layer

Dawsonite-bearing sandstones are widespread in the Upper Cretaceous strata (Fig. [3\)](#page-4-0). During the Late Cretaceous, as a regional transgression prevailed, many types of delta deposits

<span id="page-3-0"></span>

Fig. 2 (A) General burial-thermal history of H75# in Honggang anticline. The time of oil and CO<sub>2</sub> gas flooding are indicated (Zou et al. [2007](#page-17-0); Yang et al. [2010\)](#page-17-0). (B) Basin development and fracture development for the south of Songliao Basin according to Zou et al. [\(2007\)](#page-17-0)

are formed, including those of the Qingshankou and Yaojia formations, Members 3 and 4 of the Nenjiang Formation, and Member 1 of the Mingshui Formation (Ge et al. [2012\)](#page-15-0).

The oil in the reservoir was sourced from the Qingshankou mudstones (Wu et al. [2006](#page-17-0); Zou et al. [2007](#page-17-0)). Recent studies on the timing of hydrocarbon accumulation carried out using conventional methods have shown that the accumulation of hydrocarbons in middepth strata of the southern Songliao Basin occurred mainly at Neijiang-Mingshui period (85–65 Ma) (Zou et al. [2005;](#page-17-0) Zou et al. [2007](#page-17-0)). However, there is an adjustment of the hydrocarbon at 50–25 Ma, due to the formation uplifting and erosion (Zou et al. [2007;](#page-17-0) Yu et al. [2014](#page-17-0)).

The  $CO_2$ -bearing gas reservoir (K1q3 + 4 and K2qn2 + 3) formation) is mainly located in the inverted structure belts that are controlled by the inversion of basement faults (Liu et al. [2018\)](#page-16-0). Most of the researchers prefer a mantle-magmatic origin for the origin of  $CO<sub>2</sub>$  in the south of Songliao Basin according to the carbon and helium isotopic data ( $\delta^{13}C_{CO2}$ : −  $9.9 \sim -4.0$  ‰, PDB;  ${}^{3}$ He/<sup>4</sup>He: 2.65–5.88 × 10<sup>-6</sup>, R/Ra: 1.9– 4.56) (Dai et al. [1995;](#page-15-0) Chen et al. [1996](#page-15-0); Lu et al. [2009;](#page-16-0) Fu et al. [2010;](#page-15-0) Qu et al. [2016](#page-17-0)). They hold that the volcanic eruption and the development of the related faults have a causal relationship with the formation of  $CO<sub>2</sub>$ -bearing gas reservoirs.

In addition, geochemistry and geochronology of volcanic rocks in the study area indicate that the Shuangliao basalts were formed (41–51 Ma) during the structural inversion stage of Songliao Basin, and this basaltic magma is considered to have been the main source of  $CO<sub>2</sub>$  in the study area (Zhang [2006;](#page-17-0) Yu et al. [2014](#page-17-0); Qu et al. [2016\)](#page-17-0). In Honggang area, the presence of high content of inorganic  $CO<sub>2</sub>$  gas has been reported in  $K_1q^4$  formation of wells H73# and H77#, which are located in the northeastern part of the field (Fig. [1\)](#page-2-0). The values of  $pCO<sub>2</sub>$  for the wells H73# and H77# are 108 and 126 bar, with the content of  $CO<sub>2</sub> 85$  and 96%, respectively. The carbon isotope values of CO<sub>2</sub> ( $\delta^{13}$ C<sub>CO2</sub>) range between – 8.05 and – 2.65‰ (PDB) (Yang et al. [2010](#page-17-0)). In Honggang, the formation waters for dawsonite-bearing reservoir appear as NaHCO<sub>3</sub><sup>-</sup>dominated waters, with a total salinity ranges of  $8508.4 \sim$ 45,385 g/L, the concentrations of  $K^+$  + Na<sup>+</sup>, and HCO<sub>3</sub><sup>-</sup> range of  $2684.1 \sim 13,152.8$  g/L and  $3905.3 \sim 27,868.4$  g/L, respectively.

# Samples and methods

This study is based on the petrographic data from dawsonitebearing sandstones in 14 wells (data of 351 thin sections, from Liu et al. [2011](#page-16-0)) and XRD data obtained from mudstones in 3

<span id="page-4-0"></span>Fig. 3 Simplified stratigraphic chart for Songliao Basin. Dawsonite-bearing sandstones accumulated in the Quantou Formation, Qingshankou Formation, and Yaojia Formation. The activity rate for Honggang fault was according to Liu et al. [\(2018](#page-16-0))



wells (37 sets of data, from Ming [2017\)](#page-16-0). In addition, 30 core samples of the Qingshankou Formation and Yaojiao Formation were collected from 6 wells and prepared for thin-section examination. These 30 core samples were analyzed to obtain statistics on the contents of dawsonite and asphaltenes with line notation, which worked for 15 views. Combined with the well-logging data, these microscope-based content data were used to investigate the relationship between dawsonite content, asphaltene content, and the stratigraphic distributions of oil, gas, and formation water.

Observations of fluid inclusions in the dawsonite-bearing sandstones were conducted on four selected samples from H143# and H146# using a Leica DMRX HC fluorescence microscope in the Analytical Laboratory of Beijing Research Institute of Uranium Geology, Beijing, China. The fluid inclusion thermometry was performed using a LINKAM THMS600 heating-cooling stage with 1 °C precision.

## Results

## Petrographic characterization of the dawsonitebearing sandstones

Dawsonite-bearing sandstones were found in drilling cuttings from 14 wells. Dawsonite is the most abundant cement in these sandstones, comprising 1–19% of the bulk rock volume. The identified dawsonite-bearing sandstones occur mainly in the Qingshankou Formation, with lower abundance in Member 4 of the Quantou Formation and in Member 1 of the Yaojia Formation (Fig. 4).

Samples of dawsonite-bearing sandstone from the Honggang anticline are poorly to moderately sorted lithic arkoses to feldspathic litharenites and contain 23–36% detrital quartz, 14–25% feldspar, and 16–35% rock fragments. Dawsonite is present as acicular crystal and radial aggregation filling pores or as bladed crystals and tufts/rosettes of fine needles replacing detrital grains or early-stage cements (Fig. [5a](#page-6-0)). Authigenic minerals in dawsonite-bearing sandstones (besides dawsonite) include quartz, feldspar, illite, kaolinite, illite-smectite, calcite, and ankerite. The order of cement growth can be summarized as feldspar overgrowth, quartz overgrowth, microcrystalline quartz I, kaolinite I,

calcite I, dawsonite, microcrystalline quartz II, kaolinite II, calcite II, and ankerite (Liu et al. [2011\)](#page-16-0).

Asphaltenes are abundant in dawsonite-bearing sandstone, comprising 0.7–7.2% of the whole rock by volume (Table. [1\)](#page-7-0). This asphaltene is dark brown to gray brown, with a "bitumenlike" appearance on thin sections, and occurs in pores following feldspar dissolution (Fig. [5b\)](#page-6-0), in small intergranular pores (Fig. [5c, e\)](#page-6-0), and in intergranular pores of residual dawsonite aggregations (Fig. [5b\)](#page-6-0). Some asphaltenes occur along cracks in minerals, constituting asphaltene veins (Fig. [5d](#page-6-0)), or as solid inclusions within ankerite cement (Fig. [5c](#page-6-0)). There is a moderate positive relationship between asphaltenes and dawsonite contents (Table. [1](#page-7-0); Fig. [6](#page-7-0)).

According to well-logging data, around 20% of the sandstones containing dawsonite are developed in oil-bearing layers. It is worth noting that asphaltenes are found in all of the dawsonite-bearing sandstones, regardless of whether they are oil-bearing or dry units.

#### Petrographic characterization of the mudstones

The mineral composition of the mudstones mainly contains quartz, clay minerals (illite, illite and smectite mixing layer), plagioclase, feldspars, pyrite, dawsonite, ankerite, and sider-



Fig. 4 Longitudinal distribution of dawsonite cements in Honggang anticline. Dawsonite-bearing sandstones accumulated in the Quantou Formation, Qingshankou Formation, and Yaojia Formation. The data in brackets is the average content of dawsonite in each well

<span id="page-6-0"></span>Fig. 5 Characteristic thin-section micrographs for dawsonite and asphaltenes in dawsonite-bearing sandstones. (a) Dawsonite filled in the porosity, present as acicular radial aggregations and bladed crystals, H146#, 1507.21 m, plane polarized light; (b) asphaltenes occur in pores following feldspar dissolution and the intergranular pores of residual dawsonite aggregations, H146#, 1507.21 m, plane polarized light; (c) disseminated asphaltenes, H146#, 1507.21 m, plane polarized light; (d) asphaltenes occur along cracks in minerals, constituting bitumen veins, H143#, 1256 m, plane polarized light; (e) asphaltenes occur in intergranular pores, H146#, 1550.41 m, plane polarized light; (f) asphaltenes occur in intergranular pores, the same site as (e), ultraviolet light. Daw, dawsonite; Bit, asphaltenes; Ank, ankerite



ite. The content of dawsonite in dawsonite-bearing mudstones ranges between 2 and 5.6% of the bulk rock volume with XRD analyzed (Table. [3\)](#page-8-0). Dawsonite is difficult to recognize in mudstones as the dawsonite crystals are so small that visual detection is usually impossible.

## Vertical distribution of dawsonite cements

In this study, we focused on the vertical distribution of dawsonite cement in the well of H145#, H146#, and H148#, as dawsonite was detected in both sandstones and mudstones from these three wells.

The identified mudstones can be divided into caprocks and mudstone interlayers. The significance of caprocks in  $CO<sub>2</sub>$  gas reservoir is to prevent the escape of  $CO<sub>2</sub>$  to other reservoirs or to the surface. The 70-m-thick mudstones above SD10 in well H148# are cap mudstones, whereas the mudstones that occur between dawsonite-bearing sandstones in wells H145#, H146#, and H148# are mudstone interlayers. Thus, in these three wells, 10 dawsonite-bearing sandstone layers (SD 1 to SD 10) and 5 dawsonite-bearing mudstone layers (MD 1 to MD 5) can be identified in the Qingshankou Formation (Table. [2,](#page-8-0) Table [3\)](#page-8-0). It is clear that dawsonite in the sandstones

usually appears as multilayered zones of cementation which are separated by mudstone interlayers. The distance between each dawsonite-bearing sandstone layer ranges from 1.8 to 26.5 m. Dawsonite also presents in the mudstones no matter for the caprocks or mudstone interlayer. Besides dawsonite, ankerite was also found in some other mudstones; these mudstone layers are named as MA 1 to MA 3. Other mudstone layers, in which illite was well developed, are named as MI 1 and MI 2 (Fig. [7;](#page-9-0) Table [3\)](#page-8-0).

#### Fluid inclusion characteristics

Four types of fluid inclusion (FI) are developed in dawsonitebearing sandstones: aqueous inclusions (hydrocarbon-bearing saline inclusions), liquid (L-type) hydrocarbon-bearing inclusions, vapor (V-type) hydrocarbon-bearing inclusions, and liquid + vapor  $(L + V$ -type) hydrocarbon-bearing inclusions.

Aqueous inclusions ( $2 \times 4$  μm to  $12 \times 20$  μm, vapor/liquid ratio < 5%) in gray, light gray, or light brown are distributed in quartz overgrowth and in cracks within dawsonite (Fig. [8b\)](#page-11-0), calcite, and detrital quartz and have scattered or zoned distributions. The homogenization temperatures of these inclusions range from 71 to 127 °C with a mean of 93.5 °C, and the <span id="page-7-0"></span>Table 1 Contents for dawsonite cements and asphaltenes combining with well-logging data in dawsonite-bearing sandstones in Yaojia and Qingshankou Formations



salinity (wt.% NaCl equivalent) ranges from 1.74 to 14.41% with a mean of 5.70% (Table. [4](#page-10-0)). The aqueous inclusions typically coexist with  $L$ - and  $L + V$ -type hydrocarbon inclusions.

L-type hydrocarbon inclusions are gray or dark gray, with some displaying light-yellow or light-blue-green

asphaltenes(%)



Fig. 6 Relationship between the dawsonite cements and asphaltenes in dawsonite-bearing sandstones

fluorescence. The L-type inclusions are abundant in intergranular quartz overgrowth and early-formed calcite, as well as along cracks in quartz overgrowth, in which they appear as discontinuous trails (Fig. [8a\)](#page-11-0).

L + V-type hydrocarbon inclusions ( $2 \times 6$  µm to  $15 \times$ 20  $\mu$ m, with vapor/liquid ratio < 5%) are distributed in the late-formed calcite and dawsonite (Fig. [8c, d\)](#page-11-0) and along cracks in detrital quartz, detrital feldspar, and quartz overgrowth (Fig. [8e, f](#page-11-0)). The inclusions normally appear transparent or light yellow, and the contained liquid hydrocarbons show intense light-yellow and light-blue fluorescence. The homogenization temperatures of these inclusions range from 67 to 108  $\degree$ C with a mean of 90.5  $\degree$ C.

V-type hydrocarbon inclusions are gray and are found in clusters in late-formed calcite cements.

Two stages of inclusions can be distinguished based on their occurrences and the homogenization temperatures of coexisting aqueous inclusions (Fig. [9](#page-11-0)). The first stage comprises mainly L-type FIs and fewer  $L + V$ -type FIs, with some

<span id="page-8-0"></span>



 $Q$  quartz,  $F$  feldspar,  $L$  lithic fragment,  $Daw$  dawsonite,  $Cc$  calcite cement,  $Qc$  quartz cement

of the inclusions displaying light-yellow fluorescence. These inclusions are distributed in the early-formed quartz overgrowth and early-formed calcite, or along cracks in earlyformed quartz overgrowth, appearing as discontinuous trails. The inclusions that are developed in early-formed quartz overgrowth are mainly L-type hydrocarbon inclusions (GOI (grains with oil inclusions):  $2-3\%$ ), with a few L + V hydrocarbon inclusions, whereas those that are developed in earlyformed calcite are L hydrocarbon inclusions. The homogenization temperatures of the aqueous inclusions coexisting with the L inclusions are between 70 and [9](#page-11-0)0  $^{\circ}$ C (Fig. 9).

The second stage of inclusions comprises mainly of  $L + V$ type FIs (60–90% of the total), which are found surrounding quartz overgrowth and in detrital quartz as well as in calcite and dawsonite. Homogenization temperatures for aqueous inclusions coexisting with these inclusions are 100 to 120 °C (Fig. [9](#page-11-0)).

The oil charging recorded by these two stages of FIs identified in the dawsonite-bearing sandstones corresponds temporally to the periods of hydrocarbon charging: the first period is the accumulation of hydrocarbons occurring mainly at Neijiang-Mingshui period (Fig. [2\)](#page-3-0), and the second stage is the late adjustment stage of the hydrocarbon reservoirs during formation uplifting. As the late-formed quartz and late-formed calcite, which contain the second-stage FIs, were formed after the dawsonite, it can be inferred that the  $CO<sub>2</sub>$  leading to the formation of the dawsonite occurred after the main period of petroleum accumulation.

## **Discussion**

#### Formation of multilayer dawsonite-cemented zones

Thermodynamic analysis (Ryzhenko [2006](#page-17-0)) and geochemical numerical simulations (Xu and Pruess [2001;](#page-17-0) Xu et al. [2004](#page-17-0); Pearce et al. [1996;](#page-16-0) Knauss et al. [2001,](#page-16-0) 2005; Neufeld et al. [2010](#page-16-0); Gherardi et al. [2012](#page-15-0); Kampman et al. [2014](#page-16-0))

Table 3 X-ray diffraction data of mudstone interlayers and caprock in H145#, H146#, and H148# of Qingshankou Formation (according to Ming [2017\)](#page-16-0)

Well	Number	Depth $(m)$	Lithology	Samples	Q	Kfs	P1	P <sub>V</sub>	Hem	Daw	Ank	Sd	$\rm{I/S}$	TII
H <sub>145</sub>	MD1	1480-1480.02	Mudstone		47	6	15	$\equiv$	5	$\overline{\mathbf{4}}$			6	17
	MD2	1435-1435.02	Mudstone		49	6	13	$\overline{\phantom{0}}$	4	2	$\qquad \qquad -$	2	$24$ (Clay)	
H <sub>146</sub>	MA1	1541-1541.04	Mudstone	3	21.3	$\overline{\phantom{0}}$	7.7	5.5	$\qquad \qquad -$	—	13.1	$\overline{\phantom{0}}$	12.1	40.3
	MI1	$1521 \sim 1523$	Mudstone		24.8	2.2	15	2.4	0.8	$\overline{\phantom{0}}$	2.6	3.2	9.5	39.5
	MI2	1516-1516.04	Mudstone	3	25.3	1.9	15.8	4.2	$\overline{\phantom{m}}$	$\mathbf{0}$	$\overline{\phantom{m}}$	1.6	6.7	44.5
H148	MD3	1480.8-1480.84	Mudstone	4	15.6	3.5	13.9	3.6	$\overline{\phantom{m}}$	3.8	5.4	3.2	25.8	25.2
	MD4	1477.5-1477.57	Mudstone	3	24.7	5.2	20.3	1.7	$\qquad \qquad -$	2.3	$\overline{\phantom{0}}$		21.3	24.5
	MD5	1474.5-1474.6	Mudstone		20.6	$\overline{\phantom{0}}$	15.8		$\qquad \qquad -$	5.6	$\qquad \qquad -$	$\overline{\phantom{0}}$	57 (Clay)	
	MA <sub>2</sub>	$1475.5 \sim 1476.56$	Mudstone	8	23.1	1.6	12.9	3.7	$\overline{\phantom{0}}$	-	4.6	5.7	21.6	26.8
	MA3	$1473.5 \sim 1473.6$	Mudstone	6	27.6	1.6	15.1	3.4			4.6	2	20.1	25.6

 $Q$  quartz, Kfs k-feldspar, Pl plagioclase, Py pyrite, Hem hematite, Daw dawsonite, Ank ankerite, Sd siderite, I/S illite and smectite mixing layer, Ill illite

<span id="page-9-0"></span>

Fig. 7 Dawsonite appears as multilayered zones of cementation that are separated by mudstone interlayers. Ten dawsonite-bearing sandstone layers can be identified in the Qingshankou Formation in H145#, H146#, and H148#

indicated that  $CO<sub>2</sub>$ , which was injected into the reservoir, would lead to the dissolution of the unstable minerals (feldspar, chlorite, carbonate minerals, etc.) and the precipitation of calcite, siderite, ankerite, or dawsonite. Combining with the paragenetic sequence, the minerals that formed after  $CO<sub>2</sub>$  flooding in Honggang are dawsonite, microcrystalline quartz II, kaolinite II, calcite II, and ankerite. The chemical reaction for the post- $CO<sub>2</sub>$ injection of authigenic mineral formation in Honggang could be listed as Eqs. 1, 2, 3, 4, and 5.

$$
albite + CO2 + H2O = dawsonite + 3 quartz
$$
 (1)

(Knauss et al. [2005;](#page-16-0) Ryzhenko [2006](#page-17-0))

albite þ 2 H<sup>þ</sup> þ 2 Na<sup>þ</sup> þ 2 CO2 ð Þþ g 3 H2O

$$
= 2 \text{ dawsonic} + 2 \text{ Ca}^{2+} + 2 \text{ quartz} + \text{koolinite}
$$
 (2)

(Ryzhenko [2006](#page-17-0))

$$
albite + 2 H2O + CO2 = calcite + kaolinite
$$
 (3)

(Gunter et al. [1997](#page-15-0); Suzanne and Spiers [2009](#page-17-0))

k f eldspar þ Na<sup>þ</sup> þ 2CO2ð Þþ aq H2O ¼ dawsonite þ 3quartz þ 2K<sup>þ</sup> ð4Þ

(Johnson et al. [2001](#page-16-0); Cantucci et al. [2009\)](#page-15-0)

chlorite + 5 calcite +  $5CO<sub>2</sub>$  = 5 ankerite + kaolinite

$$
+\text{quartz} + 2H_2O\tag{5}
$$

(Watson et al. [2004](#page-17-0))

The formation of dawsonite requires elevated  $CO<sub>2</sub>$  partial pressure or abundant  $CO_3^2$ <sup>-</sup>/HCO<sub>3</sub><sup>-</sup> anion, which means that the precipitation of dawsonite is usually found to be associated with massive  $CO<sub>2</sub>$  influx. The mineralogical assemblages (dawsonite and the other precipitated minerals) after  $CO<sub>2</sub>$  flooding are at thermodynamic equilibrium with a high  $pCO<sub>2</sub>$ . As a function of the analysis on carbon-oxygen isotopic, it has been confirmed that the mantle-magmatic  $CO<sub>2</sub>$  provided the carbon sources for the deposited of dawsonite, calcite II, and ankerite (Liu et al. [2011\)](#page-16-0).

<span id="page-10-0"></span>



Dawsonite presenting in mudstones could also be a product of a CO<sub>2</sub>-water-rock system. Except for appearing as the product of the fracture filling, dawsonite, developing in mud sediments, was also reported in soil (Hay [1963\)](#page-15-0), kaolinite mudstone (Limantseva et al. [2008\)](#page-16-0), and oil shale (Smith and Milton [1966\)](#page-17-0), and all of them had been considered to be related with the carbonate fluid induced by evaporation concentration. The stratum developing dawsonite in H145# and H148# is in fan delta front and shallow lake sedimentary system. In the stratigraphic sequence of southern Songliao Basin, there is no calcium crust which develops in the dawsonite-bearing soil as reported by Hay ([1963\)](#page-15-0) in Tanganyika (Oduvai) Gorge, or the characteristic minerals indicating evaporation environment (such as natural alkali and soda) developed in the dawsonite-bearing oil shale as Smith and Milton [\(1966](#page-17-0)) reported in the Green River Formation, Piceance Creek Basin of Colorado. Therefore, dawsonite developing in the mudstones of Honggang was probably the product induced by the upward diffusion of supercritical  $CO<sub>2</sub>$  through the underlying sandstones.  $CO<sub>2</sub>$  diffusion into clay-rich caprocks containing reactive phyllosilicate minerals and precipitation of carbonates was a suggested mechanism as previously predicted elsewhere (Haszeldine et al. [2005;](#page-15-0) Gherardi et al. [2012](#page-15-0); Higgs et al. [2013](#page-15-0), [2015;](#page-15-0) Watson et al. [2004](#page-17-0); Xu et al. [2005](#page-17-0)).

<span id="page-11-0"></span>Fig. 8 Petrographic characteristics of fluid inclusions in dawsonite-bearing sandstones. (a) Dark gray L-type fluid inclusions in quartz overgrowth, H143#, 1599.15 m, plane polarized light; (b) aqueous fluid inclusion in dawsonite, H146#, 1518.65 m, plane polarized light; (c)  $L + V$ -type fluid inclusion in dawsonite, H146#, 1518.65 m, plane polarized light; (d)  $L + V$ type fluid inclusion in dawsonite, the same site as (c), ultraviolet light; (e)  $L + V$ -type fluid inclusion in quartz overgrowth, H146#, 1550.41 m, plane polarized light; (f)  $L + V$ -type fluid inclusion in quartz overgrowth, the same site as (e), ultraviolet light. Q, quartz; Qo, quartz overgrowth; Daw, dawsonite; V-type liquid hydrocarbon-bearing inclusions;  $L + V$ -type liquid + vapor hydrocarbon-bearing inclusions



The injection of mantle  $CO<sub>2</sub>$  occurred in Paleogene, during that time the Qingshankou and Quantou Formation were with in situ pressures and temperatures in the range of 100–200 bar and 80–110 °C. With this pressure and temperature,  $CO<sub>2</sub>$  was in the supercritical state. The precipitation of a measurable quantity of minerals needs a significant quantity of water. If the reservoir is dry due to the presence of hydrocarbons (oil and gas) and/or water-free supercritical  $CO<sub>2</sub>$  (scCO<sub>2</sub>), the



Fig. 9 Frequency histogram of the homogenization temperature in dawsonite-bearing sandstones

precipitations of minerals are impossible and no record of the conditions is feasible, whereas, with the in situ pressures and temperatures, the dissolution of  $\mathrm{scCO}_2$  into bulk formation water generates carbonic acid, bicarbonate, and carbonate anions, leading to the bleaching of sandstones and formation of ferruginous carbonate concretions (Lewicki et al. [2007;](#page-16-0) Loope and Kettler [2015](#page-16-0)). In addition, the formation water will also be dissolved in  $\sec O_2$ , forming a wet  $\sec O_2$ phase (Lin et al. [2008](#page-16-0); Pearce et al. [2016\)](#page-16-0), with the thickness of this phase measuring only a nanometer or angstrom on the surface of the mineral (Lin et al. [2008](#page-16-0)), leading mineral dissolution and precipitation induced by the wet  $\sec O_2$  phase limited.

Normally the fractures could be the obvious migration "pathway" for  $\secO_2$ ; moreover  $CO_2$  can also migrate laterally along the connected sandstone layers or diffused upward through the low-permeability mudstone layers. During the upward diffusion,  $\sec O_2$  could migrate through the mudstone interlayer from the underlying sandstones and then transfer to the overlying sandstones. Ideally, the dissolved  $\sec O_2$  would have continued to diffuse into the overlying layers until it was exhausted. Simultaneously, dawsonite would have been precipitated in the sandstone and the mudstone interlayer, with

the content of dawsonite decreasing in the upper layers as the hypothesis shown in Fig. 10. In fact, the vertical distribution of the content of dawsonite in H145#, H146#, and H148# does not seem to change with the depth.

With the buffer of mudstones,  $\sec O_2$  tends to migrate laterally along the interworking sandstone layers. During the lateral migration,  $\sec O_2$  in the sandstones would have been distributed by the mudstone interlayer, following which multilayer dawsonite cementation would have occurred (Eqs. [1](#page-9-0), [2,](#page-9-0) and [4\)](#page-9-0) (Fig. [11](#page-13-0)).

Thereby, a multilayered dawsonite could be one of the geological produces for  $\sec O_2$  flooding through the heterogeneous rock, which acts as the lateral migration and upward diffusion.

According to the distribution of the dawsonite in caprocks and the mudstone interlayers, we can estimate the upper limit on the distance of diffusion of the dissolved  $\sec O_2$ . Currently, we are not able to determine whether the formation of the

ankerite and illite in the mudstones was related to the upward diffusion of  $\sec O_2$ . The depth of MD5 is 1474.5 m, if dawsonite is assumed to be present in all of the mudstone interlayers from MD5 downward to the top of the underlying sandstone (1478 m), then the vertical distance of diffusion for this dissolved  $\sec O_2$  in the caprock mudstone is 3.5 m. If the whole mudstone interlayers (1480.5–1481.5 m) of MD3 contained dawsonite, then the distance of diffusion for this dissolved  $\sec CO_2$  in the interlayered mudstone is only 1 m. Reactivity of the mudstone is generally shown to be low and limited to the vicinity of the  $CO_2$ -mudstone interface (Liu et al. [2012](#page-16-0)) and is related to the original mineralogical and petrophysical properties. The upward diffusion for  $\sec O_2$  to the low-permeability mudstone is limited. In the mudrock seals overlying a natural  $CO<sub>2</sub>$ reservoir in the North Sea Miller Oil Field, a total of 12 m vertically above the interface influenced by  $CO<sub>2</sub>$  was reported by Lu et al. [\(2009](#page-16-0)), which was evidenced by a strong linear upward decreasing trend of  $\delta^{13}$ C.



Fig. 10 Ideal pattern diagram for the upward diffusion of water-saturated supercritical CO<sub>2</sub> from underlying sandstone. Note the contents of dawsonite should be increased with depths

<span id="page-13-0"></span>

Fig. 11 Lateral migration and the upward diffusion of supercritical CO<sub>2</sub> from underlying sandstone lead to the formation of the multilayer dawsonitecemented zones

### Migration of  $CO<sub>2</sub>$  in dawsonite-bearing sandstones

As a function on the role of " $CO<sub>2</sub>$  trace mineral" (Liu et al. [2009;](#page-16-0) Gao et al. [2009](#page-15-0)), the existence of dawsonite can record such a scenario, where a large-scale  $CO<sub>2</sub>$  is injected or resided in the geological history.

A typical  $CO<sub>2</sub>$ -bearing reservoir is composed of upper water-free  $\sec O_2$  and lower dissolved  $\sec O_2$  into formation water. The geological record for water-free  $\sec O_2$  is rare, whereas dissolved  $\sec O_2$  can be recorded by the formation of carbonate minerals such as dawsonite and ankerite. Therefore, if dawsonite and  $\sec O_2$  coexisted in a  $CO_2$ -bearing reservoir, then the dawsonite cement layers can be regarded as the layers where the  $\sec O_2$  is dissolved in a sufficient quantity of water. If the reservoir is found to be with exhausted  $CO<sub>2</sub>$ , then the dawsonite cement layers can be regarded as an ancient CO2-bearing reservoir.

Dawsonite-bearing sandstone is normally well developed in  $CO_2$ -bearing reservoirs. For example, wells Su2# (1368– 1450 m) and Wu10# (1811–1821 m) in the Hailar Basin (China) (Xu et al. [1994](#page-17-0)), Gu7# (1549.28–1577.14 m), Gu9# (1573.5–1579.5 m), Gu48# (1207.5–1515.7 m) in the Huazijing Step of the southern Songliao Basin (China) (Yu et al. [2014](#page-17-0)), and 22-1X State (462–472 m) in the Springerville–St. Johns  $CO<sub>2</sub>$  gas field (US) (Moore et al.  $2005$ ) all contain abundant dawsonite. However,  $CO<sub>2</sub>$  that is preserved in a dawsonite-bearing reservoir will eventually disappear by migrating to a new trap or leaking to the surface.  $CO<sub>2</sub>$  has been reported to have migrated to a new trap in wells Tong 1# and Wu 2# in the Hailar Basin (China) (Xu et al.

[1994\)](#page-17-0) and undergone small-scale leakage in the Shabwa Basin (Yemen) (Worden [2006\)](#page-17-0), Fuxin Basin (China) (Liu et al. [2008\)](#page-16-0), and Tamtsag Basin (Mongolia) (Liu et al. [2009](#page-16-0)).

Dawsonite-bearing sandstones are widespread in 14 wells, but most wells in the anticline do not contain  $CO_2$ .  $CO_2$  is distributed in several wells which are mostly on the northeastern part of the anticline, such as H73# and H77# (Zou et al.  $2007$ ), with dawsonite-bearing sandstones and  $CO<sub>2</sub>$  gas coexisting only in well H73#. The C isotope values ( $\delta^{13}C$ , PDB) of dawsonite in the sandstones of the Honggang anticline range from  $-3.42$  to 3.29‰, whereas the C isotope values of  $CO<sub>2</sub>$  in isotopic equilibrium with dawsonite  $(\delta^{13}C_{CO2}$ , PDB) are calculated to be in the range of −9.92 to − 4.23‰ (Liu et al. [2011\)](#page-16-0). This is calculated using the calcite- $CO<sub>2</sub>$  carbon isotope fractionation equation of Ohmoto and Rye (1979), and assuming there is zero carbon isotope fractionation between calcite and dawsonite, the temperature for this equation was calculated by the depth of dawsonitebearing sandstones  $(1256 \sim 1830 \text{ m})$  and the average geothermal gradient (4.26 °C/100 m). The calculated  $\delta^{13}C_{CO2}$  values are similar to the carbon isotope values ( $\delta^{13}$ C, PDB) of the residual CO<sub>2</sub> in the gas reservoir (−8.05 to −2.65‰) (Hou et al.  $2009$ ), suggesting that  $CO<sub>2</sub>$  for dawsonite genesis and residual  $CO<sub>2</sub>$  in the gas reservoir of the Honggang anticline had the same carbon source. Dawsonite could provide a permanent mineral storage host only in systems that maintain high  $CO<sub>2</sub>$  pressures; once high  $CO<sub>2</sub>$  pressure dissipates, dawsonite may be an ephemeral phase in dynamic setting (Hellevang et al. [2005\)](#page-15-0). This means that in addition to the  $CO<sub>2</sub>$  trapped by the precipitation of dawsonite, the remaining

free or dissolved  $CO<sub>2</sub>$  would still be existing in the reservoir. Combined with the truth that most of the present  $CO<sub>2</sub>$  gas reservoirs (in K1q4) are in the deeper layers than the dawsonite-bearing sandstone reservoirs without  $CO<sub>2</sub>$  (K1q4- $K2y1$ , we can deduce that  $CO<sub>2</sub>$  was at some time abundant in the Honggang anticline (in K1q4-K2y1) but had now part of  $CO<sub>2</sub>$  been migrated to the north part of the anticline or to other traps, with the other part consumed by the reaction with the primary rock, producing new carbonates. With the basic thermodynamic fraction equation and geological numerical simulations,  $CO<sub>2</sub>$  sequestered by dawsonite-bearing sandstones was calculated to be  $89.73 \sim 99.51$  kg/m<sup>3</sup> (Liu et al. [2011\)](#page-16-0).

Hydrocarbon filling events were also recorded in the dawsonite-bearing sandstones by the paragenesis and compositions of fluid inclusions. In Honggang, parts of the dawsonite-bearing sandstones are developed in oil-bearing or oil-water layers. Two stages of hydrocarbon-bearing (oilgas) inclusions were found in the dawsonite-bearing sandstones, with the later-stage inclusions (presenting the adjustment stage of the hydrocarbon) being contained in the microcrystalline quartz II, calcite II, and dawsonite, as well as in fractures in the quartz grains, quartz overgrowth, and detrital feldspar (Fig. [8\)](#page-11-0). The diagenetic sequence indicates that dawsonite, microcrystalline quartz II, and calcite II were formed after  $CO<sub>2</sub>$  flooding. Therefore, we infer that the injection time of  $CO<sub>2</sub>$  and the adjustment stage of the hydrocarbon were separated by only a very short time interval. The secondstage FIs, most of which were  $L + V$ -type hydrocarbonbearing inclusions and distributed in fractures/cracks in quartz grains and their overgrowth, were found to contain not only  $CO<sub>2</sub>$  in both gaseous and liquid phases but also  $CO<sub>3</sub><sup>2−</sup>$  with CH<sub>4</sub> (Qu et al. [2013](#page-17-0)). Inorganic CO<sub>2</sub> was detected in the northeastern part of the anticline (well H73#), with  $\delta^{13}C_{\text{PDB}}$ values between  $-5.32$  and  $-5.80\%$  (Hou et al. [2009](#page-15-0)), indicating that inorganic  $CO<sub>2</sub>$  has dissolved in the oil. The physical and chemical properties of crude oil and the ionic concentration of formation water were also changed after the  $CO<sub>2</sub>$ injection (Yu et al., 2016). The change of crude oil shows the decrease of density, viscosity, freezing point, and initial boiling point, while the change of formation water is the increase of salinity,  $K^+$ +Na<sup>+</sup>, and  $HCO_3^-$ .

Asphaltenes, abundant in the dawsonite-bearing sandstones, might be a product induced by deasphalting of crude oil through injection of mantle-derived  $CO<sub>2</sub>$ . The principal processes for the asphaltene formation generated with crude oil include thermal alteration and deasphalting (Rogers et al. [1974](#page-17-0); Leythaeuser and Anf Rückheim [1989;](#page-16-0) Larter et al. [1990](#page-16-0); Wilhelms and Larter [1994,](#page-17-0) [1995;](#page-17-0) Hunt [1996;](#page-15-0) Huc et al. [2000](#page-15-0); Liu et al. [2020b](#page-16-0)). The process for the direct thermal cracking of petroleum hydrocarbons usually occurs at great depths (temperatures of  $\geq$  170 °C; Milner et al. [1977](#page-16-0); Huc et al. [2000;](#page-15-0) Waples [2000](#page-17-0)). However, the maximum burial temperature from the burial-thermal history models ( $\sim$  117 °C) or the higher temperature recorded in fluid inclusions (122 °C) does not exceed the lowermost temperature boundary for thermal alteration (170 °C). This indicated that very little thermal alteration of crude oil occurred in the Qingshankou Formation reservoir.

It is well known that the flooding of  $CO<sub>2</sub>$  into an oil reservoir could cause the precipitation of asphaltenes (Novosad and Costain [1990;](#page-16-0) Monger and Trujillo [1991](#page-16-0); Liu et al.  $2020a$ ). As the solubility of  $CO<sub>2</sub>$  in oil is nearly 30 times higher than that in pure water,  $CO<sub>2</sub>$  dissolved in oil reduces the viscosity of the oil and increases its volume, thereby providing the internal driving energy for this oil. Characterizing such mechanisms will assist in enhanced oil recovery  $(CO<sub>2</sub>$ -EOR), which has been applied to projects in various countries (Blunt et al. [1993](#page-15-0); Kovscek and Cakici [2005](#page-16-0); Han and McPherson [2009;](#page-15-0) Lindeberg et al. [2017;](#page-16-0) Lee et al. [2019\)](#page-16-0). When  $CO<sub>2</sub>$  dissolves in oil, the dynamic equilibrium of the original chemical composition of the oil is altered, followed by fractionation of light components and enrichment of heavy components, causing the precipitation of asphaltenes.

In Honggang, asphaltenes develop in the intergranular pores of residual dawsonite aggregations, and there is a moderate positive relationship between the contents of asphaltenes and dawsonite cements. We can deduce that the crude oil in this area was deasphalted after the injection of  $CO<sub>2</sub>$ , with the residual lighter oil trapped as hydrocarbon fluid inclusions in carbonate minerals such as dawsonite. This is in turn suggested that  $CO<sub>2</sub>$  could be stored as carbonate minerals after the termination of a  $CO<sub>2</sub>$ -EOR project.

## Conclusions

We examined the occurrence of dawsonite cements as well as the characteristics of fluid inclusions in dawsonite-bearing sandstones of the Honggang anticline, southern Songliao Basin, to establish a petrological record of magmatic  $CO<sub>2</sub>$ migration in the heterogeneity reservoir. Our conclusions are as follows:

- 1. Dawsonite normally appears as multilayered zones of cementation in the sandstones which are separated by mudstone interlayers. These multilayered dawsonite could be one of the geological produces for mantle-derived  $CO<sub>2</sub>$ flooding through the heterogeneous rock, which acts as the lateral migration and upward diffusion.
- 2. Dawsonite was detected in the mudstone interlayers, which implied  $CO<sub>2</sub>$  could migrate through the thinner mudstone interlayer from the underlying sandstones and then transfer to the overlying sandstones. The vertical distance of diffusion for this dissolved  $\sec O_2$  in the mudstones is limited. Caprock is still efficient to prevent the escape of  $CO<sub>2</sub>$  to other reservoirs or to the surface.

<span id="page-15-0"></span>3. Both of the hydrocarbon and mantle  $CO<sub>2</sub>$  injection events have been recorded in the dawsonite-bearing sandstones. Combined with the truth that the injection time of  $CO<sub>2</sub>$  is later than that of hydrocarbon, the deasphalting of crude oil by injection of mantle-derived  $CO<sub>2</sub>$  should occur, with the asphaltenes as the deasphalting product, abundant in dawsonite-bearing sandstones. Therefore,  $CO<sub>2</sub>$  could also be stored as long-term carbonate minerals, such as dawsonite, after the termination of a  $CO<sub>2</sub>$ -EOR project.

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