Marine and Petroleum Geology 75 (2016) 220–239

Contents lists available at ScienceDirect

Marine and Petroleum Geology

journal homepage: www.elsevier.com/locate/marpetgeo

Research paper

Origin and distribution of hydrogen sulfide in the Yuanba gas field, Sichuan Basin, Southwest China

Pingping Li [a,*], Fang Hao [b], Xusheng Guo [c], Huayao Zou [a], Yangming Zhu [d], Xinya Yu [a], Guangwei Wang [a]

[a] State Key Laboratory of Petroleum Resources and Prospecting, China University of Petroleum, Beijing, Changping, Beijing 102249, China
[b] Key Laboratory of Tectonics and Petroleum Resources, Ministry of Education, China University of Geosciences, Wuhan, Hubei 430074, China
[c] SINOPEC Exploration Company, Chengdu, Sichuan 610041, China
[d] Department of Earth Sciences, Zhejiang University, Hangzhou, Zhejiang 310027, China

A R T I C L E I N F O

Article history:
Received 20 November 2015
Received in revised form
21 April 2016
Accepted 22 April 2016
Available online 23 April 2016

Keywords:
Hydrogen sulfide
Thermal sulfate reduction
Carbon dioxide
Stable carbon isotopes
Yuanba gas field
Sichuan Basin

A B S T R A C T

The Yuanba gas field in the Permian Changxing Formation (P_2c), which exhibits wide variations in its hydrogen sulfide (H_2S) concentration (1.20–12.16%), is a typical sour gas field in the northern Sichuan Basin. The sulfur-rich reservoir's solid bitumen (atomic S/C ratios are 0.032–0.142), and late calcite cement $\delta^{13}C$ values, which are smaller than the $\delta^{13}C$ values of the host dolostone, indicate that the H_2S originated from thermal sulfate reduction (TSR) and oil was involved in TSR. The gas souring index (GSI) of P_2c's gases is generally lower than 0.1. The ethane $\delta^{13}C$ values increase as the GSI increases, although no obvious increase was observed in the methane $\delta^{13}C$ values. The calcite cements' $\delta^{13}C$ values (−15.36 to +4.56‰) in dolostone are heavier than the typical reported values, which implies that only limited heavy hydrocarbon gases were involved in TSR. No anhydrites developed in P_2c's reservoirs, and dissolved sulfate anions (SO_4^{2-}) were mainly enriched during dolomitization. Insufficient dissolved SO_4^{2-} most likely caused the lower H_2S concentrations in the Permian to Triassic reservoirs in the northeastern Sichuan Basin compared to the Permian Khuff Formation in Saudi Arabia and the Jurassic Smackover Formation in Mississippi. Except for the SO_4^{2-} in residual water in paleo-oil zones, SO_4^{2-} from bottom water may also be involved in TSR; therefore, oil reservoirs with bottom water have more SO_4^{2-} and can produce more H_2S than pure oil reservoirs. This phenomenon may be the main cause of the great difference in the H_2S concentrations between reservoirs, while gravitational differentiation during late uplift most likely creates differences in H_2S concentrations in a single reservoir. Carbon dioxide (CO_2), which has a relatively heavy $\delta^{13}C$ value (−3.9 to −0.3‰), may be the combined result of TSR, the balance between CO_2 and inorganic fluid systems, and carbonate decomposition.

1. Introduction

H_2S is toxic and corrosive and can increase the handling costs of natural gas. Thus, the origins and distribution predictions of H_2S are crucial topics in the petroleum industry. Numerous laboratory studies (e.g., Kiyosu and Krouse, 1990, 1993; Cross et al., 2004; Yuan et al., 2013), geological case studies (e.g., Worden et al., 1995; Heydari, 1997; Cai et al., 2004; Hao et al., 2008), and comprehensive studies and reviews (e.g., Goldstein and Aizenshtat, 1994; Machel, 2001; Hao et al., 2015) have been conducted over the past 40 years.

The main sources of H_2S in hydrocarbon reservoirs are as follows: (1) the thermal decomposition of organic sulfur compounds in kerogen or oil (also termed thermal chemical alteration, TCA, e.g., Kelemen et al., 2008), (2) bacterial or microbial sulfate reduction (BSR), and (3) thermochemical sulfate reduction (TSR) (Orr, 1974; Machel, 1987, 2001). In most cases, TSR mainly contributes to the high concentrations of H_2S (>10%) in deeply buried gas reservoirs (Orr, 1974, 1977; Worden and Smalley, 1996; Mougin et al., 2007).

TSR is a reaction between hydrocarbons and dissolved sulfate (Machel et al., 1995; Worden et al., 1996; Bildstein et al., 2001). Dissolved SO_4^{2-} is highly stable because of its symmetrical tetrahedral molecular structure (Ma et al., 2008). Therefore, energy absorption is essential to break its sulfur–oxygen bonds. Most

* Corresponding author.
E-mail address: lpp@cup.edu.cn (P. Li).

http://dx.doi.org/10.1016/j.marpetgeo.2016.04.021
0264-8172/

experimental studies determined or estimated relatively high activation energies of 140–250 kJ/mol (Kiyosu, 1980; Cross et al., 2004; Ma et al., 2008; Zhang et al., 2012), which implies that TSR would occur at relatively high temperatures. The onset temperature to initiate TSR in the laboratory is generally above 200 °C (Toland, 1960; Kiyosu and Krouse, 1993; Cross et al., 2004; Xia et al., 2014). Although still controversial, the commonly believed lowest temperature for TSR is 100–140 °C based on laboratory experiments and case studies (Orr, 1974; Worden et al., 1995, 1998; Cai et al., 2004).

The initiation mechanism, reaction process, and products of TSR have been studied intensively (Orr, 1974; Machel et al., 1995; Worden and Smalley, 1996; Zhang et al., 2007, 2008a; Amrani et al., 2008; Yuan et al., 2013). A three-stage TSR has been proposed by Hao et al. (2008): liquid-hydrocarbon-involved TSR (R1), heavy-hydrocarbon-gas-dominated TSR (R2), and methane-dominated TSR (R3). If the respective metals are available, pyrite, saddle dolomite, ankerite, siderite, witherite, and strontianite can form during these reactions (Machel, 1987, 2001; Krouse et al., 1988; Heydari and Moore, 1989):

$$\text{Liquid hydrocarbons} + SO_4^{2-} \rightarrow \text{NSO-compound} + \text{bitumen} + H_2S + CO_2 \quad \text{(R1)}$$

$$nCaSO_4 + C_nH_{2n+2} \rightarrow nCaCO_3 + H_2S + (n-1)S + nH_2O \quad \text{(R2)}$$

$$CH_4 + CaSO_4 \rightarrow CaCO_3 + H_2S + H_2O \quad \text{(R3)}$$

The Sichuan Basin, which has relatively high H_2S concentrations (generally >5.0%) in its marine Permian to Triassic reservoirs, is a typical sour gas province in southern China. Previous studies mainly focused on Permian to Triassic gas reservoirs in the eastern Sichuan Basin and proved that the H_2S originated from TSR (Cai et al., 2003, 2010; Li et al., 2005; Zhu et al., 2005, 2007; Hao et al., 2008). However, whether intense methane-dominated TSR occurred remains controversial (Hao et al., 2015). The newly discovered Yuanba gas field in Permian Changxing Formation (P_2c), which exhibits wide variations in its H_2S concentration (1.20–12.16%), is located in the northern Sichuan Basin. Many isolated gas reservoirs with isolated gas-water contacts are present here, and the H_2S concentration varies greatly between different reservoirs and even in a single reservoir. The hydrocarbon gases are mainly derived from secondary oil cracking (Li et al., 2015a). No anhydrite is present in P_2c's gas reservoir in the Yuanba gas field, which is obviously different from commonly reported case studies (Worden and Smalley, 1996; Heydari, 1997; Jenden et al., 2015). Therefore, the Yuanba gas field is a suitable geological example to examine the essential conditions and stages of TSR.

The purpose of this paper is to address the following questions: (1) What is the origin of the H_2S and CO_2 in the Yuanba gas field? (2) Was methane involved in TSR? (3) What is the source of the sulfates that are required for TSR? (4) What are the factors that control the distribution of H_2S? (5) Why are the H_2S concentrations relatively low in the Yuanba gas field and adjacent areas in the Sichuan Basin?

2. Geological setting

The Sichuan Basin, which has an area of 180,000 km^2, is a rhombic basin in southwestern China (Fig. 1). The general evolutionary history and stratigraphy of the basin have been reviewed by Ma et al. (2007), Hao et al. (2008), and Li et al. (2015a). The Sichuan Basin has experienced several tectonic cycles and movements (Zhai, 1989; Tong, 1992) (Fig. 2). Before the early Indosinian movement, the basin was mainly characterized by subsidence and uplift, while large-scale lateral compression has been occurring since the late Indosinian movement, and strong lateral compression occurred during the Himalayan movement (Ma et al., 2007).

The total thickness from the Sinian to the Quaternary in the Sichuan Basin is 6000–12,000 m (Fig. 2). The Lower Sinian consists of piedmont and fluvial deposits to the southwest; eruptive materials to the west; and fluvial, offshore, and shallow sea deposits to the southeast. The Upper Sinian-Lower Permian mainly consists of marine carbonate and shale. The Upper Permian Longtan Formation (P_2l) developed in a continental to marine transitional environment in the southwestern part of the basin and consists of mudstone that is interbedded with coal; simultaneously, the Wujiaping Formation (P_2w) developed in a restricted embayment in the northeastern basin and consists of marine mudstone and muddy limestone. The P_2c layer to the Lower Triassic Feixianguan Formation (T_1f) developed in an open and shallow platform and consists of limestone and dolostone. During the deposition of P_2c, a northwest- to southeast-trending shelf developed in the northern and eastern Sichuan Basin, and platform edges developed in both the western and eastern regions of the shelf (Fig. 3A). During the deposition of the second member of the Feixianguan Formation (T_1f^2), the shelf closed in the northwestern part and the range of the shelf decreased (Fig. 3B). Near the end of T_1f, the shelf completely disappeared and a completely restricted platform formed. The Lower Triassic Jialingjiang (T_1j) and Middle Triassic Leikoupo (T_2l) Formations developed in restricted and evaporite platforms and consist of limestone and widespread anhydrite. The Upper Triassic-Quaternary Xujiahe Formation (T_3x) developed in a fluvial-lacustrine environment and consists of coal, mudstone, sandstone, and local conglomerate.

Five potential petroleum source rocks developed in the Sichuan Basin, including Lower Cambrian shale and mudstone; Lower Silurian shale; Upper Permian coal, mudstone, and muddy limestone; Upper Triassic mudstone and coal; and Lower-Middle Jurassic mudstone (Fig. 2). The Upper Permian source rocks have been confirmed to have contributed abundant natural gases from T_1f and P_2c in the northeastern Sichuan Basin (Li et al., 2005; Hao et al., 2008, 2009; Zou et al., 2008).

The Yuanba gas field, which was discovered in 2007, is located in the northern Sichuan Basin (Fig. 1) and contains its main gas production interval in P_2c's dolostone reservoir (Guo, 2011). Platform margin reefs and shoals traps developed in P_2c, and open sea limestone in the first member of T_1f is the direct cap rock. The hydrocarbon gases in P_2c's reservoirs in the Yuanba gas field are mainly secondary cracking gases that were derived from P_2w's sapropelic source rock (Guo, 2011; Duan et al., 2013; Li et al., 2015a). P_2c's reservoirs reached maximum burial depths of approximately 8000 m and temperatures of approximately 240 °C at 100 Ma during the Late Cretaceous before being uplifted to a present depth of 6500–7000 m. The reservoirs exhibit a present-day thermal maturity above 3.0% and have equivalent vitrinite reflectance (Ro) (Fig. 4, Li et al., 2015a).

3. Samples and methods

The chemical composition of the natural gas and carbon isotope, reservoir porosity and water saturation data were collected from the SINOPEC Exploration Southern Company. All the gas samples were collected during drill stem testing by using standard techniques in the industry and were analyzed with standard techniques at the Key Laboratory of Gas Geochemistry, Lanzhou Institute of Geology, Chinese Academy of Sciences. The chemical composition of the natural gas samples was analyzed by using a Finnigan MAT-271 mass spectrometer, and the stable carbon isotope compositions of methane, ethane, and CO_2 were measured by using a Finnigan