Organic Geochemistry 101 (2016) 63–71

Contents lists available at ScienceDirect

Organic Geochemistry

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

UV Raman spectroscopy of hydrocarbon-bearing inclusions in rock salt from the Dongying sag, eastern China

Yong Chen [a,b,*], Xintao Wang [a], Robert J. Bodnar [c]

[a] School of Geosciences, China University of Petroleum (East China), Qingdao 266580, Shandong Province, China
[b] Laboratory for Marine Mineral Resources, Qingdao National Laboratory for Marine Science and Technology, Qingdao 266071, China
[c] Fluids Research Laboratory, Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA

ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 2 July 2016
Accepted 13 August 2016
Available online 20 August 2016

Keywords:
UV Raman spectroscopy
Hydrocarbon-bearing inclusions
Aqueous inclusions
Petroleum migration
Sealing capacity
Rock salt

ABSTRACT

Compositions of hydrocarbon-bearing inclusions in rock salt (halite) from the Shahejie Formation in the Dongying sag, Bohai Bay Basin, eastern China have been analysed by Raman spectroscopy coupled with a 244 nm UV laser source. The fluorescence effect caused by the conventional visible laser excitation of the aromatic fractions of HC-bearing inclusions can be effectively avoided. Six types of HC-bearing inclusions belonging to two generations have been identified in halite according to their hydrocarbon types and petrographic characteristics. The presence of HC-bearing inclusions in halite provides evidence of crystal fracturing and healing, plastic deformation and dynamic recrystallization of rock salt in the Dongying sag. This proves that rock salt may have repeatedly lost and then recovered its sealing capacity during two stages of oil emplacement. Water and hydrocarbons were detected by UV Raman spectroscopy in the studied samples, in both HC-bearing inclusions and aqueous inclusions. These results are important for understanding the formation conditions of these fluid inclusions and the interactions between the formation water and petroleum in reservoirs. Our results show that UV Raman spectroscopy has a potential to become a powerful tool for analyzing hydrocarbon-bearing fluid inclusions trapped in various elements of a petroleum system.

1. Introduction

Hydrocarbon-bearing (HC-bearing) inclusions are ubiquitous in petroleum reservoirs and/or migration pathways (Burruss, 1981; Munz, 2001). HC-bearing inclusions contain important information about petroleum generation, migration, and accumulation because of their sealing capacity (Goldstein and Reynolds, 1994; Goldstein, 2001; Munz, 2001). Petroleum migration can be inferred from compositional differences between inclusions in successive growth zones of fracture cement samples (Bodnar, 1990; George et al., 1997), or from the presence of different populations of inclusions in different generations of cements (Burruss et al., 1983; George et al., 1998). The compositions of the oil or source rock bitumen are the keys to identify the types, maturity and origin of oil. However, when these sorts of sample are unavailable or the petroleum has been mixed, biodegraded or water-washed, the inclusions can then be the key (George et al., 1998; Munz, 2001; Guilhaumou et al., 2004). Accurately determining the composition or types of HC-bearing inclusions is critical for identifying the types, maturity, and origin of oil.

Up to now, the composition of group or bulk hydrocarbon inclusions can be only acquired by gas chromatography–mass spectrometry (GC–MS) through on-line or off-line crushing inclusions or extracting hydrocarbons under a vacuum system via laser ablation (Karlsen et al., 1993; George et al., 1996; Jones and Macleod, 2000; Volk et al., 2000). However, as the samples are extracted in bulk, distinguishing the geochemical signature of different fluid inclusion assemblages in the same mineral is not possible. Therefore, analytical methods for probing the chemical compositions of individual inclusions are required for understanding the evolution of fluids during petroleum migration and emplacement. For individual hydrocarbon inclusions with large size, their compositions can be obtained by using laser ablation GC–MS (Volk et al., 2010; Zhang et al., 2012) or using time-of-flight secondary ion mass spectrometry (TOF-SIMS) (Siljeström et al., 2013). Also, individual hydrocarbon inclusions can be identified non-destructively by UV fluorescence spectroscopy (Kihle, 1995), micro-infrared spectroscopy (FT-IR) (Pironon and Barres, 1990; Pironon et al., 2001), and Raman spectroscopy (Wopenka et al., 1990; Burke, 2001; Jehlička and Edwards, 2008). A single inclusion needs to be at least ~200 μm^2 in cross-section for detection by FT-IR analysis

---

[*] Corresponding author at: School of Geosciences, China University of Petroleum (East China), Qingdao 266580, Shandong Province, China.

E-mail address: yongchenzy@upc.edu.cn (Y. Chen).

http://dx.doi.org/10.1016/j.orggeochem.2016.08.010
0146-6380/

(Wopenka et al., 1990). Raman spectroscopy offers a laser-spot-size of 1–2 μm, which allows us to work on small inclusions or at the scale of individual phases in a fluid inclusion (Bourdet et al., 2011). Although the size requirement ($\geqslant$ 3 μm) of inclusions is easily satisfied for Raman spectroscopy (Wopenka et al., 1990), the fluorescence induced by the excitation laser (such as the 514.5 nm wavelength laser) is in the visible range and overlaps Raman shifts. Because the intensity of fluorescence is orders of magnitude stronger than the Raman signal over a wide range of Raman spectra, it is difficult to obtain good Raman spectra of hydrocarbon inclusions using visible laser excitation. Therefore, visible Raman micro-spectroscopy can only be applied in the case of non-fluorescent inclusions (Pironon et al., 2001). Near-infrared FT-Raman can be applied in the case of weakly fluorescent inclusions, but is still affected by strong background fluorescence for most inclusions (Pironon et al., 1991).

Nevertheless, UV Raman sheds light on the analysis of HC-bearing inclusions. Asher and Johnson (1984) were the first to show that significantly improved spectra of hydrocarbons can be obtained by exciting within the UV region of the spectrum. The more significant advantage was the realization that fluorescence can be avoided altogether by going to energies typically higher than the first excited state, from which most fluorescence arises (Kasha, 1950; Asher, 1984). Shoute et al. (2002) and Loppnow et al. (2004) successfully obtained UV Raman spectra on a variety of hydrocarbon samples with excitation wavelengths between 214 and 234 nm with little or no interference from fluorescence. All of these results argued that UV Raman spectroscopy was potentially a powerful tool in probing the chemical compositions in HC-bearing inclusions.

Rock salt usually serves as a good cap rock for petroleum reservoir systems; it forms the top and side seals for major hydrocarbon accumulations. However, the hydrocarbon inclusions found in halite of rock salt indicate that oil can enter into rock salt under special geological conditions (Pironon et al., 1995a, 1995b; Grishina et al., 1998; Schoenherr et al., 2007b; Chen et al., 2014). In this study, we attempted to analyze and characterize HC-bearing inclusions with UV Raman spectroscopy, in order to better understand the petroleum types and the compositional changes of these fluid inclusions trapped in rock salt during oil migration and emplacement in the Dongying sag, Bohai Bay Basin, eastern China.

2. Samples

Our studied samples were rock salt collected from the Paleogene Shahejie formation in the Dongying sag, Bohai Bay Basin, eastern China. The geological background of the Dongying sag had been introduced by many papers (Guo et al., 2012; Yuan et al., 2015), and the geochemistry of evaporites in studied area was reported in detail by Chen et al. (2013). All 41 samples were from drilling cores from Dongfeng 3 (DF3), Dongfeng 5 (DF5), and Haoke 1 (HK1) wells, which are located in the central uplift belt zone in the Dongying sag. In core samples directly above or below some oil stringers, the rock salt is stained black by crude oil, suggesting that oil migrated through the rock salt. More information about the samples can be found in the paper reported by Chen et al. (2014). Many HC-bearing fluid inclusions were found in halite, indicating that the rock salt interacted with migrating oil and water. In order to understand the geological process of oil migration, it is essential to know the compositions or types of the oil in the fluid inclusions.

3. Method and instrumentation

The rock salts were cut into about 500 μm thin wafers with double side polished. Fluid inclusion petrographic analysis was undertaken to understand the occurrence, sizes, phase(s), shapes, colours, and petrographic relationships. Hydrocarbon inclusions were identified by their fluorescence under UV illumination. The fluorescence of hydrocarbon inclusions was checked by UV light microscopy, using an Axioskop 40 microscope (Carl Zeiss). Two-phase (liquid + vapor) fluid inclusions were selected to test the homogenization temperatures. Microthermometry was conducted using a Linkam THMSG 600 heating and cooling stage. The stage was mounted on a microscope equipped with a 50× long working-distance objective for visible light. After calibration of the stage, the precision and accuracy of temperature measurements was approximately ± 0.5 °C at the conditions of this study. The heating or cooling rate was < 5 °C/min when approaching the homogenization temperature, and we used the method of cycling (e.g., Goldstein and Reynolds, 1994) to determine homogenization temperatures.

HC-bearing inclusions were identified with micro-fluorescence, and their components were analyzed by UV Raman spectroscopy. Experiments were conducted in the fluids lab of the Virginia Polytechnic Institute and State University, USA. The Raman spectrometer was LabRam HR800-UV of JY Horiba. The Raman system is equipped with 2400 and 300 groove/mm gratings; a 5 W, 514 nm Argon ion laser and a 100 mW, 244 nm UV laser; electronically cooled, back-illuminated CCD detector optimized for the UV region. The systems are equipped with Olympus microscopes with a range of objective lenses and filters. We collected Raman signals of HC-bearing inclusions under a 400 μm hole, 2400 groove/mm grating, and 40× objective lens. The accumulation time was 60 s, and every measurement point was measured three times. Because the field-of-view of the UV Raman spectrometer is quite limited, it could not show the entire outline for some inclusions in the micrographs.

4. Analytical results

4.1. Petrography and fluorescence of HC-bearing inclusions in halite

HC-bearing inclusions were identified by weak fluorescence under ultraviolet illumination, showing the changes of their abundance in different regions. Based on their petrographic and fluorescence characteristics, HC-bearing inclusions in the halite studied can be classified into two generations in the Dongying sag. The first generation was formed by healing of micro-fractures and distributed along a straight line. These fluid inclusions mostly contain one liquid phase or gas–liquid (two) phases, but several inclusions display three phases containing gas, oil, and brine. HC-bearing inclusions of the first generation show light yellow or yellow-green fluorescence under ultraviolet light, as shown in Fig. 1a–f. The color of fluorescence indicates that the maturity of oil in the inclusions is low (Blamey and Ryder, 2007; Guo et al., 2012). The second generation HC-bearing inclusions are distributed in planar form, and they contain a liquid phase or gas-liquid two phases. The liquid phase shows light blue[1] color under UV light (Fig. 1g–h), indicating a relatively high maturity of oil. The population of HC-bearing inclusions in the first generation is much bigger than the second one.

4.2. Homogenization temperatures of hydrocarbon-bearing inclusions

The experimental results show that the homogenization temperatures (Th) of HC-bearing inclusions are different for each generation. The Th values for the first generation vary from 83 to 106.4 °C with an average of 95.4 °C, while that of the second

---

[1] For interpretation of color in Figs. 1 and 6, the reader is referred to the web version of this article.