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Water, is it necessary for fluid inclusions forming in calcite?

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ABSTRACT

It is important to know how did hydrocarbon inclusions form and respond for accumulation of oil and gas in petroleum reservoirs. Also, the process of formation of fluid inclusions in reservoirs can offer the physical and chemical information about diagenesis, which are helpful to evaluate property of reservoirs. In order to understand the formation of fluid inclusions in oil-saturated carbonate reservoirs, we had done experiments on synthetic hydrocarbon inclusions in calcite using pure crude oil system. This article reports that some hydrocarbon fluid inclusions were synthesized in pure crude oil system without adding water in calcite. Reproduced experiment was done to confirm the reliability. The experimental results show that water contained in crude oil could play an important role in transferring materials for calcite growth and formation of fluid inclusions, even though only 0.4 wt% water in experimental crude oil. Some polar components and organic acid in oil can promote dissolution and re-precipitation of calcite. Although we still do not know the details of material transfer and growth of calcite in nearly pure oil fluids, our experimental results provided evidence for that diagenesis may be not completely stopped, and hydrocarbon inclusions can be formed by healing of cracks and record the information of oil accumulation even the carbonate rock reservoirs were saturated with oil. This study indicates that formation fluids can react with calcite or limestone under oil-saturated condition in carbonate reservoirs, which process may be contribute to secondary porosity forming in carbonate reservoirs.

1. Introduction

There are currently some debates on the processes of diagenesis under hydrocarbon-bearing conditions in petroleum reservoirs. Dixon et al. (1989), Gluyas et al. (1993), Neilson et al. (1998), Marchand et al. (2001, 2002) proposed that mineral growth was limited by petroleum accumulation in a reservoir, whereas Walderhaug (1990), Ramm (1992), Saigal et al. (1992), Midtbø et al. (2000), Yuan et al. (2007), Ni and Wang (2007), Ni and Meng (2008), and Ge et al. (2009a, 2009b) suggested that petroleum does not affect diagenesis remarkably. Debates surround how oil-rich versus water-rich fluids affect diagenesis in reservoirs. One of debate focuses is whether the mineral grows in oil-saturated reservoir. Experimental studies may help shed some light on these questions. We know that in some cases, fluid inclusions are trapped during mineral growth. Therefore, we have conducted experiments on synthesis of hydrocarbon inclusions in calcite, in order to understand fluid inclusion formation and mineral growth under conditions of oil-saturated in reservoirs.

It is well known that water plays an important role in the transport of materials during crystal growth. Usually, minerals are more hydrophilic rather than oleophilic (Pan et al., 1996). Many studies have shown that water can be detected not only in synthetic hydrocarbon inclusions, but also in natural oil inclusions (Kihle and Johansen, 1984; Pironon and Barres, 1990; Teinturier and Pironon, 2004; Cao et al., 2006; Pironon and Bourdet, 2008). Most previous studies focused on synthetic hydrocarbon (oil) inclusion in quartz, but only a few studies have described synthesized hydrocarbon inclusions in calcite (Pironon and Bourdet, 2008). Teinturier and Pironon (2004) reported that petroleum inclusions were synthesized in quartz in a pure oil system (without water) at 350 °C and 400 bars; but, the silica gel used in those experiments contain on average about 10 wt% water, which may have played an important role in the cementation of quartz. In order to understand the effect of oil on growth of calcite in a reservoir during the accumulation of oil and gas, we ever synthesized fluid inclusions in calcite under various volume ratios of oil to water, from 0:1 to 9:1 (Ge et al., 2009a, 2009b). As there are some oil fields produce heavy oil in carbonate reservoirs in Bohai bay basin, China, we did some synthetic fluid inclusions experiments under the condition near to real reservoir's temperature and pressure. In this study, we tried to synthesize hydrocarbon

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inclusions in pure crude oil system aim to understand the growth of calcite and the diagenesis process in oil-saturated reservoir which was filled with heavy oil.

2. Experimental procedures

The method in our experiments is that synthetic fluid inclusions were formed in healed fractures in calcite. The calcite crystal was cut into chips and cleaned using the ultrasonic bath to eliminate contamination. Primary inclusions in calcite were destroyed by heating up to 450 °C. The calcite crystals were fractured by thermal shock by dropping them into cold water after heating in a furnace at 450 °C, and then dried at 120 °C for more than 10 h. Experiments were done in gold capsules (length-50 mm; outside diameter-5 mm, wall-0.2 mm). Oil, calcium carbonate powder ($CaCO_3$), and calcite chips were loaded into the capsule, and the capsule was welded shut. After welding, the capsule was laid in an oven to check for leaks. Then the capsule was placed in the high temperature-pressure vessel. To avoid leakage, the capsule was weighed before and after welding, after drying and post-experiment. Synthetic fluid inclusions experiments were done at 150 °C and 40 MPa, temperature and pressure conditions close to the conditions in the reservoir about 4000 m beneath the surface in the Bohai Bay Basin, eastern China. Experiments were done with the set temperature and pressure held constant for 15 days. The experiments were stopped by quick cooling in 20 min. After the temperature and pressure were down, took out the capsule and weighed it for checking its closure. Replicates of this “water-free” experiment have been performed to confirm that hydrocarbon fluid inclusions can be formed without any aqueous liquid phase present. Experimental parameters were listed in Table 1. The crude oil used in our experiments was heavy crude oil provided by the State Key Laboratory of Heavy Oil. Analyses result showed that the oil contained 0.4% water. The density of the experimental oil was 0.9320 g/cm^3. The heavy crude oil was chosen from one oil field in Baihai Bay basin, China. In our experiments, we tried to make experimental condition near natural reservoir environment. The composition of crude oil was analyzed by chromatography and mass spectrometry, and listed in Table 2.

3. Characteristics of synthetic hydrocarbon inclusions

The calcite was cut into thin flakes after each experiment. We observed the synthetic fluid inclusions using microscopy, to understand the occurrence, size, phase(s), shape, color, and petrographic relationships. Hydrocarbon inclusions were identified by their fluorescence under UV illuminaion. Photomicrographs of some fluid inclusions are shown in Fig. 1. Most hydrocarbon inclusions are distributed along the cleavage planes of calcite (Fig. 1a). The inclusions have various shapes: some are nearly square while others are irregular in shape. The color of the liquid phase in most synthetic hydrocarbon inclusions is yellow (Fig. 1c), but some are colorless (Fig. 1d). The bubble is usually black under transmitted light (Fig. 1d). The fluorescence color is mostly buff (Fig. 1b and d), but several hydrocarbon inclusions have blurry-white fluorescence (Fig. 1b and f). The results show that hydrocarbon bearing inclusions were synthesized in the pure oil system in our experiments. Combined with our previous studies (Ge et al., 2009a, 2009b), these results suggest that hydrocarbon inclusions can be formed and record the whole process of oil accumulation with increasing volume ratio of oil to water from 0:1 to 9:1 in carbonate reservoirs. The microscopic and fluorescent characteristics of hydrocarbon inclusions demonstrate that calcite keeps growing and trapping inclusions even in fluid media of nearly pure oil (oil saturated) during oil accumulation in carbonate reservoir.

Table 1
Experiment parameters of synthetic hydrocarbon inclusions in crude oil system.

Experimental number	No. 1	No. 2
Weight of gold capsule (g)	3.3156 ± 0.001	3.2460 ± 0.001
Weight of calcite (g)	0.2251 ± 0.001	0.1987 ± 0.001
Weight of calcium carbonate powder (g)	0.0270 ± 0.001	0.0204 ± 0.001
Volume ratio of oil to water	1:0	1:0
V_{oil} (ml)	0.08500	0.2267
V_{water} (ml)	0	0
Total weight (g)	3.6462 ± 0.0010	3.6755 ± 0.0010
Weight after welding (g)	3.6448 ± 0.0010	3.6752 ± 0.0010
Weight after drying (g)	3.6440 ± 0.0010	3.6748 ± 0.0010
Weight after finishing experiment (g)	3.6443 ± 0.0010	3.6752 ± 0.0010
Experimental temperature (°C)	150.0	150.0
Experimental pressure (MPa)	40.0	40.0
Experimental time (days)	15	15

Table 2
The composition of crude oil (Example: The C14 includes all moleculars which have fourteen carbon atoms.).

Composition	Weight percent (wt%)
C14	5.692
C15	5.882
C16	3.474
C17	2.381
C18	7.020
C19	12.309
C20	7.563
C21	4.023
C22	1.451
C23	1.254
C24	1.118
C25	2.402
C26	3.065
C27	4.350
C28	6.492
C29	10.905
C30	9.787
C31	0.852
C32	9.608
C33	0.372

4. Discussion on trapping mechanisms of fluid inclusions in calcite

Under real geological conditions, minerals can be precipitated from formation water or brine in reservoirs before the charge of oil. Fluid inclusions are mainly trapped in the presence of an aqueous phase with gas. Most minerals appear to be hydrophilic under inorganic conditions. But during the oil was charging into reservoirs, if some new fractures may be formed in minerals because of hydro-fracture effect or activity of fault, fractures will have some opportunity to interact with water and oil. Our previous studies showed that calcite has similar wetting properties with water and crude oil (Chen et al., 2011). Therefore, the type of fluid inclusions depends on which fluid arrived first into a fracture. This phenomenon is similar to that described by Teinturier and Pironon (2004).When we first added oil into the gold capsule, more hydrocarbon inclusions were produced. Because of immiscibility of water and oil, we usually see hydrocarbon inclusions and aqueous inclusions distributed in different zone in petroleum reservoirs.

Previous reports indicated that water preferentially wetted the surfaces of minerals rather than oil, and that the presence of water