

IDENTIFICATION OF MULTIPLE GENERATION OIL INCLUSIONS TRAPPED IN QUARTZ SINGLE CRYSTALS USING STEPWISE HEATING CHEMICAL IONISATION MASS SPECTROSCOPY

SCHUBERT, F.¹, M. TÓTH, T.¹, KELE, Z.², VISKOLCZ, B.³

¹University of Szeged, Department of Mineralogy, Geochemistry and Petrology, H-6701 Szeged, P.O. Box 651, Hungary.

²University of Szeged, Institute of Medical Chemistry, H-6720, Szeged, Dóm tér 8., Hungary.

³University of Szeged, Department of Chemistry, Juhász Gyula Teacher's Training College, H-6701 Szeged, P. O. Box 396, Hungary.

E-mail: schubert@sol.cc.u-szeged.hu

Introduction

Quartz is one of the most important cement phases both in sedimentary and fractured hydrocarbon reservoirs. It may form at a wide range of physical and chemical conditions and rather often entraps fluid inclusions of the co-genetic fluid phases. Besides H₂O-bearing inclusions, commonly HC-bearing inclusions also occur, which report about hydrocarbons migrated through the reservoir during quartz precipitation episodes (e.g. Munz et al., 1999, Teinturier et al., 2002). These inclusions can give information both about the PVT properties of charging of the reservoir and the composition of the migrating fluids. HC-bearing fluid transport usually takes place in successive migration events, which can be recorded by fluid inclusion (FI) generations trapped along growth zones or as secondary inclusion planes within diagenetic minerals, like quartz. As a result even a single crystal may contain HC fluids of significantly different composition. There are several possible methods on bulk chemical analysis of HC-bearing fluid inclusions (e.g. GC, GC-MS, Karlsen et al., 1993), most of which, however cannot provide valuable information if oil inclusions of different compositions are present side by side. Some spectroscopy techniques also are available for quantitative analysis of certain components. The visible Raman microspectroscopy can be used even for minute inclusions, but the usually strong fluorescence of the HC inclusions hinder its applicability. The most accurate information about the composition of a single HC inclusion can be obtained by FT-IR spectroscopy (Pironon et al, 2001), although this approach is limited in quartz due to its strong absorption above 2000 cm⁻¹.

In the present study we introduce a novel approach for measuring compositions of different hydrocarbons in single crystals. After decrepitating inclusions under closed system conditions we aim detecting liberated fluids by a highly sensitive mass spectrometer. Hydrocarbons of different compositions are separated by a programmed stepwise heating procedure. The method is tested on fracture-filling quartz crystals from the Variscan basement of the Pannonian Basin, Hungary. The fractured metamorphic rock bodies in the study area are excellent HC-reservoirs (Nelson, 1985).

Geological background

Békés basin, the deepest sub-basin of the Pannonian Basin system (SE Hungary) is surrounded by metamorphic basement highs, which produce significant amount of hydrocarbons from their fractured crystalline rocks. One of the largest fractured basement reservoirs is the Szeghalom dome (SzD), which consists of medium- to high-grade metamorphic rocks; essentially gneiss and amphibolite. Due to the multiphase subsidence of the Pannonian Basin, the SzD shows a rather complex Neogene evolution history. The dominantly steeply dipping conjugated microfaults are filled in by a well-defined fracture-filling mineral sequence. The first cement phase of considerable amount is a free-standing, hydrocarbon-inclusion bearing quartz phase. Based on stratigraphic, stable isotope chemical and palynological observations, this quartz phase formed prior to the most exhumed state of the SzD (Juhász et al., 2002) and trapped hydrocarbon traces, which should not be identical to the oil produced from the metamorphic basement at present.

The quartz crystals trapped HC FIs in several growth zones; in some cases even 15 zones occur. In some drilling cores the HC FIs do not show any change from the inner growth zones to the external ones based on petrography, UV fluorescence and Raman microspectroscopy analysis (Schubert, 2003). However, in other cases a clear difference can be recognized from one zone to another in both fluorescence and optical properties (colour, V/L ratio, etc.). In these samples, the HC inclusions of the inner zones can usually be characterised by a dark brown liquid phase in normal light and an intense, greenish blue fluorescence colour under the UV excitation (V/L=0.2-0.3). With an abrupt change, in the outer growth zones a new fluid phase becomes dominant. It can be characterised by translucent liquid and vapour phases of a very weak, bluish fluorescent colour (V/L =0.8-0.9).

Strategy

Previous studies clearly inferred presence of fluid inclusions representing different types of HC in fracture filling quartz crystals of the SzD. As mass spectroscopy is a method to detect even extremely low amount of material, this approach was used measuring compositions of the multiply generation oil inclusions. To decrepitate inclusions we prefer heating to mechanical crushing because mixing of different hydrocarbons must be avoided. Using this method we aim determining the temperature of the decrepitation of different inclusion types and detecting their MS spectra independently.

In each crystal studied inclusions differ both in V/L ratio and composition of the entrapped oil. Assuming identical compositions, material of the inclusion has larger volume to expand at higher V/L during heating and will decrepitate at higher

T. Assuming identical V/L and diverse compositions, the inclusion, which contains hydrocarbon mixture of lower boiling point, should open earlier. As a result, it can be presumed that multiply generation oil inclusions in a single crystal open at different temperatures, and so they can be detected independently.

Before measurement, the quartz crystals were purified and selected by standard methods. In a chemical ionisation mass spectrometer (CI-MS) the crystals were heated with a stable 10 K/s velocity and the mass spectra were detected at every 500 milliseconds. Simultaneously, the continuous total ion current was recorded too in order to trace the decrepitation temperature of the inclusions.

The MS spectra run on a Finnigan TSQ 7000 mass spectrometer (Finnigan MAT Ltd, San Jose, USA). Samples were introduced to the ion source via a direct insertion probe that was operated at a temperature between 320 and 700 K. Chemical ionization (CI) ion source conditions were as follows: temperature 423 K; electron energy, 40eV; filament current 200 μ A; CI gas: isobutane; the pressure of the ion source: 8 torr.

Results

The most important results of the experiment can be concluded as follows:

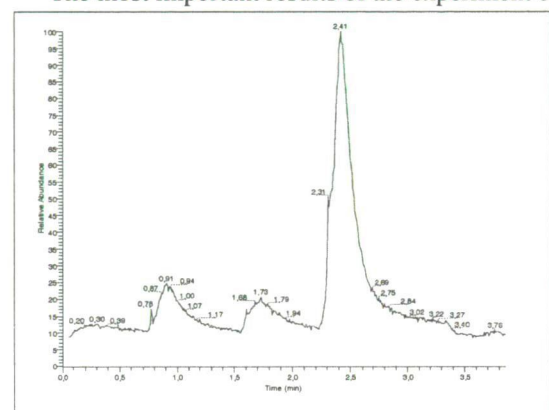


Figure 1. Typical ion current curve with three peaks

1) Ion current curves generally exhibit only a few sharp peaks rising from the base line. Each peak belongs to a well-defined temperature value, most probably defined by decrepitation of a certain FI generation (Fig. 1.).

2) Comparative analysis of MS spectra, belonging to the different peaks of the total ion current, suggests that they associate with CH mixtures of different compositions (Fig. 2.).

3) In all studied cases, inclusions rich in high molecule weight components open earlier, even if these FIs occur in the internal zones of the crystals.

4) In case of the SzD quartz crystals one can recognize the same oil type based on MS spectra in different drilling cores. Such a classification might lead to characterize different fluid regimes in the reservoir.

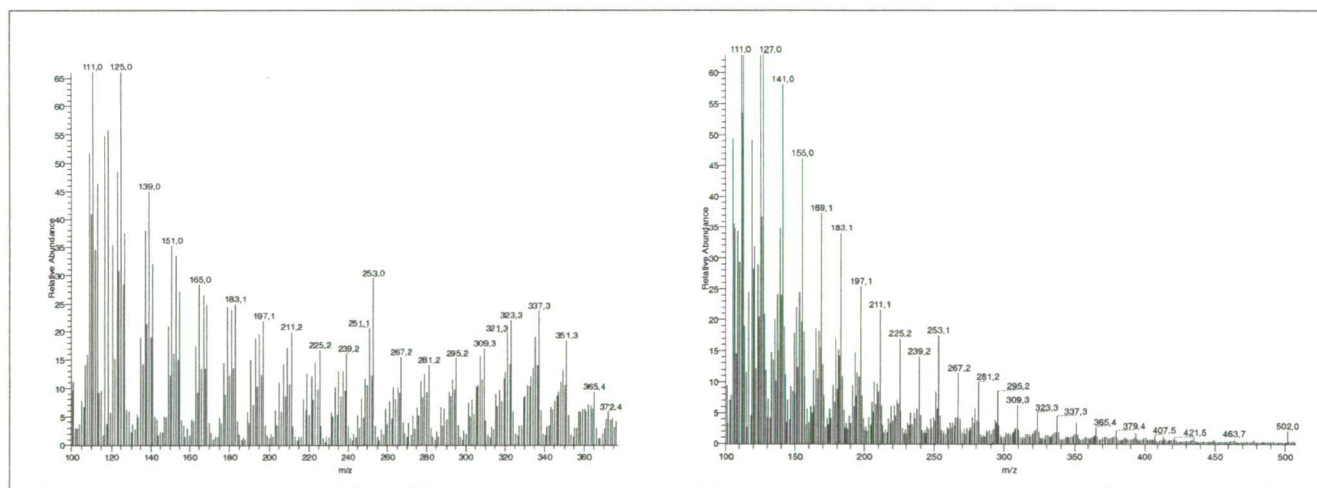


Figure 2. MS spectra of two different oil types from the same quartz crystal

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