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Geochemical assessment of hydrocarbon migration phenomena: Case studies from the south-western margin of the Dead Sea Basin

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ABSTRACT

Calcite veins with fluid and solid bitumen inclusions have been discovered in the south-western shoulder of the Dead Sea rift within the Masada-Zohar block, where hydrocarbons exist in small commercial gas fields and non-commercial fields of heavy and light oils. The gas–liquid inclusions in calcite are dominated either by methane or CO_2, and aqueous inclusions sometimes bear minor dissolved hydrocarbons. The enclosed flake-like solid bitumen matter is a residue of degraded oil, which may be interpreted as "dead carbon". About 2/3 of this matter is soot-like amorphous carbon and 1/3 consists of *n*-C_8—C_{18} carboxylic acids and traces of *n*-alkanes, light dicarboxylic acids, and higher molecular weight (>C_{20}) branched and/or cyclic carboxylic acids. Both bitumen and the host calcites show genetic relationship with mature Maastrichtian chalky source rocks (MCSRs) evident in isotopic compositions ($\delta^{13}C$, $\delta^{34}S$, and $\delta^{18}O$) and in REE + Y patterns. The bitumen precursor may have been heavy sulfur-rich oil which was generated during the burial compaction of the MCSR strata within the subsided blocks of the Dead Sea graben. The $\delta^{18}O$ and $\delta^{13}C$ values and REE + Y signatures in calcites indicate mixing of deep buried fluids equilibrated with post-mature sediments and meteoric waters. The temperatures of fluid generation according to Mg–Li-geothermometer data range from 55 °C to 90 °C corresponding to the 2.5–4.0 km depths, and largely overlap with the oil window range (60–90 °C) in the Dead Sea rift (Hunt, 1996; Gvirtzman and Stanislavsky, 2000; Buryakovsky et al., 2005). The bitumen-rich vein calcites originated in the course of Late Cenozoic rifting and related deformation, when tectonic stress triggers damaged small hydrocarbon reservoirs in the area, produced pathways, and caused hydrocarbon-bearing fluids to rise to the subsurface; the fluids filled open fractures and crystallized to calcite with entrapped bitumen. The reported results are in good agreement with the existing views of maturation, migration, and accumulation of hydrocarbons, as well as basin fluid transport processes in the Dead Sea area.

1. Introduction

Hydrocarbons and aqueous fluids entrapped, at different stages of basin evolution, as fluid inclusions in minerals of reservoir rocks (quartz and feldspar), as well as calcite or quartz in veins and diagenetic cements, have important implications for characteristics of petroleum systems. These inclusions can provide clues to the charge history, sources and maturity of paleo-oils, and to time, environments, and pathways of oil migration (McLimans, 1987;

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Burruss, 1999; Munz, 2001; Chi et al., 2006; Coelho et al., 2008; Li et al., 2011, 2013).

However, reconstructing the reservoir history and physico-chemical parameters of oil generation solely from fluid inclusion data may be problematic and intrinsically ambiguous (McLimans, 1987). This may happen if the inclusions encapsulate bitumen and/or non-fluorescent products of severe biodegradation rather than crude oil. The nature of bitumen and biodegradation products in fluid inclusions remained poorly understood and debated until the production of hydrocarbon gases, light oil, and semi-liquid or solid bitumen by the interaction of oil with thermal waters was experimentally simulated (McLimans, 1987; Balitsky et al., 2007, 2012). Crystal growth in this case occurs in a heterogeneous mixture of aqueous solutions and hydrocarbons while the latter become entrapped as fluid inclusions with variable phase ratios. Therefore, studies of such inclusions should focus mostly on their organic component which stores record of geochemistry, migration pathways, and potential sources of hydrocarbons.

Entrapment of oil inclusions has been studied in quartz, feldspar, fluorite, and topaz, but the inclusions hosted by calcite are the most abundant and largest in size (Balitsky et al., 2007, 2012). Calcite can inherit information of the physico-chemical environments of petroleum generation and migration in trace-element (Li, B, Sr, Ba, As, Mo, Zn, Cr, Ni, V) and REE signatures, as well as in Li, C, and O isotope compositions (Khoury, 2007; Feng et al., 2009; Lavrushin, 2012; Webb et al., 2009; Himmler et al., 2010; Fleurance et al., 2013; Li et al., 2013).

Extracting genetic information from very small fluid inclusions in vein calcites and from crude oil fully degraded to solid bitumen has been a challenge of this study. To solve the problem, we explore various approaches and combine the conventional analytical techniques of organic geochemistry with methods for reconstructing the formation history of carbonate minerals. The samples come from the south-western flank of the young Dead Sea Basin which, though having quite a poor petroleum potential, has been exhaustively documented with respect to local geology, stratigraphy, tectonic history, and geochemistry and can provide good reference for testing the reconstruction results. The basin is remarkable as a natural laboratory for studying the palaeo-groundwater flow regime, maturation, migration, and accumulation of hydrocarbons, as well as fluid transport processes (Nissenbaum and Goldberg, 1980; Garfunkel, 1997; Rullkötter et al., 1985; Girdler, 1990; Braester et al., 1991; Gvirtzman and Stanislavsky, 2000; Möller et al., 2007).

2. Geological setting and sample locations

2.1. Tectonics and geology

The Dead Sea is located in a pull-apart basin bordered by the fault system of the Dead Sea Transform, a prominent shear zone in the Middle East separating the Arabian plate from the Sinai microplate (Fig. 1). The transform system originated in the Miocene, ~17 Ma ago, during the break-up of the Afro-Arabian continent, and has accommodated left-lateral motion between the two plates, with ~105 km of total displacement. The modern Dead Sea Transform system consists of at least six major overlapping left-stepping strike-slip faults with deep rhomb-shaped depressions between each fault pair. The Dead Sea Basin is the largest one (Garfunkel, 1997; Girdler, 1990; Maercklin et al., 2004). This long-lived fault zones control the subsurface fluid flow (brines or meteoric waters), either by localizing it or by impeding cross-fault flow (Caine et al., 1996; Gvirtzman and Stanislavsky, 2000).

The Dead Sea rift basin is filled with a Holocene to Miocene sediments that range from continental clastics through marine and lacustrine deposits to evaporates and reach a thickness of about 10 km (Nissenbaum and Goldberg, 1980; Garfunkel, 1997; Hassouneh, 2003; Hall et al., 2005). The rocks on the uplifted rift shoulders were deposited in different settings from Cambrian through Cenozoic time. Cambrian to Lower Cretaceous (Nubian-type) sandstones are exposed along the eastern shore, while the western margin is composed of Permian to Upper Cretaceous and Paleocene sandstone, limestone, dolomite, marl, and chalk, about 4 km thick in total. Over the greatest part of the area, there are outcrops of a Senonian sedimentary sequence composed mainly of carbonate (including organic-rich chalks), chert and phosphorite (Zeigler, 2001; Hall et al., 2005).

Southwest of the basin, there is the Masada-Zohar block (Fig. 1 and 2), where small commercial gas fields (Zohar, Kidod and Haqanaim), as well as non-commercial heavy (Gurim 1 and 2) and light (Zuk-Tamrur-1) oils were found (Nissenbaum and Goldberg, 1980; Gardosh et al., 1996). A part of the block is occupied by the Hatrurim Basin, the largest area of the Mottled Zone rocks (Burg et al., 1991). Not being a separate stratigraphic unit, the Mottled Zone sequence encompasses Cretaceous and Paleogene calcareous sediments subjected to strong post-depositional alteration. The sedimentary parent rocks have been affected by brecciation, low-temperature hydrothermalism, and exceptionally broad high-temperature combustion metamorphism. This specific sequence tops the Cretaceous section of the area (Bentor and Vroman, 1960; Gross, 1977; Khoury and Nassir, 1982; Khoury, 2007; Burg et al., 1991; Hall et al., 2005; Techer et al., 2006; Sokol et al., 2010, 2011). Since post-Paleogene time, the strata have lied above the water table representing the unsaturated (vadose) zone (Möller et al., 2007).

2.2. Hydrocarbons in the Dead Sea area

The Dead Sea rift is a relatively poor basin, but a variety of non-commercial asphalts, light and heavy oils have been found from the surface to a depth of 4000 m in its south-western part (Nissenbaum and Goldberg, 1980; Tannenbaum and Aizenshtat, 1984; Rullkötter et al., 1985; Gardosh et al., 1996, 2008; Gvirtzman and Stanislavsky, 2000; Connan and Nissenbaum, 2004). Oil pockets exist in the Hatrurim Basin (Fig. 1 and 2): light oil from a thin sand layer of Triassic Gevanim Fm. in Zuk Tamrur-1 well in the southeastern periphery of the basin, approximately 3000 bbl of heavy oil from the Jurassic Inmar sandstone in the Gurim anticline (western margin), and about 9000 bbl of sulfurous heavy oil from the youngest Lower Cretaceous Kurnub sandstone (Nissenbaum and Goldberg, 1980; Gardosh et al., 1996). The heavy oils more likely are secondary alteration products derived from conventional oils by water-washing, incipient biodegradation or physical loss of volatile components. The light oils (Zuk Tamrur and Massada) lack geochemical signatures of biodegradation (Spiro et al., 1983a; Rullkötter et al., 1985).

Asphalts found in the Dead Sea area are of two types. One is immature (intact) asphalt representing the very early maturation grade of kerogen, which appears either as huge floating blocks on the Dead Sea or in deep boreholes (Tannenbaum and Aizenshtat, 1984; Rullkötter et al., 1985). The floating asphalts and asphalts from Amiaz-1 borehole at 3460 m contain *n*-alkane envelopes rich in asphaltic material (more than 50%) and in sulfur (~10%). Asphalt of the other type occurs as seepages along the rift faults (e.g., Massada and Nahal Heimar asphalts). They consist of 60% asphaltenes and 10% sulfur, a composition attributed to gradual removing of saturated and aromatic hydrocarbons toward the land surface due to meteoritic water washing and thereby of biodegradation (Nissenbaum, 1978; Tannenbaum and Aizenshtat, 1984; Rullkötter et al., 1985).