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Geochemical analysis techniques and geological applications of oil-bearing fluid inclusions, with some Australian case studies

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Abstract

Reliable geochemical information of similar quality to conventional analyses of crude oils and source rocks can be obtained from oil-bearing fluid inclusions (FI). Carefully controlled analytical procedures including sample clean-up, procedural blanks and attention to detail are essential for the successful analysis of inclusion oils. The procedures are technically challenging, but if they are carefully followed, successfully analysed samples can include not only those with high abundances of oil inclusions, such as in current or palaeo-oil reservoirs, but also samples with low amounts of oil inclusions, such as those from oil migration pathways or from Proterozoic or even older rocks. A full range of hydrocarbons can be measured from inclusions, including low molecular weight hydrocarbons, *n*-alkanes, aliphatic biomarkers such as isoprenoids, hopanes and steranes, and aromatic hydrocarbons.

There are many geological applications of the analysis of FI oils, which contribute to reducing regional exploration risk. This paper uses Australian case histories to illustrate the main applications of FI oil analysis. These include better constraining oil charge histories of reservoirs and identifying active source rocks previously unknown in a particular basin. The effects of oil-alteration by biodegradation and/or water-washing in the reservoir can be removed, mixing episodes in reservoirs can be deconvoluted, and the effects of drilling mud additives or other contaminants can be eliminated. Furthermore, the hydrocarbon composition and diversity of Earth's early biosphere can be constrained, and secondary migration pathways can be mapped across prospects or basins.

Keywords: Fluid inclusions; Oil; Biomarkers; Hydrocarbons; Australia

1. Introduction

Oil-bearing fluid inclusions (FI) are small samples, often <10 μm in diameter, of pore fluid trapped during the crystallisation of minerals such as quartz, feldspar and carbonate. Oil inclusions typically occur in diagenetic cements, such as quartz overgrowths, and in healed microfractures within detrital grains, diagenetic cements, or both. Oil inclusions form during the crystallisation of diagenetic minerals and through the fracturing during burial compaction of framework minerals (detrital or diagenetic). In many cases, if oil saturation was high in a reservoir, oil inclusions can be formed. The presence of oil inclusions in water-wet reservoir sandstones provides a record of palaeo-oil migration (e.g. Burruss, 1981; McLimans, 1987; Eadington et al., 1991). However, since not all oil accumulations are associated with oil inclusions, the

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absence of oil inclusions cannot be used as evidence for the absence of a palaeo-oil column.

The tiny amounts of oil trapped in FIs can be analysed using gas chromatography–flame ionisation detection (GC–FID; e.g. Horsfield and McLimans, 1984; Jensenius and Burruss, 1990; Jochum, 2000; Volk et al., 2002b) and gas chromatography–mass spectrometry (GC–MS; e.g.; Karlsen et al., 1993; Lisk et al., 1996; George et al., 1996; Jones and Macleod, 2000; Volk et al., 2002b; Karlsen et al., 2004). Data from oil inclusion geochemistry can be used in petroleum systems analysis, to compare present and palaeo-oils and to examine migration events and alteration processes that have affected oil composition over time. The advantage of using FIs is that once oil is trapped within mineral grains, it is physically isolated from the main pore system of the reservoir rock. Therefore, subsequent events in the reservoir such as loss of charge, water-washing, biodegradation and drilling do not affect the composition of the inclusion oil. Furthermore, oil inclusions survive within fractured core and within cuttings, even if these materials are dried by heating, subjected to experiments such as core-floods, or stored for several years.

The purpose of this paper is firstly to review the analytical methodologies that are applicable to describing the geochemical composition of oil inclusions. Particular attention will be applied to the techniques that have been developed and refined at CSIRO, which enable direct comparison between inclusion oil geochemistry and crude oils or source rocks. Secondly, several geological applications arising from the knowledge of the chemical composition of oil inclusions will be discussed; these will be illustrated with reference to previously published work by CSIRO.

2. Screening of samples

Prior to geochemical analysis of oil inclusions, it is advisable to ascertain that sufficient oil inclusions are present in the sample for analysis. This can be achieved by using various petrographic or geochemical methods, some of which are described in the next two sections.

2.1. Grains containing oil inclusions (GOI) method

The distribution of oil inclusions can be determined using the GOI method (Lisk and Eadington, 1994; Eadington et al., 1996; Lisk et al., 2002). In brief, this petrographic method, designed for analysis of sandstones, measures the abundance of quartz and feldspar grains containing oil-bearing FIs in sandstone samples and relates this parameter to an empirical database of GOI values from known oil fields to determine the extent of oil saturation in the geological past. Oil accumulation in the geological past can generally be differentiated from oil on migration pathways, irrespective of the current fluid phase. GOI values >5% are indicative of palaeo-oil zones (Lisk and Eadington, 1994; Lisk et al., 1998), whilst GOI values between 0.1 and 5% may indicate oil migration pathways (Lisk et al., 2000, 2001; Liu et al., 2004). If no oil has been present in a reservoir, GOI values are generally <0.1%. However, low GOI values are not uncommon in current oil zones, due to different timings of oil occurrence and oil inclusion formation processes.

Note that GOI values provide only a rough guide to the amount of oil that can be expected to be extracted from oil inclusions (George et al., 2001a). This is because (1) GOI deliberately does not count total numbers of oil inclusions (as it is an oil saturation-related parameter), and (2) no reference is made in GOI to the size of the oil inclusions. Because of the cube root factor, one 20 μm diameter inclusion contains the same amount of oil as 8000 inclusions of 1 μm diameter (George et al., 2001a). Most inclusion oils previously analysed at CSIRO have contained 100–4000 ng *n*-alkanes/g mineral crushed, and any recovery >40 ng/g is generally regarded to be reliable and easily interpretable (George et al., 2001a). Recent work on oil migration pathways succeeded in analysis of very low GOI samples (<1.5% GOI), with 7–23 ng/g quartz recovery of interpretable oil from inclusions (Liu et al., 2004; George et al., 2004b).

2.2. Other screening techniques

Limited geochemical data on FI oils can be obtained from bulk rock-crushing mass spectrometric techniques (Barker and Smith, 1986) such as “Fluid Inclusion Stratigraphy” (FIS; Barclay et al., 2000) and can indicate transient oil migration (Liu et al., 2004). The FIS data can be used to screen many samples in a well, so as to select the best intervals for detailed geochemical analysis of inclusion oils. The FIS method, however, does not involve chromatographic separation prior to mass spectrometry and only analyses the low molecular weight hydrocarbon range. Consequently, this method provides none of the biomarker data typically used to make oil–source rock and oil–oil correlations.

Another way of screening samples is using the quantitative grains with fluorescence (QGF) method (Liu et al., 2003; Liu and Eadington, 2005; Liu et al., 2007-this issue). This technique uses UV spectroscopy