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## First on-line analysis of petroleum from single inclusion using ultrafast laser ablation

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### ABSTRACT

For many years, geochemical analysis of petroleum from single inclusions has been a challenging objective for fluid inclusion studies. In this study, individual petroleum inclusions have been selectively opened and analysed, for the first time, by coupling an on-line femtosecond laser with a gas chromatograph–mass spectrometer (GC–MS).

GC–MS chromatograms show straight chained, branched and cyclic alkanes and aromatic hydrocarbons with carbon numbers ranging from 4 (*iso*-butane) to 19 (pristane). The distribution of these compounds is similar to that observed by on-line bulk crushing, and pyrolysis artefacts such as alkenes and ketones were not detected. Hydrocarbons with higher carbon numbers appear to have remained in the extraction chamber, a limitation that may be overcome by improvements to the inlet system.

This pilot study proves that ultrashort laser pulses can be used to liberate unaltered oil from individual inclusions, thereby creating exciting opportunities for further research aimed at determining the nature of different hydrocarbon palaeo-fluids trapped within single minerals.

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### 1. Introduction

Petroleum fluid inclusions are tiny, usually <10 μm sized vacuoles that are filled with petroleum and their occurrence in rocks and minerals is well documented (Burruss, 1981). They are commonly found in quartz crystals and sand grains of petroliferous basins, where they occur in healed fractures and along crystal growth zones. The petroleum in these perfectly sealed vessels provides a snap shot of the fluid composition in the geological past, as it is shielded from contamination and alteration that usually affects hydrocarbons over time. Thus, unique information on the fluid's evolution can be obtained by analysing the trapped hydrocarbons. To date, the chemical composition of petroleum trapped in fluid inclusions can be inferred using spectroscopic methods (e.g. measurement of epifluorescence when excited with ultraviolet light, Raman spectroscopy, and Fourier-transform infrared spectroscopy) and microthermometry (Munz, 2001). Alternatively, it may be determined directly by mechanical crushing or thermal decrepitation of bulk samples followed by solvent or thermal extraction of the petroleum for analysis by gas chromatograph–mass spectrometer (GC–MS) (George et al., 2007). However, fluorescence microscopy and heating–freezing experiments commonly indicate that

these crystals contain several fluid inclusion assemblages which hold information from different geological events (e.g. Schubert et al., 2007). While spectroscopic methods, sometimes combined with volumetric measurements and modeling (e.g. Thiéry et al., 2000), can constrain the composition of hydrocarbons in fluid inclusions without losing the spatial resolution provided by a microscope, detailed molecular and isotopic data that hold the key to the source and maturity of the oil can so far only be obtained by using the crushing/GC–MS analysis approach. However, as the samples are extracted in bulk, distinguishing the geochemical signature of different fluid inclusion assemblages in the same mineral is not possible.

The extraction of fluid inclusions using laser systems can potentially bridge this gap. In some previous studies lasers have been used to extract oil from fluid inclusions, yet these approaches were not selective enough to differentiate individual inclusions. Greenwood et al. (1998) analysed 10–100 random inclusions using thermal decrepitation induced by an infrared Nd:YAG laser beam with a wavelength of 1064 nm coupled on-line to a GC–MS system. Hode et al. (2006) extracted fluid inclusion oil in a vacuum chamber using an infrared Er:YAG laser with a wavelength of 2940 nm and condensation of this oil onto a cold finger. The condensed oil was subsequently dissolved in hexane and analysed off-line by GC–MS. While their approach could extract oil from a group of inclusions and individual inclusions could be opened with this la-

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ser, it is not possible to analyse volatile or gaseous hydrocarbons in this manner. Moreover, the infrared wavelengths of both the Nd:YAG and Er:YAG lasers couple with the petroleum trapped in the fluid inclusion rather than with the transparent host mineral, such that the inclusions are explosively decrepitated. We found decrepitation of selected inclusions using a Nd:YAG laser hard to control and suspect that the decrepitation mechanism is likely to cause other inclusions to open, as probably occurs in healed, yet still structurally defective, zones of the mineral.

In the present work, individual petroleum inclusions have been selectively opened and analysed for the first time, by coupling a femtosecond laser on-line to a GC–MS instrument.

## 2. Experimental setup

The laser extraction GC–MS setup was a modified version of that used by Greenwood et al. (1996). It comprises an Agilent 6890 gas chromatograph (GC) interfaced to an Agilent 5973 mass selective detector (electron energy 70 eV, electron multiplier 1200 V, source temperature 250 °C, 0.1 amu resolution) and an Olympus BX60 M system microscope with a custom built laser chamber and inlet system. The microscope was used with a long working distance objective (20× with numerical aperture of 0.4). The Nd:YAG laser of this existing laser micropyrolysis (LaPy)-GC–MS system was replaced by a high energy femtosecond oscillator system (Femtsource scientific XL 200, Femtolasers GmbH). The pulses emitted by this laser have a spectral width of about 50 nm centred in the near infrared around 800 nm. In contrast to continuous wave radiation or *q*-switched (nanosecond) laser pulses, the energy in this case is concentrated into an extremely short time interval, i.e. only about 50 femtoseconds (fs). This results in an ultrahigh peak intensity at the laser focus ( $>10^{14}$  W/cm<sup>2</sup>) that induces nonlinear (multiphoton) absorption of the radiation, a process which is virtually independent of the central wavelength of the laser (Lenzner, 1999; Martin et al., 2003).

The minimum energy that is required to exceed the ablation threshold and to drill micro holes into quartz can be reduced if ultrashort laser pulses are used. For pulses of 50 fs duration, the threshold fluence is only about 3 J/cm<sup>2</sup> (Lenzner, 1999). Combined with the fact that with the long working distance objective used in our setup the laser can be focussed to a minimum spot diameter of about 2 μm, a pulse with energy in the order of 100 nJ is required. However, standard femtosecond oscillators (laser systems that are

relatively inexpensive, compact and user friendly) only offer pulse energies of up to about 10 nJ. To our knowledge, so far only femtosecond amplifier systems have been employed for the ablation of transparent dielectric media. However, such laser systems are expensive, complex and require a well controlled laboratory environment, with minimal variations in temperature and humidity, and have to be placed on vibration free optical tables. Moreover, it has been shown that the required spatial resolution in the range of a few micrometers can only be achieved during the ablation process if the pulse energy is adjusted just above the actual ablation threshold of the material to be processed (Gattass and Mazur, 2008). This implies that the output of femtosecond amplifiers, typically in the mJ range, has to be strongly attenuated for high precision micromachining, which greatly reduces the penetration rate.

In this work we have chosen to use a novel and unique laser system that avoids these drawbacks (Fig. 1). It can deliver pulse energies in the order of hundreds of nanojoules while offering the same excellent performance in terms of compactness and user friendliness as standard oscillators. By introducing a Herriott type multi-pass cell into the resonator of a standard femtosecond oscillator, its repetition rate can be reduced by more than an order of magnitude. At constant average output power, this results in a substantially increased energy per laser pulse that can be sustained inside the cavity by utilising an innovative dispersion management scheme (Fuerbach et al., 2005).

The GC–MS was operated in full scan mode (50–550 amu) and chromatography was carried out using a DB-5 column (J&W, 25 m, 0.32 mm I.D, 0.52 μm film thickness) with helium as a carrier gas (1.5 ml/min). The sample chamber was held at ca. 100 °C, and helium at 100 ml/min flushed petroleum liberated by the laser ablation process into a coiled nickel loop immersed in liquid nitrogen. After 2 min of trapping and cryo-focussing, the helium flow through the nickel trap was reduced to 1 ml/min by switching a 6-port Valco valve, the cryotrap was removed and the nickel trap heated to 320 °C. Products were then re-focussed in a loop of GC column immersed in liquid nitrogen. Once this trap was removed, the GC oven was programmed from an initial temperature of 40 °C (2 min. hold), followed by heating at 4 °C/min to 310 °C (30 min. hold).

## 3. Sample

Our new analytical approach was tested on a well characterised idiomorphic clear bipyramidal quartz crystal of ca. 3 mm size that

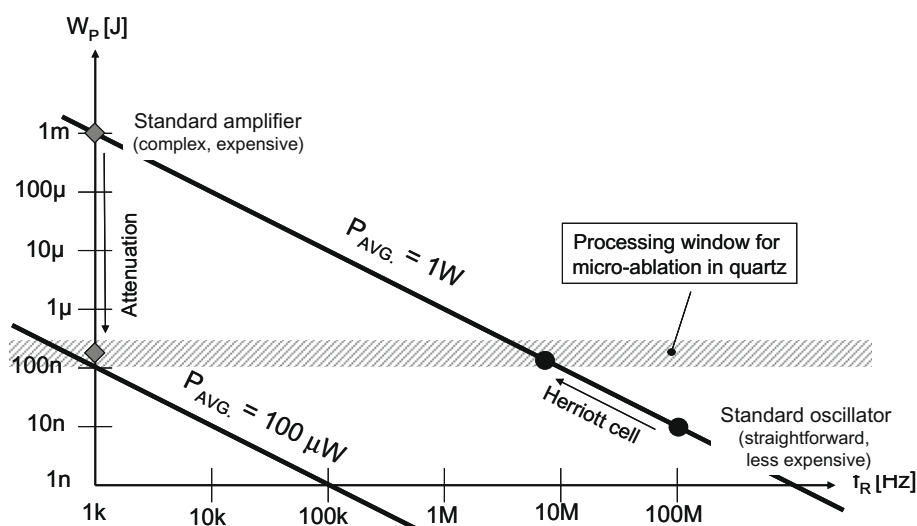


Fig. 1. Cross plot of dependency of work per pulse and pulse frequency. The use of a Herriott type multi-pass cell leads to an increase of the cavity length of a femtosecond oscillator and hence the energy per pulse.

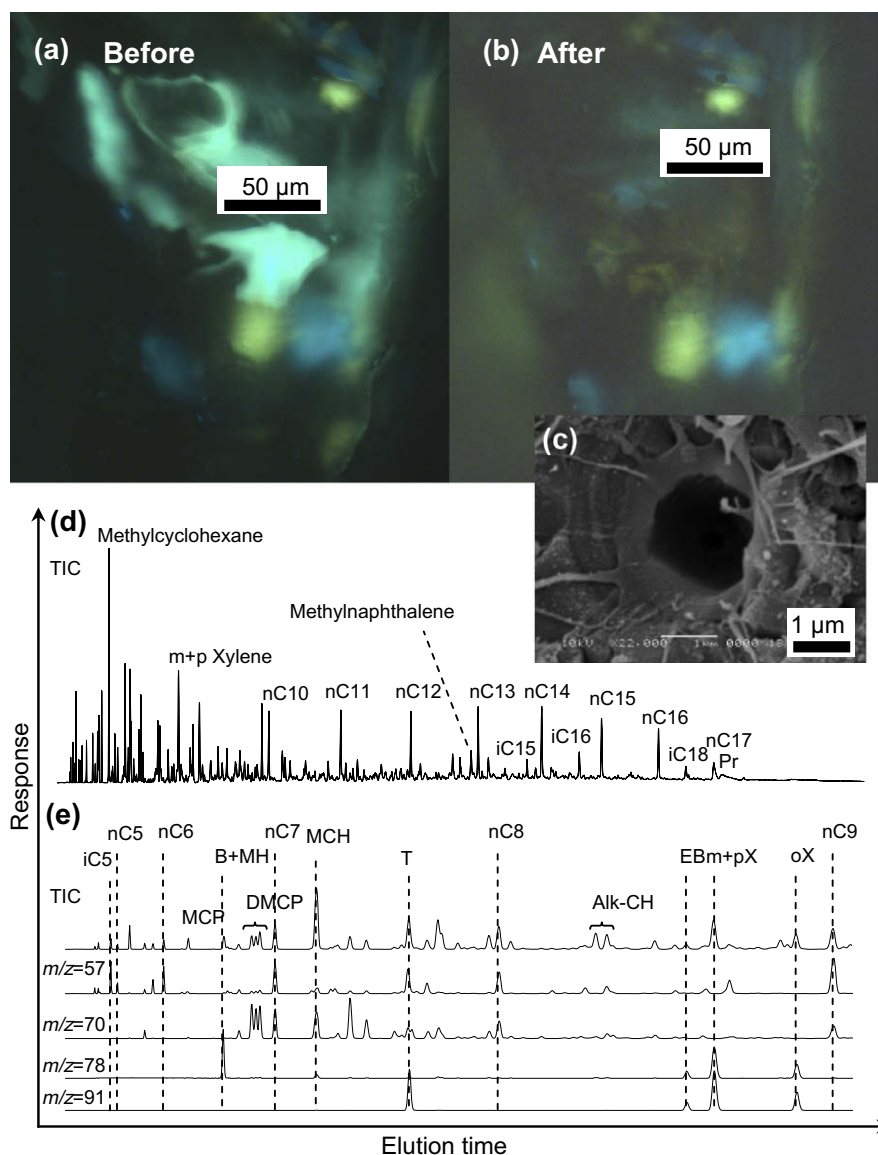
was isolated from a volcanic dyke cross-cutting organic rich Silurian graptolite shales of the Kopanina Formation at the Kosov quarry in the Barrandian Basin (Czech Republic). Petroleum inclusions in this crystal are abundant and can reach a maximum size of up to 100  $\mu\text{m}$  in diameter. Inclusions are dominated by abundant blue fluorescing inclusions with some larger and irregular shaped inclusions showing a yellow fluorescence colour. More detailed descriptions of the fluid inclusion assemblages in the test sample (KQ7-Qz) and geochemical results from on-line bulk crushing are provided in Volk (2000) and Volk et al. (2002).

#### 4. Results

In our first attempt to selectively open a single inclusion we have specifically targeted a small (<10  $\mu\text{m}$ ) blue fluorescing inclusion. We focused laser pulses with an energy of 160 nJ and a dura-

tion of about 50 fs at a repetition rate of 11 MHz onto the crystal, thereby ablating the quartz and successfully opening the inclusion. This did not appear to affect nearby inclusions. However, the amount of petroleum that was liberated was too small for confident detection on our GC–MS system.

We then focused on a different and larger (>50  $\mu\text{m}$ ) blue fluorescing inclusion that is shown in Fig. 2a. Again, we extracted the petroleum from this single inclusion without affecting adjacent inclusions, including one with a more yellowish fluorescence colour deeper in the crystal (see Fig. 2b). The extraction hole ablated into the quartz crystal had a diameter of about 2  $\mu\text{m}$  (Fig. 2c). For this larger inclusion, the amount of extracted hydrocarbons was sufficient to produce a clear signal on the GC–MS. The resulting chromatograms show straight chained, branched and cyclic alkanes and aromatic hydrocarbons with carbon numbers ranging from 4 (*iso*-butane) to 19 (pristane) (Fig. 2d), while gases were



**Fig. 2.** Petroleum trapped in fluid inclusions in quartz sample KQ7-Qz before (a) and after (b) ultrafast laser ablation. UV epifluorescence photomicrographs. (c) Extraction crater ablated into quartz, scanning electron microscope photomicrograph. (d) Total ion chromatogram (TIC) of the extracted petroleum. nC10 = *n*-decane etc., iC15 = isopentadecane, etc., Pr = pristane. (e) TIC and selected  $m/z$  chromatograms providing more detail for compounds in the C<sub>5</sub>–C<sub>9</sub> elution range. MCP = methylcyclopentane, B = benzene, MH = methylhexane, DMCP = dimethylcyclopentane, MCH = methylcyclohexane, T = toluene, Alk-CH = alkylcyclohexanes, EB = ethylbenzene, *m* + *p* + *o*X = meta-, para- and orthoxylene.

not monitored with the chosen GC–MS scan rate. The distribution of low to mid-molecular weight compounds is similar to that observed by on-line bulk crushing (Volk et al., 2002). However, C<sub>19+</sub> compounds (with retention times up to that of the C<sub>31</sub> *n*-alkane) which were recovered in the on-line crushing approach could not be detected using our laser approach. As in previously reported laser extraction methods (e.g. Greenwood et al., 1998; Hode et al., 2006), pyrolysis artefacts such as alkenes and ketones were also not detected when using the pulsed laser system. This proves that the laser pulses themselves do not alter the oil's composition and do not introduce any thermal artefacts. This in turn can be explained by the fact that, due to their extremely high peak intensities, femtosecond laser pulses transfer their energy to the sample via nonlinear optical processes rather than via thermal absorption, and thus alter the material by 'cold ablation' (Keller, 2003). More details on the distribution of low molecular weight hydrocarbons in the C<sub>5</sub>–C<sub>9</sub> range are provided in Fig. 2e.

## 5. Outlook

It appears as if hydrocarbons with carbon numbers >20 have remained in the extraction chamber, possibly due to the relatively low thermal extraction temperature (ca. 100 °C) and/or cold spots in the transfer line. Improvements to the inlet system may overcome these problems, and thus enhance analytical sensitivity and the recovery of high molecular weight components. While increasing the thermal extraction temperature may improve extraction efficiency, it may also lead to unintentional thermal decrepitation of some of the inclusions. Coupling fluid inclusion extraction with time-of-flight secondary ion mass spectrometry for the detection of biomarkers (as proposed by Siljeström et al., 2009) may be another way of significantly enhancing the sensitivity of the system, although this approach will lack the chromatographic resolution currently used to obtain a maximum of information on petroleum. Nevertheless, this pilot study proves the concept that ultrashort laser pulses can be used to liberate unaltered oil from individual fluid inclusions. In so doing it creates opportunities for exciting new research aimed at de-convoluting the information retained in different hydrocarbon palaeo-fluids trapped within single minerals.

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