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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 fluid 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, which opens exciting research opportunities to deconvolute information on the nature of different hydrocarbon palaeo-fluids from single minerals.

**Keywords**
- Fluid inclusion; petroleum inclusion; femtosecond laser; laser ablation

**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 can often be found in quartz crystals and sand grains of petrolierous 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 evolution can be obtained by analysing the chemical composition of the trapped hydrocarbons. To date, the chemical composition of petroleum trapped in fluid inclusions can be determined by inference from spectroscopic (e.g. measurement of epifluorescence when excited with ultraviolet light, Raman spectroscopy, Fourier-transform infrared spectroscopy) and microthermometric methods (Munz, 2001) and by mechanical crushing or thermal decrepitation of bulk samples followed by solvent or thermal
extraction for analysis by gas chromatography – mass spectrometry (GC-MS) (George et al., 2007). However, fluorescence microscopy and heating – freezing experiments commonly indicate that these crystals contain several fluid inclusion assemblages that hold information from different geological events (e.g. Schubert et al., 2007). While spectroscopic methods, sometimes combined with volumetric measurements and modelling (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 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 laser, 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.

**Experimental setup**

The laser extraction GC-MS setup was a modified version of that used by
Greenwood et al. (1996). It comprises a Hewlett Packard 6890 gas
chromatograph (GC) interfaced to a Hewlett Packard 5973 mass selective
detector (electron energy 70 eV, electron multiplier 1200 V, source
temperature 250 °C, 0.1 amu resolution) and an Olympus BX60M system
microscope with a custom-built laser chamber and inlet system. The
microscope was used with a long-working-distance objective (20x 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 (Femtosource 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, i.e. only about 50 femtoseconds long time interval. This results in an ultrahigh peak intensity at the laser focus (>1014 W/cm²) that induces nonlinear (multiphoton) absorption of the radiation, a process that is virtually independent on the actually centre 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 with a duration of 50 fs, the threshold fluence is only about 3 J/cm² (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 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 only femtosecond amplifier systems have been employed for the ablation of transparent dielectric media so far. Such laser systems, however, are expensive, complex and require a well controlled laboratory environment, with minimal variations in temperature and humidity, and have to be set-up on vibration-free optical tables.
Moreover, it has been shown that the required spatial resolution in the few-
micrometer range can only be achieved in 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 Herriot-type multipass 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 m 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 minutes of trapping and
cryofocussing, 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 ºC. 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 ºC (2 min. hold), followed by heating at 4 ºC/min to 310 ºC (30 min. hold).

**Sample**

Our new analytical approach was trialled on a well-characterised idiomorphic clear bipyramidal quartz crystal of ca. 3 mm size that was isolated from a volcanic dyke cross-cutting organic-rich Silurian graptolite shales of the Kopanina Formation at the quarry Kosov in the Barrandian Basin (Czech Republic). Petroleum inclusions in this crystal are abundant and can reach a large size of up to 100 µm 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).
Results
In our first attempt to selectively open a single inclusion we have specifically targeted a small blue fluorescing (<10 µm sized) inclusion. We focused laser pulses with an energy of 160 nJ and a pulse duration 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 µm) 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 µm (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 not monitored with the chosen GC-MS scan rate. The distribution of low- to mid-weight molecular compounds is similar to that observed by on-line bulk crushing (Volk et al., 2002), however, C_{19+} compounds that were detected up to n-C_{31} in the on-line crushing approach could not be detected using our laser approach. Similar to 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 composition and do not introduce any thermal artefacts. This 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 detail on the distribution of low-molecular-weight hydrocarbons in the C5-C9 range is provided in Fig. 2e.

**Outlook**

It appears as if hydrocarbons with carbon numbers > 20 have remained in the extraction chamber, possibly due to the relatively cool 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 recovery. While increasing the thermal extraction temperature may improve extraction efficiency, it may lead to unintentional thermal decrepitating 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, which opens exciting research opportunities to de-convolute information on the nature of different hydrocarbon palaeo-
fluids from single minerals.

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Chirped-pulse oscillators for the generation of high-energy


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Figure captions

Figure 1: Cross-plot of dependency of work per pulse and pulse frequency.

The use of a Herriott-type multipass cell leads to an increase of the cavity length of a femtosecond oscillator and hence the energy per pulse.

Figure 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 C5-C9 elution range. MCP = methylcyclopentane, B = benzene, MH = methylhexane, DMCP = dimethylcyclopentane, MCH= methylcyclohexane, T= toluene, Alk-CH = alkylcyclohexanes, EB = ethylbenzene, m+p+oX = meta-, para- and orthoxylene.
Figure 1

[Diagram showing a graph with axes labeled \( W_p [J] \) on the y-axis and \( f_R [Hz] \) on the x-axis. The graph includes two lines: one representing \( P_{AVG} = 100 \mu W \) and another representing \( P_{AVG} = 1 W \). The graph indicates two different regions: one for standard amplifiers (complex, expensive) and another for standard oscillators (straightforward, less expensive). There is also a shaded area labeled "Processing window for micro-ablation in quartz." ]
Figure 2

a) Before
b) After

(c) Image with 1 μm scale bar

(d) Chromatogram with peaks labeled:
- TIC
- nC5, nC6, nC7...
- MCH
- DMCP
- T
- Alk-CH
- EB m+pX
- oX

(e) Graph with elution time on x-axis and response on y-axis, showing peaks at m/z values of 57, 70, 71, and 91.