

POTENTIAL OF SHORT WAVELENGTH LASER ABLATION OF ORGANIC MATERIALS

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INTRODUCTION

Although the literature contains several articles on UV laser ablation of synthetic polymers [1] and human tissue for surgical applications, to our knowledge there is no published record on organic geochemical applications for UV laser pyrolysis–gas chromatography–mass spectrometry (LA-GC-MS). In this study we have investigated the use of a 213 nm UV laser for ablating kerogens and organic rich rocks to liberate and analyse hydrocarbon signatures and compared the results against IR laser pyrolysis and traditional Py-GC-MS.

It is possible to equate laser wavelength to electron volts where 1064 nm (IR) = 1.2 eV and 213 nm (UV) = 5.8 eV. Most chemical bonds have an energy between 2 to 4 eV and C-C bonds are ~3.6 eV. Organic materials can absorb radiation from a UV laser and chemical bonds can be cleaved cleanly by complex photochemical pathways by a single photon [2]. Ablation occurs with almost no heating of the sample and hence the term laser ablation instead of pyrolysis. Visible or IR lasers have insufficient energy to break bonds with a single photon this results in the heating of sample by the absorption of energy into the vibrational modes of the molecule which can then result in pyrolysis.

EXPERIMENTAL

Laser ablation work was performed using a Nd:YAG 213 nm laser (New Wave Research) and an off-line static helium filled cell, the cell was subsequently solvent extracted. Laser ablation pits were ~300 μm × 300 μm. Separate analysis of the same samples using a more traditional flash pyrolysis approach was performed with a CDS Pyroprobe and IR laser pyrolysis [3] for comparative purposes.

A solvent-extracted kerogen consisting mainly of higher plant material (Brownie Butte, Montana, ~ 70 Ma) and extracted chip of Green River Shale were used for initial experiments.

RESULTS

As can be seen in Fig 1 and 2 UV laser ablation is able to liberate relatively high molecular weight fragments with only small amounts of alkenes or other pyrolysis artefacts detected. SEM images of ablation pits indicate there is no obvious thermal alteration of the sample (Figure 3). The results of the pyrolysis techniques (on-line and IR laser pyrolysis) are similar and display a number of artefacts related to the pyrolysis process.

Laser ablation of a number of samples has also shown that the distributions of biomarkers are comparable with the solvent extracts. Product yields although not quantified appear to be much higher than traditional pyrolysis techniques.

These initial results are interesting, in theory C-C bonds should be broken in these experiments we only have limited evidence for this in the very low concentration of alkenes present in the extracts, although hydrogenation has been observed in other experiments involving UV sources. The *n*-alkanes released from the kerogen can be explained by the breaking of C-O bonds; this kerogen sample contains abundant ester linked C₂₆ to C₃₂ even fatty acids that could yield the distribution of odd *n*-alkanes observed. The Green River Shale laser ablation extract appears so similar to the solvent extract of the same sample that a reasonable conclusion is that the mineral matrix has been ablated away releasing occluded free organic compounds.

PLANNED WORK

Future work will include ablation of model compounds, synthetic polymers, experiments with shorter wavelength lasers and development of an on-line system.

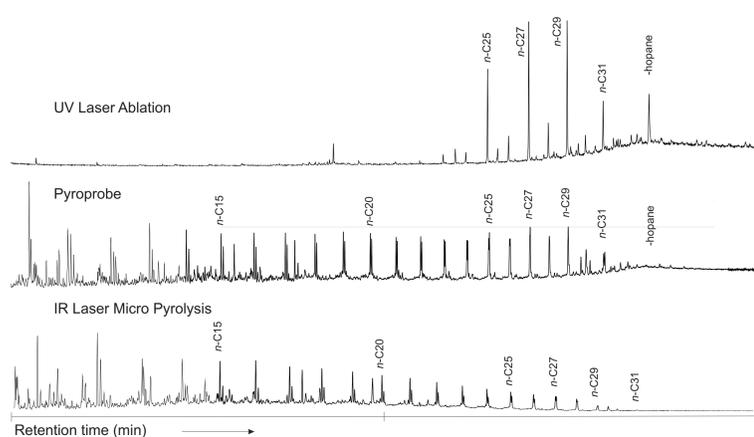


Figure 1 :UV laser ablation and pyrolysis of Brownie Butte solvent extracted kerogen.

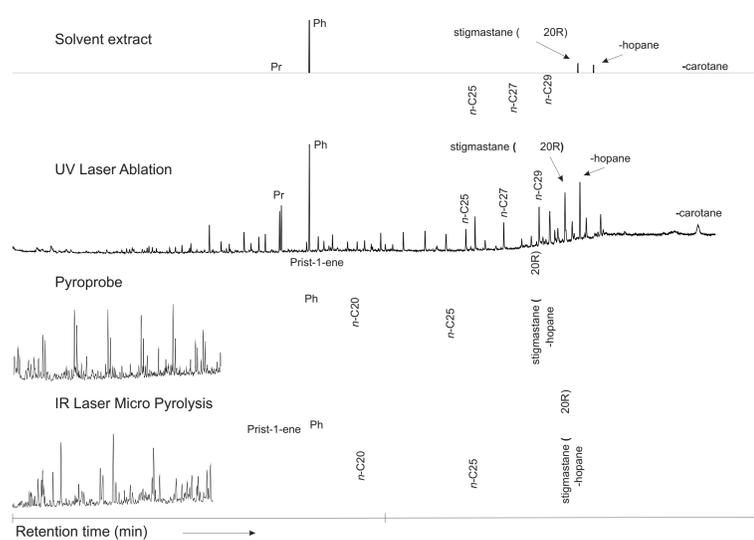


Figure 2 :Solvent extract and UV laser ablation and pyrolysis of Green River Shale solvent extracted rock chip.

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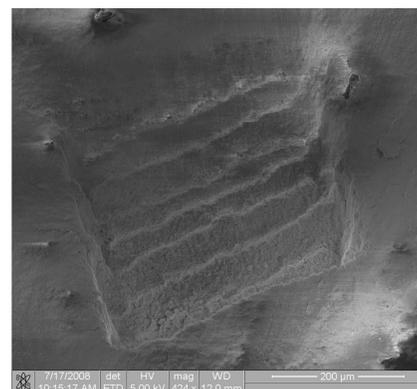


Figure 3: SEM image of laser ablation pit from a Green River Shale sample showing no evidence of heating.