

## Petroleomics: Molecular characterization of petroleum crude oil

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Until recently, characterization of petroleum crude oil was limited to bulk measurements. Electrospray ionization and atmospheric pressure photoionization high-field Fourier transform ion cyclotron resonance measurement of molecular mass to within ~100 ppb now makes it possible to resolve and identify up to 30,000 individual elemental compositions,  $C_nH_nN_nS_nO_n$ , up to ~1,000 Da in a single mass spectrum [1]. As for dissolved organic matter [2], even heavy crude oils are mainly composed of species less than ~1,200 Da in mass. Higher molecular weight species can result from non-covalent multimers, as seen by time-of-flight mass spectrometry and by gas-phase dissociation experiments. The compositions are conveniently sorted by graphical images based on heteroatom class ( $N_nS_nO_n$ ), double bond equivalents (rings plus double bonds), H/C and O/C ratios, and total number of carbons. Molecular composition can in turn be related to crude oil geographic origin, maturity, biodegradation, deposits, and processing. Work supported by NSF (DMR-06-54118) and the State of Florida.

[1] Marshall & Rodgers (2008) *Proc. Natl. Acad. Sci. U.S.A.* **105**, 18090–18095. [2] D'Andrilli, Dittmar, Koch, Purcell, Marshall & Cooper (2010) *Rapid. Commun. Mass Spectrom.* **24**, 643–650.

## A new approach to molecularly characterize the biology and economic utility of oil shales

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Oil shales are often divided into six different categories, based on the environment of deposition and the state of preservation of the organic matter [1]. Of these six types, five are thought to be derived from algal material. Furthermore, three of the types are thought to derive from specific types of algae: oil shales that were deposited in a marine environment and contain the algal cyst *Tasmanites punctatus* are tasmanites, oil shales that formed in a lacustrine environment and contain the remains of the green algae *Botryococcus braunii* are torbanites while lacustrine rocks containing the remains of *Gloeocapsomorpha prisca* are kukersites [1]. However, here we show that not all organic-walled microfossils preserved in these oil shales derive from the three species, and some might not be algae at all. It is of crucial importance to determine what types of organisms formed an oil shale deposit, not only to understand the interplay of ecology and biota through time, but to ascertain the best way to unlock these vast reservoirs of organic carbon locked in the rock record.

### Novel micro-analytical approaches

Organic petrography, Rock-Eval pyrolysis, and Fisher assay are traditionally used to evaluate oil shales [1]. However, these techniques only give information about the potential yield of volatile oil, not on the molecular composition of the oil shale or the oil derived from it. Thus, the application of novel micro-analytical techniques, including chemical oxidation of the organic material and infrared micro-spectroscopy, to these organic-rich rocks allows an exploration of biologic compounds and biopolymers, both extractable and recalcitrant, preserved in the rocks. In combination with careful studies of geological context, these data enable a more robust assessment of the micro-organisms responsible for the formation of these deposits, as well as the environment in which they once dwelled. We demonstrate that, while the traditional oil shale classification seems straightforward, it is, however, a vast oversimplification and has led to the propagation of a great number of misconceptions.

[1] Hutton *et al.* (1994) *Energy & Fuels*. **8**, 1478–1488.