

## Petroleum decomposition under redox-controlled aqueous conditions

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Petroleum coexists with water and redox sensitive minerals at elevated temperatures and pressures in sedimentary basins. A series of laboratory experiments have been conducted to constrain the role of inorganic sedimentary components during geochemical processes responsible for petroleum maturation and the formation of natural gas. Experiments were conducted at 325-350°C and 350 bar over a broad range of water/oil ratios to allow comparison of organic transformations occurring in an oil phase with reactions involving oil dissolved in water. Fe-bearing mineral assemblages and anhydrite were added to some experiments to regulate the redox state of the fluid.

Experiments conducted in the absence of added minerals were characterized by high aqueous hydrogen concentrations indicative of extremely reducing conditions. Oil decomposition produced a methane-poor assemblage of low molecular weight hydrocarbons consistent with thermal cracking of longer-chain hydrocarbons. Despite the presence of water as an oxygen source, relatively minor amounts of carbon dioxide were produced. Low molecular weight products generated from oil dissolved in water were enriched in branched compounds relative to products generated in an oil phase.

In the presence of a suitable oxidizing agent such as a hematite-magnetite-pyrite mineral buffer, oil decomposition produced substantial amounts of carbon dioxide in addition to a methane-rich assemblage of low molecular weight hydrocarbons. Formation of alteration products that are both oxidized and reduced relative to the original oil is consistent with a reaction pathway involving stepwise oxidation of *n*-alkanes to produce alkenes, alcohols, ketones, and carboxylic acid reaction intermediaries. Depending on the oxidation state of the chemical system, carboxylic acids may either decarboxylate to produce *n*-alkanes and carbon dioxide or undergo complete oxidation to carbon dioxide. In general, these results are consistent with observations from natural environments where oxidative oil degradation associated with thermochemical sulfate reduction is occurring.

Decomposition of short-chain *n*-alkanes by stepwise oxidation is significantly faster than thermal cracking and produces a more methane-rich assemblage of low molecular weight products. These data suggest that water and redox reactive minerals facilitate reaction pathways that are not available in a pure oil system. The presence of numerous oxidizing agents in sedimentary basins suggests oxidative degradation of low-molecular weight *n*-alkanes may play a key role in the formation of "dry" natural gas.

## Sources and processes of nitrogen along the lower Jordan River

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### Introduction

We report the results of collaboration between Palestinian, Jordanian, and Israeli research groups investigating the lower Jordan River between the Sea of Galilee (Lake Tiberias) and the Dead Sea. The research objectives focus on the level of nitrogenous pollutants in the river, their sources and modifications. The study is based on chemical analyses, flow rate measurements, and isotopic analyses of <sup>18</sup>O and <sup>15</sup>N in the dissolved nitrate and ammonium molecules.

### Results and discussion

The river begins with high levels of ammonium and organic nitrogen derived from sewage inputs. Ammonium decreases from 20 to 0-5 mg-N/L along the first 20 km of the river, while nitrate increases from nearly zero to 10-15 mg-N/L.

Mass balance calculations were obtained along several river segments. Calculations were based on NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> analyses and measurements of the river and tributaries flow rate. The role of nitrogen transformations and mixing processes was determined and quantified. It was found that both mineralization and nitrification are significant. In addition, it was found that a non-point water source enters the river, affecting both its water quantity and quality.

Isotopic analysis showed an increase in the δ<sup>15</sup>N<sub>(NO3)</sub> values from less than 5‰ to 15-20‰ with no significant change in δ<sup>18</sup>O<sub>(NO3)</sub>. The δ<sup>15</sup>N<sub>(NH4)</sub> values vary from 10‰ to 40‰.

### Conclusions

The simultaneous increase in nitrate and δ<sup>15</sup>N<sub>(NO3)</sub> along the flow of the Jordan River is explained by a nitrification of <sup>15</sup>N-enriched ammonium resulting in an enriched nitrate. In addition, non-point groundwater discharge affects the nitrate level at some of the river sections.