

## Opening the black box: Imaging nanoparticle transport through rock with MRI

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### Introduction

Magnetic Resonance Imaging (MRI) is perhaps best known for its use in medicine. However, its ability to non-invasively image inside materials that are opaque to other imaging methods is of benefit to the geological and environmental sciences. Here we report on the application of MRI to image transport of nanoparticles through sandstone. This approach is beneficial as it enables 2D and 3D 'videos' of nanoparticle transport inside rock to be collected, providing spatially resolved data from which we can enhance our understanding of nanoparticle transport in groundwater systems.

### Methods

Commercially available nano-magnetite nanoparticles with an organic polymer cap were used. The superparamagnetic nature of these nanoparticles ensured they were visible to MRI. These were pumped through bentheimer sandstone rock core and MR images were collected every 5 minutes. Images were calibrated to maps of actual nanoparticle concentration using the MRI parameter  $T_2$  (the spin-spin relaxation of  $^1\text{H}$  nuclei), as  $1/T_2$  is proportional to nanoparticle concentration.

### Results and conclusion

Transport of positive and negatively charged nanoparticles were successfully imaged, with transport of positively charged nanoparticles retarded significantly due to electrostatic attraction to quartz surfaces. Images collected after flushing with nanoparticle free water showed negative nanoparticles were successfully removed from the sandstone, while significant quantities of positive nanoparticles remained. Concentration profiles were evaluated with CXTFIT and colloid filtration theory at regular distances along the length of the sandstone core to test for variations in dispersivity, dispersion coefficient, recovery, deposition rate constant, collision efficiency and transport –attachment efficiency. MRI's ability to collect spatially resolved data ensures it can act as a useful tool to unpick nanoparticle transport heterogeneity and test and develop transport models.

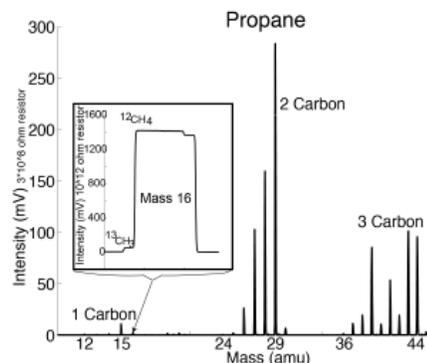
## Direct Mass Spectrometric Analysis of Position Specific $\delta^{13}\text{C}$ in Organics

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It is recognized that natural organic molecules can exhibit position-specific isotopic fractionations (i.e., differences in isotopic composition for a single element between non-equivalent molecular sites). For example, lipids can exhibit up to ~30 ‰ difference in  $^{13}\text{C}/^{12}\text{C}$  between adjacent carbons as a result of fractionations arising during decarboxylation of pyruvate in lipid biosynthesis [1]. Little in detail is known about such isotope effects in natural products, but it seems possible that observations of isotopic ordering of carbon could distinguishing among the mechanisms and conditions of biosynthetic reactions. And, such position specific isotope effects may be inherited by alkanes produced from thermal degradation fatty acid chains, perhaps modified as functions of the conditions and mechanisms of thermal maturation.

Here we examine the potential of the MAT 253 Ultra, a new kind of high resolution gas source isotope ratio mass spectrometer [2], to make measurements that will permit reconstruction of position specific carbon isotope compositions in organic molecules, as preserved in alkanes. We focus on propane, the smallest alkane that could exhibit position specific carbon isotope differences. Electron impact ionization of propane yields three families of product ions:  $\text{C}_1\text{H}_n$ ,  $\text{C}_2\text{H}_n$  and  $\text{C}_3\text{H}_n$ ; fragments made by H loss are abundant, including bare carbon ions and clusters. H adducts are present but rare. An analysis of the  $^{13}\text{C}/^{12}\text{C}$  ratio of any two of these families of product ions constrains the position specific C isotope fractionation in propane, provided such fragment species can be analyzed stably and reproducibly and one has accounted for exchange through recombination. We have demonstrated that  $^{13}\text{C}\text{H}_3/^{12}\text{C}\text{H}_3$ ,  $^{13}\text{C}^{12}\text{CH}_4/^{12}\text{C}_2\text{H}_4$ , and  $^{13}\text{C}^{12}\text{C}_2\text{H}_8/^{12}\text{C}_3\text{H}_8$  ratios can be analyzed with sub-per mil precision (as good as 0.1 ‰ for the most abundant species), and zero-enrichments yield accurate results. It remains to be seen whether this approach accurately reproduces independently known position-specific isotopic differences, though the low abundance of adducts suggests recombination will not be a significant artifact; i.e., accuracies similar to the precisions reported here are expected.



**Figure 1:** Full spectra of propane as measured on MAT253-Ultra [1] DeNiro, Epstein (1977) *Science* **Volume 197**, 261-263. [2] Eiler et. al (2012) **this volume**.