# Final Report
## DOE Project DE-SC0006623
### July 30, 2015

## 1. Background

The purpose of this project was to construct a gas-source isotope ratio mass spectrometer with sufficient mass resolving power to measure the relative abundances of rare isotopic species of methane gas. The science goal was to provide a new isotopic tool for sourcing methane. In particular, the new instrument was designed to measure the relative abundances of both $^{13}CH_3D$ and $^{12}CH_2D_2$, two very stable but very rare doubly-substituted isotopologues with the same cardinal mass of 18 atomic mass units, allowing us to move beyond temperature of formation as the sole information to be obtained from $^{13}C$-D bond ordering. Studies made possible with this novel instrument should provide new information about the mode of formation, presence of mixing, and importance of migration of natural $CH_4$ gas. Results will facilitate sourcing fugitive methane as well as helping to specify the origin of gas where provenance is uncertain.

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## 2. Status

The new mass spectrometer, called the *Panorama*, was delivered to UCLA in early March of 2015 (Figure 1). It is currently functioning beyond expectations in the purpose-built laboratory at UCLA.
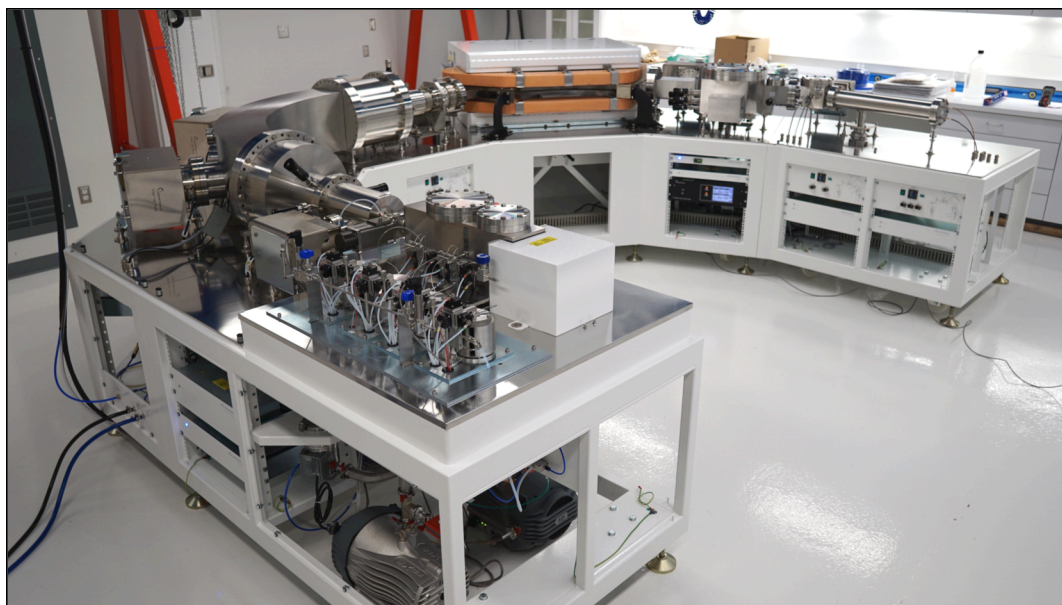


**Figure 1**. Panorama installed in the laboratory at UCLA.

This instrument, the largest of its kind in the world, was developed for our laboratory at UCLA and is unique. The basic components are shown schematically in Figure 2. The magnetic sector has a radius of 800 mm that, when combined with typical slit widths and aberrations yields an operational mass resolving power of ~ 45,000, more than 40 times that of conventional gas-source isotope ratio mass spectrometers and three times the operational value for the next highest resolution instrument of its kind. Sensitivity is provided by an ion counter on the central channel (Figure 2). With this instrument we measure $\Delta^{13}CH_3D$ and $\Delta CH_2D_2$, where $\Delta$ here refers to per mil departures from the stochastic relative abundances of these rare species, with virtually no mass spectrometric interferences and no corrections.
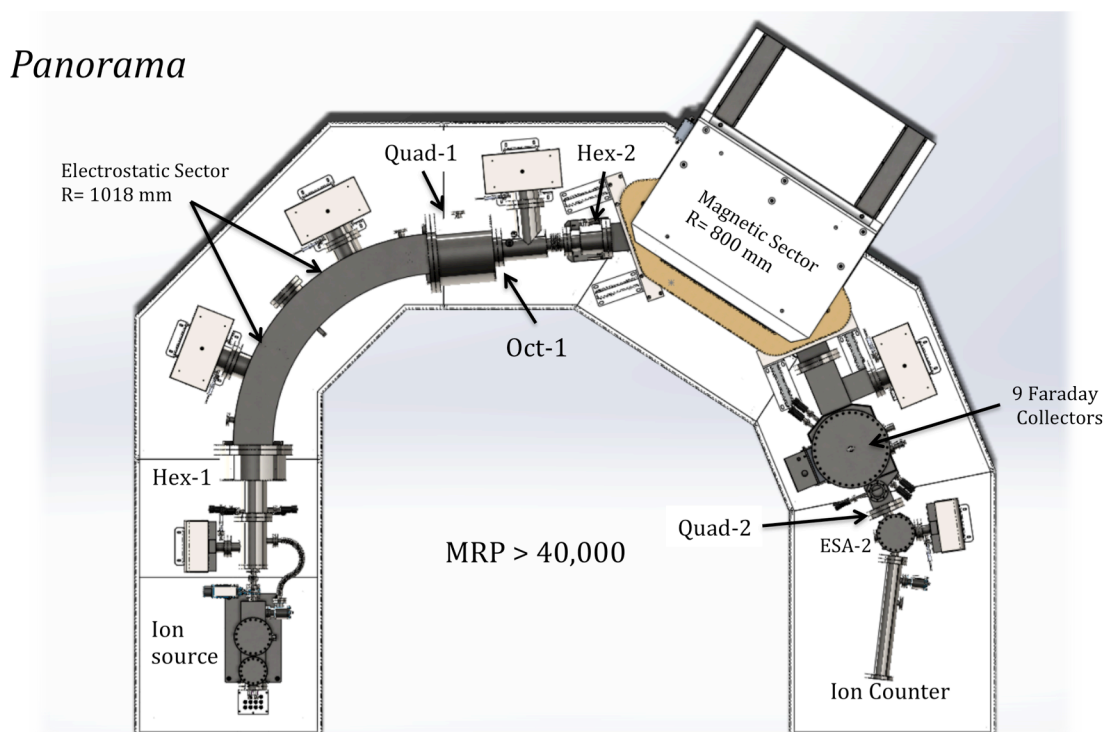


**Figure 2**. Plan view schematic showing the essential ion optical components of the Panorama mass spectrometer.

We have run numerous tests on the instrument that verify its accuracy and precision, including comparisons of bulk D/H and $^{13}C/^{12}C$ relative to other methods for measuring these isotope ratios in methane gas, with excellent agreement (Figure 3). It is important to recognize that these measurements are made on the methane gas itself as the analyte. Previous methods require converting the $CH_4$ to $CO_2$ for carbon isotope ratio analysis and $H_2$ for D/H. In addition, the internal precision we obtain for D/H is ~ 0.01 per mil, an extraordinary value compared with other methods.

A strategy for validating the results was constructed based on the non-linear nature of mixing gases with different bond ordering and bulk isotopic compositions. Using this property of mixing, we have been demonstrating accuracy and precision by measuring mixtures of two gases that are in thermodynamic equilibrium with respect to bond ordering at very different temperatures and with

different bulk isotopic compositions. Indeed, one of the powerful applications of measuring both $\Delta^{13}CH_3D$ and $\Delta CH_2D_2$ in real samples is the significant departures from thermodynamic equilibrium that arise from simply mixing multiple sources of gas with different isotopic compositions. Figure 4 shows our results to date for two gases that differ in D/H by 150 per mil, a reasonable variation for natural samples. Mixtures fall off of the loci of thermodynamic bond ordering compositions at various temperatures represented by the heavy black curve in Figure 4. The correspondence between the theoretical mixing curve and the measurements demonstrates that we are obtaining precise and accurate measurements of natural abundances of $^{13}CH_3D$ and $CH_2D_2$. In the case of the latter, these are the first such measurements ever made. The results in Figure 4 verify the concept that a sample of methane gas can be identified as being the product of a mixture of sources even without knowing the isotopic compositions of the distinct sources.
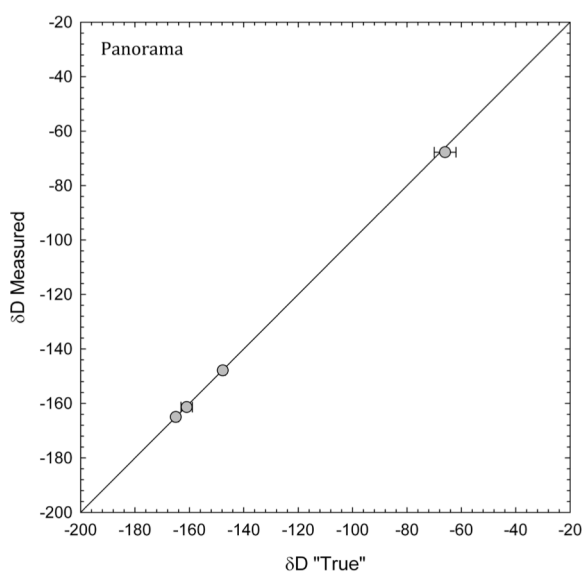


**Figure 3**. Plot of measured D/H using the Panorama vs. accepted D/H for methane samples.
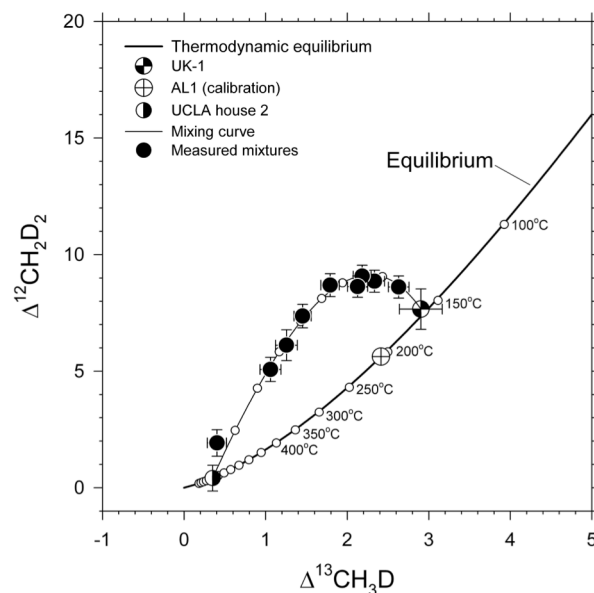
**Figure 4.** Plot of $\Delta^{13}CH_3D$ vs. $\Delta CH_2D_2$ showing measurements of mixtures of a low-temperature gas and a high-temperature gas. Adherence to the calculated mixing curve shown as the thin solid line illustrates accuracy of measurements obtained using the Panorama instrument.

## 3. Future Applications

As part of this project we are constructing a vacuum line for purification of $CH_4$ gases for isotopic analysis. In the meantime, we continue to analyze samples provided to us from several laboratories where the analyte methane has already been purified. Once the vacuum system is complete, the Panorama installation at UCLA will be poised to explore methane provenance in a wide range of samples.

Measuring the temperature of formation of natural methane gas using rare isotopologues will be of use in determining provenance. For example, candidate sources that can be distinguished on the basis of temperature include microbial methanogenesis in sedimentary source rocks with an upper temperature limit of 70 to 90°C and higher-temperature thermogenic methane production that often occurs at > 140°C. However, temperature alone will not be entirely diagnostic. Thermogenic methane

can be produced at temperatures as low as 60 to 70$^{\circ}$C (catagenesis), overlapping with methanogenesis. Serpentinization, a source of hydrogen to produce methane, occurs at temperatures as low as 50$^{\circ}$C (Schrenk et al. 2013 and references therein), and so abiogenic methane production also overlaps with methanogenesis in temperature (Etiope and Sherwood Lollar 2013). Overlap occurs at high temperatures between thermogenic gas from biotic sources and abiogenic processes like high-temperature oxidation-reduction in the deep crust or mantle (e.g., higher-$T$ serpentinization) and catalyzed abiogenic hydrocarbon production by Fischer-Tropsch-Type reactions, FTT (Horita and Berndt 1999; Foustoukos and Seyfried 2004) .

Rather than relying on temperature alone, we seek to characterize the effects of various reactions and transport mechanisms on the distributions of rare isotopologues, including mixing. The need for such tracers is clear when considered in the context of previous work. For example, a decrease in $\delta^{13}$C with increasing carbon number for gaseous n-alkanes (C1-C4) is taken as evidence of abiotic formation, while a strongly positive trend reflects a thermogenic origin (Sherwood Lollar et al. 2002; McCollom and Seewald 2007). Furthermore, Fischer-Tropsch synthesis has been suggested to induce $^{12}$C-H isotope enrichment due to the preferential elimination of the $^{12}$C-D bond during abiotic polymerization (Sherwood Lollar et al. 2002). Thus, existing isotope proxies used to identify methane origins are dependent on trends imposed by the isotopic compositions of other higher chain alkanes. By characterizing the bond ordering of $^{13}$C and D in CH$_4$, the role of methane formation mechanism on the C-H bond could be assessed in the absence of polymerization reactions. Interestingly, the $^{13}$C and D isotopic composition of hydrocarbons experimentally formed during Fischer-Tropsch synthesis under hydrothermal conditions (McCollom and Seewald 2006; Fu et al. 2007) and measured in the alkaline vent fluids of Lost City (Proskurowski et al. 2008) appears to deviate from the "abiotic" trends referred to above. This suggests that the magnitude of fractionations and isotopic trends among light alkanes are likely affected by mineral-catalyst composition and the kinetic rates of FTT reactions.

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