

# **PS Noble Gas Geochemistry at the La Barge Platform, Wyoming, USA: CO<sub>2</sub> Source and Potential Total Petroleum System Investigation Tool\***

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## **Abstract**

Initial analyses of noble gas isotopes, major element isotopes, and gas composition data from high carbon dioxide (CO<sub>2</sub>) natural gas samples at the La Barge Platform, Wyoming, USA, indicate that the CO<sub>2</sub> has a strong crustal signature. This finding is in line with geochemical, mineralogical, and fluid inclusion analyses that suggest that inorganic thermochemical sulfate reduction (TSR) is the source of La Barge's CO<sub>2</sub>. Isotopes of noble gases released from hydrocarbons during TSR carry the isotopic signature of the air-saturated seawater and crustal environment of the hydrocarbon source rock. Helium isotope ratios reported relative to their concentrations in air ranged from 0.077 to 0.085 (R/Ra); these values as well as those of neon and argon indicate crustal origin. La Barge Platform is the largest source of CO<sub>2</sub> used in enhanced oil recovery (EOR) at oil and gas fields across the northern Rocky Mountains. The field is located in southwestern Wyoming, west of the towns of Big Piney and La Barge. The field produces natural gas (21% average) and CO<sub>2</sub> (65% average) from the Mississippian-age Madison Limestone. In this initial round of sampling, three gas samples were collected from 14,500 to 16,500 feet of depth at three different well heads. These results are an initial effort towards describing the total CO<sub>2</sub> system at La Barge; this includes source, reservoir extent, connectivity, and differentiability or fingerprinting. CO<sub>2</sub> generated from TSR is chemically related to the source hydrocarbon and its total petroleum system. Noble gas isotope analyses may be another tool in defining extents and tracing migration in total petroleum systems and associated CO<sub>2</sub> systems.

# Noble Gas Geochemistry at the LaBarge Platform, Wyoming, USA: CO<sub>2</sub> Source and Potential Total Petroleum System Investigation Tool

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## Introduction

### Abstract

Initial analyses of noble gas isotopes, major element isotopes, and gas composition data from high carbon dioxide (CO<sub>2</sub>) natural gas samples at the LaBarge Platform, Wyoming, USA, indicate that the CO<sub>2</sub> has a strong crustal signature. This finding is in line with geochemical, mineralogical, and fluid inclusion analyses that suggest that inorganic thermochemical sulfate reduction (TSR) is the source of LaBarge's CO<sub>2</sub>. Isotopes of noble gases released from hydrocarbons during TSR carry the isotopic signature of the air-saturated sea water and crustal environment of the hydrocarbon source rock. Helium isotope ratios reported relative to their concentrations in air ranged from 0.077 to 0.085 (R/R<sub>A</sub>); these values as well as those of neon and argon indicate crustal origin.

LaBarge Platform is the largest source of CO<sub>2</sub> used in enhanced oil recovery (EOR) at oil and gas fields across the northern Rocky Mountains. The field is located in southwestern Wyoming, west of the towns of Big Piney and LaBarge. The field produces natural gas (21% average) and CO<sub>2</sub> (65% average) from the Mississippian-age Madison Limestone. In this initial round of sampling, three gas samples were collected from 14,500 to 16,500 feet of depth at three different well heads.

These results are an initial effort towards describing the total CO<sub>2</sub> system at LaBarge; this includes source, reservoir extent, connectivity, and differentiability or fingerprinting. CO<sub>2</sub> generated from TSR is chemically related to the source hydrocarbon and its total petroleum system. Noble gas isotope analyses may be another tool for defining extents and tracing migration in total petroleum systems and associated CO<sub>2</sub> systems.

### Goals of the study

- 1) To use isotope geochemistry to explore the generation, migration, and trapping history of the gases (CO<sub>2</sub>, CH<sub>4</sub>, He<sub>2</sub>, and H<sub>2</sub>S) at LaBarge.
- 2) To compare the chemistry of the gases at LaBarge to other large CO<sub>2</sub> producing fields in the Rocky Mountains.
- 3) To investigate the possibility of using noble gas isotopes to define a regional extent for the LaBarge total CO<sub>2</sub> system (Brennan and others, 2005) in future sampling plans.



Figure 1. LaBarge Platform location in the Greater Green River Basin (figure from Johnson, 2005).

### LaBarge geology

The LaBarge Platform is located in Sublette County, Wyoming, on the northern end of the Moxa Arch, a 124-mile-long, basement-involved anticline, along the boundary between the Greater Green River Basin and the Wyoming–Idaho–Utah Thrust Belt Province (fig. 1). Hydrocarbons produced from the field fall into two broad classes: sour Paleozoic and sweet Cretaceous petroleum (Becker and Lynds, 2012). The former Paleozoic reservoirs, and in particular the hydrocarbons and gases of the Mississippian Madison Limestone, are the focus of this investigation. The petroleum is sourced from organic materials in the Permian Phosphoria Formation (fig. 2) and has migrated eastward in multiple Paleozoic reservoirs (Sheldon, 1967; Stilwell, 1989, and references therein). LaBarge's Paleozoic reservoirs are of scientific and economic interest as they are a source of significant reserves of CO<sub>2</sub> and helium in addition to natural gas.



Figure 2. Extent of the Permian Phosphoria Formation, the source of Paleozoic oil and gas at LaBarge (figure from Johnson, 2005).

## Results

### LaBarge geochemistry

Gas composition and major element stable isotope data were generated by a commercial laboratory. Sample gas was collected from the well head in 500 ml steel cylinders that were treated for H<sub>2</sub>S bearing gas. Samples for noble gas isotope work were collected from the steel cylinders and transferred into copper tubes by Intertek. Noble gas analyses were performed by Andrew Hunt at the USGS in Denver, Colorado. Sulfur isotope samples were collected from gas in the cylinders using ISOTrap sampling devices.

Sample	Gas Composition and Stable Isotopes								Noble Gas Isotopes							
	N	CO <sub>2</sub>	H <sub>2</sub> S	Methane	δ <sup>13</sup> C Methane	δ <sup>13</sup> C CO <sub>2</sub>	δD Methane	δ <sup>15</sup> N Nitrogen Gas	δ <sup>34</sup> S	<sup>4</sup> He ccSTP/cc (x 10 <sup>-6</sup> )	<sup>20</sup> Ne ccSTP/cc (x 10 <sup>-6</sup> )	<sup>36</sup> Ar ccSTP/cc (x 10 <sup>-6</sup> )	<sup>40</sup> Ar ccSTP/cc (x 10 <sup>-6</sup> )	<sup>84</sup> Kr ccSTP/cc (x 10 <sup>-9</sup> )	<sup>132</sup> Xe ccSTP/cc (x 10 <sup>-9</sup> )	
LaBarge 1	6.154	71.438	2.712	19.689	-43.67	-4.21	-160.5	-0.68	9.7	6992	0.003	0.048	676	6.60	0.317	
LaBarge 2	6.097	70.948	2.519	20.431	-43.8	-4	-161	-0.95	10.3	7280	0.005	0.047	660	6.21	0.339	
LaBarge 3	6.327	65.176	4.89	23.605	-43.77	-3.96	-161.5	-0.94	9.6	7284	0.005	0.049	645	6.90	0.434	
Air										5.240	16.45	31.5	9308	650	23	

Sample	Noble Gas Isotope Ratios															
	CO <sub>2</sub> <sup>2</sup> He	R R <sub>A</sub>	<sup>20</sup> Ne <sup>22</sup> Ne	<sup>21</sup> Ne <sup>22</sup> Ne	<sup>36</sup> Ar <sup>36</sup> Ar	<sup>40</sup> Ar <sup>36</sup> Ar	<sup>84</sup> Kr <sup>84</sup> Kr	<sup>136</sup> Xe <sup>132</sup> Xe	<sup>20</sup> Ne <sup>36</sup> Ar	<sup>4</sup> He <sup>40</sup> Ar*	<sup>4</sup> He <sup>21</sup> Ne*	<sup>4</sup> He <sup>20</sup> Ne (xair)	F <sup>4</sup> He	F <sup>20</sup> Ne	F <sup>84</sup> Kr	F <sup>132</sup> Xe
LaBarge 1	6.66x 10 <sup>6</sup>	0.080	7.32	0.2176	0.175	14227	0.304	0.186	0.069	10.6	82.83	6.675x 10 <sup>6</sup>	8.817x 10 <sup>6</sup>	0.132	6.711	8.957
LaBarge 2	5.90x 10 <sup>6</sup>	0.085	8.82	0.2200	0.176	14085	0.339	0.141	0.117	11.3	61.13	4.143x 10 <sup>6</sup>	9.305x 10 <sup>6</sup>	0.224	6.397	9.707
LaBarge 3	6.07x 10 <sup>6</sup>	0.077	8.33	0.1617	0.181	13044	0.311	0.171	0.105	11.5	87.97	4.382x 10 <sup>6</sup>	8.820x 10 <sup>6</sup>	0.201	6.739	11.779
Air		1.000	9.800	0.0290	0.188	295.5	0.305	0.151	0.522			1.0	1.000	1.000	1.000	1.000

Table 1. Results from geochemical analyses of three gas samples from LaBarge Platform.

## Discussion

### Gas composition

Gas composition (mole %) in the Madison Limestone at LaBarge is approximately 65% CO<sub>2</sub>, 24% CH<sub>4</sub>, 7% N<sub>2</sub>, 3% H<sub>2</sub>S and 0.7% He<sub>2</sub> (table 1) and in line with numbers reported by Stillwell (1989), Johnson (2005), and Huang and others (2007). Small variations in well chemistry were present, however more data is needed to investigate potential trends.

### Stable majors

Delta (δ) <sup>13</sup>C for CO<sub>2</sub> in the samples are approximately -4‰ (table 1) and could be explained by the thermal breakdown or TSR of inorganic carbonate materials in the presence of CH<sub>4</sub> and sulfate. Carbon (δ<sup>13</sup>C = -43‰) and deuterium (δD = -160‰) isotopes ratios in the methane point to thermogenic gas formation. Sulfur isotope ratios (δ<sup>34</sup>S) values in the H<sub>2</sub>S gas of +10‰ corroborate results from King and others (2014), who based on other data, suggest this is evidence of TSR from Mississippian sulfate.

### LaBarge vs. other CO<sub>2</sub> fields

Noble isotope investigations of gas from CO<sub>2</sub>-producing fields in the Northern Rockies are not available in the literature. Studies of fields from the Southern Rockies (Gilfillan and others, 2008) and Merrill and others (unpublished) are available for comparison. As indicated in figures 3–6, LaBarge does not show similar noble gas isotope geochemistry to CO<sub>2</sub>-producing fields in the Southern Rockies. Gilfillan and others (2008) have indicated that CO<sub>2</sub>-rich fields of the Colorado Plateau are associated with a mantle (rather than crustal) source of CO<sub>2</sub>. Karlstrom and others (2014) have also shown the proximity of the southern fields to igneous geology that may have sourced the gas in question. LaBarge, however, is different as it is not associated with any known nearby igneous geology and it also plots more closely to the crustal endmember than the Southern Rockies fields do. However, numerous deep faults could allow for migration of gas from farther and deeper areas.

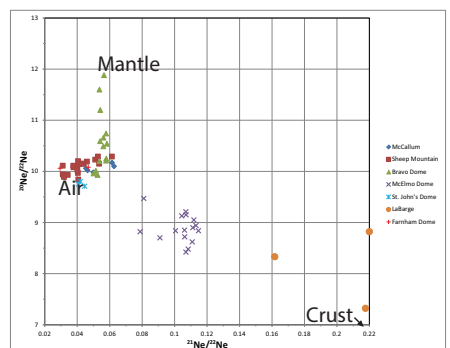


Figure 3. Neon isotope plot for LaBarge and southern Rockies fields.

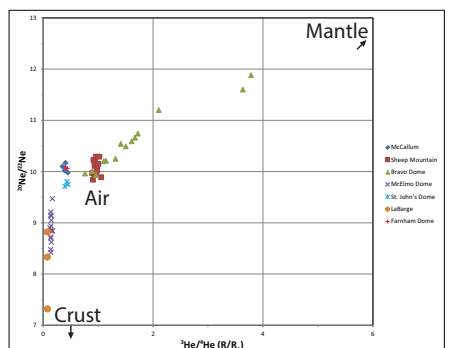


Figure 4. Neon-helium isotope plot for LaBarge and southern Rockies fields.

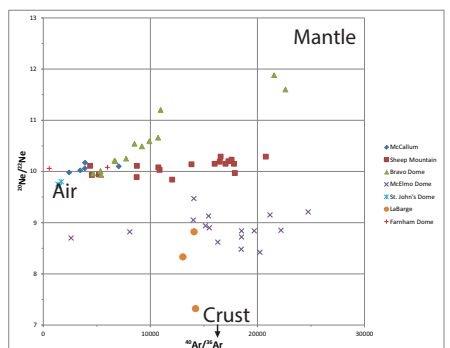


Figure 5. Neon-argon isotope plot for LaBarge and southern Rockies fields.

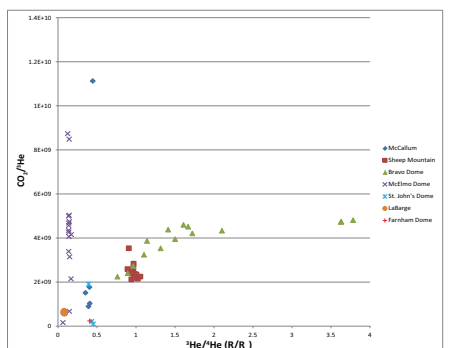


Figure 6. CO<sub>2</sub>-helium isotope plot for LaBarge and southern Rockies fields.

### Phases of fluid movement and noble gas chemistry

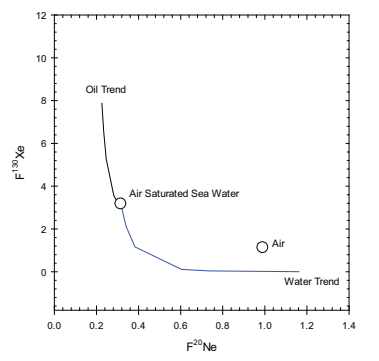


Figure 7. Modelled xenon and neon noble gas isotope chemistry based on Rayleigh fractionation model.

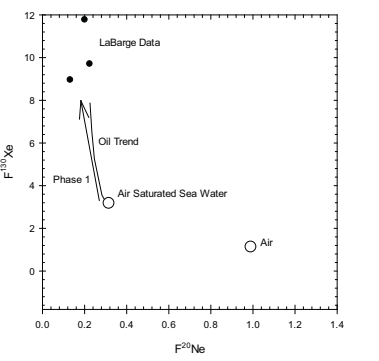


Figure 8. LaBarge xenon and neon phase 1 fractionation.

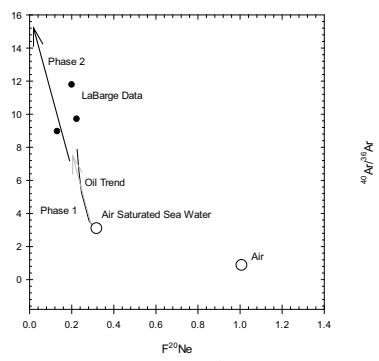


Figure 9. Xenon and neon phase 2 fractionation.

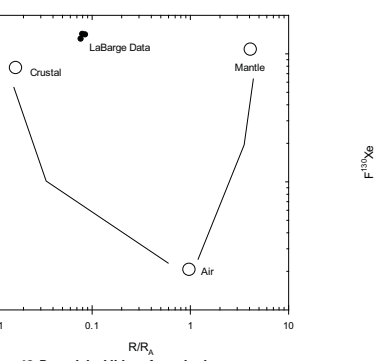


Figure 10. Potential addition of mantle signature.

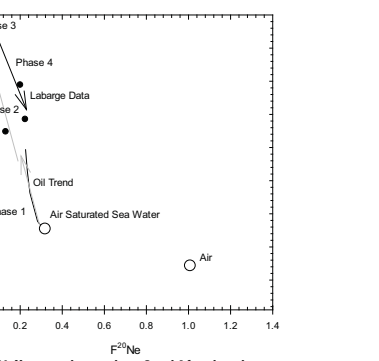


Figure 11. Xenon and neon phase 3 and 4 fractionation.

	Phase 0: Deposition	Phase 1: Oil generation	Phase 2: Oil migration	Phase 3: Oil trapping	Phase 4: Gas generation
Geology	Sediments of the Phosphoria Formation are deposited in a marine and near shore environment across much of today's Northern Rockies (fig. 2).	Oil is generated from the burial of Permian Phosphoria sediments in the early Cretaceous (Sheldon, 1967; Stilwell, 1989, and references therein; Johnson, 2005). Oil moves from Phosphoria to other Paleozoic formations including down section Mississippian Madison Limestone. It is possibly driven there by abnormal pressures during maturation (Johnson, 2005).	Oil migrates to the east upon generation along west-dipping depositional flow units. Differential stacking of sediments during the Jurassic increased the regional dip and further facilitated migration (Johnson, 2005).	Laramide tectonics halted migration as thrust faults and uplifts blocked pathways. At LaBarge, oil became trapped under Moxa Arch structures and a thrust Paleozoic hanging wall. Faults and volcanism during this period may have provided a path and source for mantle-derived gases to enter the LaBarge system (Huang and others, 2007).	Oil begins cracking to gas in the late Cretaceous (Johnson, 2005 and references therein). The gas is partially converted to CO <sub>2</sub> and H <sub>2</sub> S through thermochemical sulfate reduction (TSR) using anhydrite in the Madison Limestone for sulfate (Becker and Lynds, 2012). Either during this phase or a previous one, the system comes into contact with some magmatic gas or fluids where the heat possibly helps drive cracking or TSR.
Geochemistry	Noble isotopes in the pore waters of the shales and carbonates take on the signature of air-saturated sea water (ASSW) (fig. 7).	Noble isotopes in Phosphoria pore waters begin with compositions of ASSW. As oil is generated, heavier nobles, mainly Xe and Kr, are enriched in the oil due to their greater solubility (fig. 8). Lighter nobles, represented by <sup>4</sup> He/ <sup>40</sup> Ar, are enriched in the water relative to the oil.	Migration separated the oil from the pore water and stopped exchange of nobles. This preserved the highly fractionated signature. As the oil migrated, <sup>84</sup> Kr and <sup>132</sup> Xe were probably enriched above levels in the samples (fig. 9). <sup>4</sup> He probably began to increase as the oil took up crustal nobles from the pore water passed during migration.	A continued buildup of crustal-derived nobles from the country rock accumulates in the oil. Lack of interaction with active fluid flow at 16,000 foot depths ends exchange with any atmospheric nobles. Magmatic sources provide a small increase in R/R <sub>A</sub> to elevate the signal from 0.02 to 0.08 and impact neon isotopes in a similar fashion (fig. 10).	Gas formation leads to enrichment in lighter nobles. As all of the oil is converted, though some solid bitumen is left over, most of the original high Xe and Kr signal is transferred to the gas (fig. 11).

## Conclusions

1) Noble isotope geochemistry from LaBarge provides evidence of petroleum generation, migration, trapping, and cracking events that corroborate organic chemistry-based results generated by the USGS for the Phosphoria total petroleum system. This provides a potentially diagnostic isotope signature that can be used to investigate other sources of CO<sub>2</sub> in the region to determine the extent of the resource.

2) In addition to corroboration, the noble gas data indicate that the economic He resource also produced at LaBarge is of predominantly crustal origin coming from the west with the migration of oil in the early Mesozoic. There is, however, also a small magmatic source of He that was probably supplied in the late Cretaceous or early Tertiary from the east.

## Future research

Field work in 2014 includes plans to collect free and dissolved gas samples from thermal springs in Paleozoic formations as well as samples from additional oil and gas wells (fig. 12).

### Overarching questions

- 1) Do all Paleozoic CO<sub>2</sub> reservoirs in the basin have the same isotope signature or are the isotope signatures location specific?
- 2) Are there isotopic fractionation trends across the basin and along migration paths?

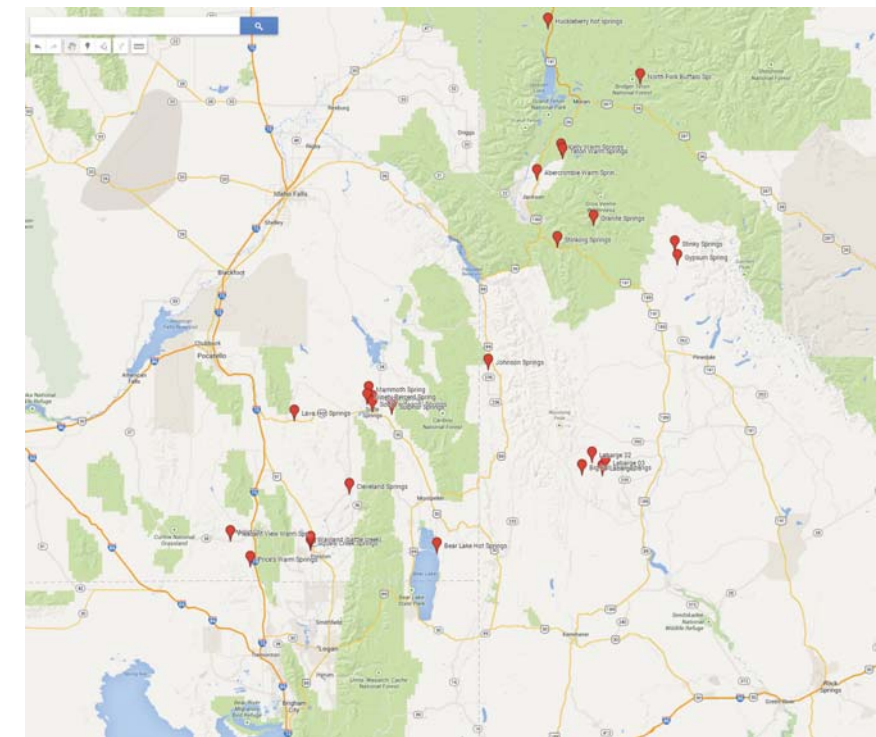


Figure 12. Planned sampling sites for 2014 field work.

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