Isotopic Analysis of Fruitland Formation Coal Bed Carbon Dioxide and Methane

John R. Doughty[*]

Abstract

Radiocarbon is found throughout the geological record, and the confirmation of this hypothesis in the cases investigated in this paper strengthens the young earth creationist paradigm. This research builds upon the work done with coal and carbon dioxide and extends it to the analysis of coal bed methane gas wells. The resulting data indicate that the carbon dioxide and methane gases trapped in the Fruitland Formation are thousands, not millions of years old.

Introduction

This paper provides another piece of evidence in support of the young earth. Those taking an evolutionary position of Earth's history often assume that natural gas, which is presumed to be an old, fossil gas, is carbon-14 "dead." One purpose of this paper is to show that such an assumption is quite false. This work experimentally verifies that significant, detectable carbon-14 (^{14}C) is found in both the CO_2 and CH_4 found in Cretaceous formation coal bed methane (CBM), that is, methane from gas wells drilled into coal beds. A subsequent work will investigate the presence of ^{14}C in deep Ordovician strata natural gas wells in the Permian Basin of Texas. Once again, the presence of the radiocarbon is reasonably explained by the flood deposition of organic material and its subsequent degradation over thousands (not millions) of years.

Background

A review of radiocarbon literature revealed that some accelerator mass spectrometer (AMS) labs use CO_2 gas as ^{14}C free baseline (also called a procedural blank) because it is presumed to be ^{14}C "dead," being derived from fossil gas. However, in all the cases reported, there was ^{14}C present in significant amounts (0.049 to 0.25 percent modern carbon; pMC). Such amounts were presumed to be due to system contamination and were subtracted from samples containing ^{14}C to obtain a "corrected" value. In the search for ^{14}C free procedural blank, Taylor and Southon (2005) used diamonds as targets in the University of California-Irvine AMS device. They obtained mean values over the range of 0.012 to 0.016 pMC, which they then attributed to "ion source crosstalk" rather than being intrinsic to the samples. Earlier, Baumgardner (2005) reported a mean uncorrected value of 0.12 (±0.01) pMC for six diamonds that were combusted in pure oxygen and converted to CO_2 for preparation for the standard analytical technique used by Isotrace AMS Lab at the University of Toronto. Still earlier, Baumgardner et al. (2003) showed ^{14}C to be present in coal. They reported a mean corrected value of 0.247 pMC for coal derived from ten different mines in the USA. The Isotrace Lab subtracted 0.077 pMC from the uncorrected values. The data set included coals from the Eocene, Cretaceous, and Pennsylvanian eras, and the close grouping of these ^{14}C concentrations indicates a single depositional event, the Flood. Therefore, I expected to find significant ^{14}C in both carbon dioxide and methane extracted from the Fruitland Formation coal bed in northwest New Mexico.

This work presents the ^{14}C and other isotopic data obtained from samples taken from three wells in the central portion of the formation area known as the Fruitland Fairway, a region known for high initial well pressures. The wells had an average production depth of 2700 feet.

---

[*] John R. Doughty, Ph.D., 532 Calle de Los Hijos NW, Albuquerque, NM 87114-2039, Tel: 505-890-5358, Email: ydmaster@swcp.com

Accepted for publication: May 8, 2006

The formation is from the Cretaceous period, and is conventionally dated as 73 to 78 million years (Ma) (Fassett, 2000). The trapping mechanism, confinement caused by hydrostatic pressure, is totally different from conventional natural gas wells. The methane is maintained in an adsorbed state in micropores (<0.5 nm diameter) within the coal matrix. The reservoir permeability is provided by fracture-like networks known as *cleats*. The cleat porosity is on the order of 0.5% to 2%. The low porosity restricts subsurface water transport (Snyder et al., 2003). When the coal bed is penetrated and water is pumped out, the hydrostatic pressure is reduced and the methane desorbs and flows out with the water.

Schoell et al. (2001) made a case based on an analysis of the stable isotope, carbon-13 ($\delta^{13}C$), for the subsurface conversion of CO_2 to methane simultaneously with a bacterial oxidative removal of C2+ hydrocarbons (alkanes). Seewald et al. (1998) have shown experimentally that CO_2 is produced when hydrocarbons are in the presence of water and mineral catalysts. Some analysts have expressed concern about the validity of ^{14}C based analyses due to possible contamination of the source material by recent meteoric groundwater containing dissolved CO_2. However, Snyder et al. (2003) and Riese et al. (2005) performed analyses of Fruitland formation coal bed brines using both the stable water-derived isotopes, oxygen ($\delta^{18}O$) and deuterium (δD), and the accompanying radioactive isotopes of iodine and chlorine (^{129}I and ^{36}Cl). They concluded that the waters are predominantly connate, that is, water trapped at the time of formation, and have not undergone extensive migration since deposition because the formation is heterogeneous.

This conclusion was based in part by the analysis of formation waters that indicated recent water flows only at the edges of the formation. Other models for the Fruitland basin assumed a significant subsurface flow through a presumed homogeneous formation. If there was indeed recent penetration of meteoric water, then it should be evidenced by both stable oxygen isotope and the radiocarbon data. The stable isotope data of Riese et al. (2005) followed the global meteoric water line (GMWL) rather well, but that data doesn't of itself provide an age estimate. They presented minimum ages derived from ^{129}I and ^{36}Cl that commonly differed by an order of magnitude with an average radioiodine age of 32 Ma and average radiochlorine age of 1.5 Ma. I expected to see ^{14}C values for both CO_2 and CH_4 obtained from Fruitland formation coal bed methane gas wells close to the uncorrected mean value of 0.286 pMC (0.21 pMC corrected) based on 12 data points obtained by Baumgardner et al. (2003) for somewhat similar Cretaceous coals. Note that a pMC value of 0.21 translates to a maximum age of 50 thousand years.

Methods and Materials

Gas Sample Preparation

The sampling apparatus is identical to that described in my previous article (Doughty, 2005) with the exception that the 10cc. closed-end sample cylinders have been replaced by double-ended 10cc. cylinders. This allowed the sample gas to flow through the system and vent it to the atmosphere. The exit valves attached to the sample cylinders are closed while the system vent valve is still open, thus providing a higher assurance for an uncontaminated sample. When the source pressure was greater than 10 psi, all valves were closed and then the system vent valve was carefully opened to reduce the internal pressure to 10 psi or below, since the AMS lab prefers samples to be less than 10 psi.

The same preparation procedure was used as in the previous work (Doughty, 2005) where 18 fill and purge cycles using high purity helium were used to eliminate any residual atmospheric CO_2 gas from the system, including all the sample cylinders. The system is then filled with 30 psi of high purity helium before it is taken to the field. However, in this work, more than one well was sampled during the field visit. Consequently, after the first sample set was taken, the first set of two sample cylinders were removed from the system. After verifying that all valves were closed, the two 10cc cylinders were removed from the system, the valve ends capped and placed in a box for transport to the University of Arizona AMS lab. The next set of sample cylinders were then attached to the system. Since a portion of the system had been opened to the atmosphere (and thus to possible contamination due to atmospheric CO_2), it had to be purged. However, only 17cc of the sampling system was exposed to the air. It was an easy matter to run a minimum of 15 purge-and-fill cycles at the low gas well pressures found in the Fruitland Formation wells. Additionally, the vent valve is opened for approximately one minute prior to opening the sample cylinder valves and is left open while the gas is also flowing through the sample cylinder. Thus, a more than ample volume exchange is provided to assure a pure sample. An example of one of the well sites where samples were taken is shown in Figure 1.

Figure 1. Sampling Fruitland Formation CBM Gas Well Vanderslice 101, August 5, 2005.

Table I. Fruitland Formation Well Gas Characteristics

Well sampled	Pressure psi	Temp. °F	CO_2, %	CH_4 %	N_2 %
Scott Com 291	9	50	7.4	92.2	0.065
Page 101R	4	50	25.2	73.3	0.271
Vanderslice 101	30	50	14.3	85.1	0.062

AMS Analysis of Gas

At the University of Arizona AMS lab, all gas samples were attached to an analysis system line, and pumped down the line before opening the sample cylinder valve. A small portion of the sample was taken for stable isotope analyses using a conventional mass spectrometer. Approximately one milligram of CO_2 was extracted and run through a cold trap to remove any traces of water. Then, downstream of the water trap, the CO_2 was trapped by a mild cryogenic cold finger. The remaining methane was collected and later passed over CuO in a furnace to convert it to CO_2 for subsequent processing into graphite targets for the AMS device. It took approximately three months to process three well sample sets (six sample cylinders). One sample set, the Page 101R well gas, was rerun because of an anomaly (a lab procedural error) yielding an abnormal result (much too high) for the methane ^{14}C value. Fortunately, there was ample gas available for the rerun and the "AM" result compared closely with the second companion "BM" sample, as it should.

Results

The physical characteristics of the well gases sampled at the wellhead of the three Fruitland Fairway wells are shown in Table I. All wells had a water separator located upstream of the sampling port. Any residual traces of water were

Table II. Fruitland Formation CBM Gas Well Sample Isotope Values

Well & Sample # *Suffix*: C=CO_2, M=CH_4	Date analyzed	Mass mg	$\delta^{13}C$, CO_2	$\delta^{13}C$, CH_4	α, $CO_2 \leftrightarrow CH_4$	$\delta^{18}O$, CO_2	$^{14}C/C$, pMC uncorrected	$^{14}C/C$, pMC corrected
Scott Com 291, #1AC	11/02/05	0.1	14.94			***7.99***	***10.51±0.2***	***7.56±0.92***
Scott Com 291, #1AM	11/02/05	1.16		-44.52	1.06223		1.18±0.03	0.90±0.1
Scott Com 291, #1BC	11/02/05	0.11	15.52			17.04	5.86±0.08	3.18±0.86
Scott Com 291, #1BM	11/02/05	1.15		-44.52	1.06284		1.05±0.03	0.77±0.14
Page 101R, #2AC	12/08/05	0.21	18.64			12.75	1.21±0.05	0.96
Page 101R, #2AM	01/24/06	0.58		-43.33	1.06478		0.62±0.03	0.46
Page 101R, #2BC	01/12/06	0.37	17.79			12.225	1.33±0.05	1.09
Page 101R, #2BM	01/24/06	0.99		-43.84	1.06446		0.79±0.03	0.59
Vanderslice 101, #3AC	11/03/05	0.2	17.13			16.72	2.69±0.16	1.18±0.51
Vanderslice 101, #3AM	11/03/05	1.15		-43.73	1.06364		0.37±0.02	0.27
Vanderslice 101, #3BC	11/03/05	0.2	17.15			16.685	2.23±0.1	0.99
Vanderslice 101, #3BM	11/08/05	1.21		-43.83	1.06378		0.28±0.03	0.21

Notes:

1. Scott Com 291 #1AC values (in ***bold italics***) were not included in mean value calculations. Sample contaminated in lab processing.
2. Stable isotope mean values: $\delta^{13}C(CO_2) = 16.86‰$ pdb, $\delta^{13}C(CH_4) = -43.96‰$ pdb, $\delta^{18}O = 15.1‰$ smow, Fractionation factor: $\alpha(CO_2 \leftrightarrow CH_4) = 1.06362$.
3. $^{14}C/C$ corrected mean values: $^{14}C/C(CO_2) = 1.48$ pMC, $^{14}C/C(CH_4) = 0.53$ pMC. $\Delta^{14}C/C = 0.95$ pMC.
4. All wells were sampled on 8/05/05.

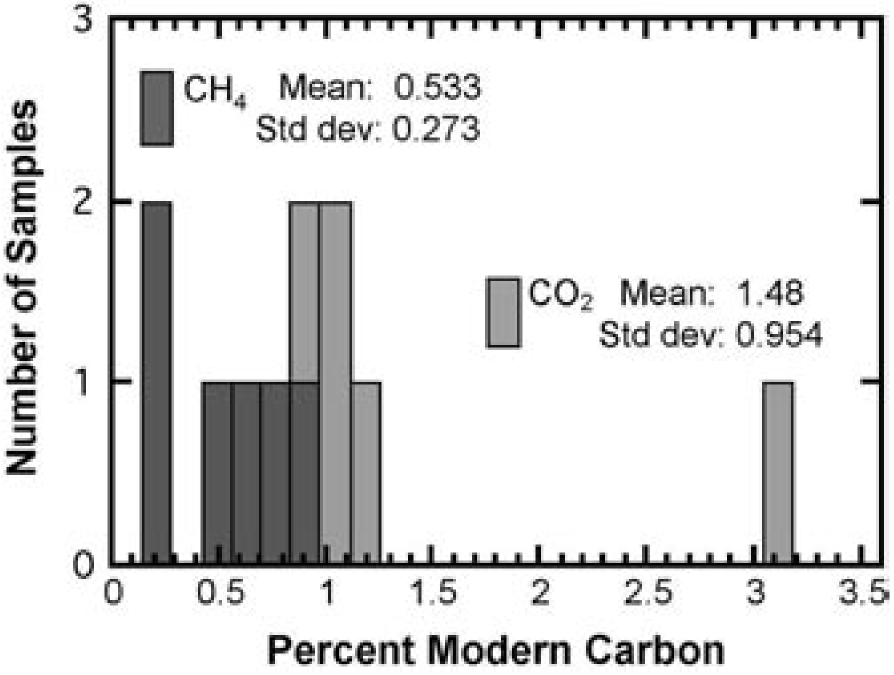

Figure 2. Distribution of ^{14}C values for the three CBM gas wells

removed at the University of Arizona AMS lab as noted above. All samples were taken from producing (flowing) wells. Two identical samples were taken at each well site. The samples were analyzed for their isotopic content of $\delta^{13}C$, $\delta^{18}O$, and ^{14}C. The results are shown in Table II. The stable isotope mean values are $\delta^{13}C(CO_2) = 16.86‰$ pdb, $\delta^{13}C(CH_4) = -43.96‰$ pdb, $\delta^{18}O(CO_2) = 15.1‰$ smow where "pdb" and "smow" are the reference standards to which the data are compared. The "pdb" standard , PeeDee Formation Belemnite, for carbon-13 is defined as 0‰, and the "smow" reference for oxygen-18 is standard mean ocean water, where $\delta^{18}O = 0‰$. The mean values for the radiocarbon results for the CO_2 are $^{14}C/C$(uncorrected) = 2.76 pMC and $^{14}C/C$(corrected) = 1.48 pMC and for the CH_4 $^{14}C/C$(uncorrected) = 0.77 pMC and $^{14}C/C$(corrected) = 0.53 pMC. The corrected values for $^{14}C/C$ (CO_2) and $^{14}C/C$ (CH_4) are shown in histogram format in Figure 2.

Discussion

First, I note that my initial hypothesis was not substantiated. The $^{14}C/C$ ratios for the carbon dioxide are a factor of three to four greater than those for the methane. They are also substantially greater than the $^{14}C/C$ mean value, 0.361 pMC, obtained from carbon dioxide gas wells (Doughty, 2005). It is assumed that the CO_2 and CH_4 were produced at essentially the same time via reactions between the coal, water, minerals, and microbes under pressure and slightly elevated temperature. The results suggest that there was some contamination of the original carbon dioxide by dissolved CO_2 brought into the coal by meteoric groundwater sometime after the deposition of the Fruitland Formation.

The isotopic mean values for $\delta^{13}C$ (CO_2) and $\delta^{13}C$ (CH_4) agree closely as expected with those of Schoell et al. (2001) who found $\delta^{13}C$ (CO_2) = 16.0‰ and $\delta^{13}C$ (CH_4) = -43.8‰. Their mean value of the fractionation factor, α ($CO_2 \leftrightarrow CH_4$), for the $\delta^{13}C$ is 1.0625, which is essentially the same as that of this work, 1.0632. Using the equation of Bottinga given in Faure and Mensing (2005, p. 775), this value of 1.0625 results in a calculated temperature of 332°K (59°C) for the formation at a time when fractionation took place. Such a temperature is conducive to microbial action. Therefore, the view of Schoell et al. (2001) that the CH_4 was produced by methanogenesis and the CO_2 was produced by bacterial oxidation of hydrocarbons is reasonable.

The $\delta^{18}O$ and ^{14}C data for the Fruitland Fairway coal bed methane gas samples did produce some unexpected results. First, the Scott Com well sample #1AC is deemed spurious because both $\delta^{18}O$ and $^{14}C/C$ values (shown in bold print in Table II) were abnormally high when compared to the other data, especially considering the fact that the Scott Com #1BC values were obtained from the same sample gas. In other words, the Scott Com #1AC $\delta^{18}O$ value should have been 17 ($\pm$1.0) and the pMC value 3.2 ($\pm$1.0). Consequently, the $\delta^{18}O$ and $^{14}C/C$ values for the Scott Com sample #1AC are not included in the mean value calculations for $\delta^{18}O$ and $^{14}C/C$. Note that the remaining $^{14}C/C$ values for CO_2 are higher than the corresponding $^{14}C/C$ values for CH_4 from the same well as shown in Table II. Note that the mean value for $\delta^{18}O$ (CO_2) is 15.1‰ SMOW, which places it well within the usual data range for sedimentary rocks, yet the data thus far suggests an additional source of ^{14}C in the carbon dioxide.

A good cross-check on the data is to calculate the $\delta^{18}O(H_2O)$ values based on the $\delta^{18}O(CO_2)$ results. The issue in doing such a calculation is the availability of a fractionation factor, α, for CO_2 gas to liquid H_20. Faure & Mensing (2005) give one for atmospheric CO_2 at 19°C as 1.04247. However, as noted above, the fractionation temperature for CO_2 and CH_4 gas is calculated to be 59°C. Consequently, I have taken the $\delta^{18}O$ values for three wells where the resident

Table III. Calculated $\delta^{18}O(H_2O)$ values compared with $^{14}C/C(CO_2)$

Sample #	$\delta^{18}O(CO_2)$ ‰ SMOW	$\delta^{18}O(H_2O)$‰ SMOW	$^{14}C/C$ (CO_2) pMC corrected
FF#1B	17.04	-8.94	3.18 (+0.86)
FF#2A	12.75	-13.13	0.96
FF#2B	12.225	-13.64	1.09
FF#3A	16.72	-9.26	1.18 (+0.51)
FF#3B	16.685	-9.29	0.99

Note: $\delta^{18}O(H_2O)$ mean value = -10.85‰ SMOW.
$^{14}C/C$ (CO_2) mean value = 1.48 pMC.

CO_2 was in contact with water as given in my previous paper (Doughty, 2005). The mean value for the $\delta^{18}O(CO_2)$ is 26.222‰ SMOW. The CO_2 gas to liquid H_20 fractionation factor, $\alpha(CO_{2g} \leftrightarrow H_2O_l)$, for CO_2 in contact with water is given by the following equation:

$$\alpha\,(CO_{2g} \leftrightarrow H_2O_l) = \frac{\delta^{18}O\,(CO_2)\,g + 1000}{\delta^{18}O(H_2O)_l + 1000}$$

By definition $\delta^{18}O(H_2O)_l$ equals zero for the SMOW standard. Therefore, $\alpha(CO_{2g} \leftrightarrow H_2O_l) = 1.02622$. The $\delta^{18}O(H_2O)$ can then be computed from the $\delta^{18}O(CO_2)$ results given in Table II. The working equation is as follows:

$$\delta^{18}O(H_2O) = \frac{\delta^{18}O(CO_2) - 26.22}{1.02622}$$

The results are shown in Table III where, as noted above, the $\delta^{18}O(H_2O)$ value for the Scott Com well sample #1AC is not included in calculating $\delta^{18}O(H_2O)$ SMOW mean value. The resulting mean value is -10.85‰ SMOW, which agrees closely with the mean value of -10.1‰ SMOW for 112 production wells in the Fruitland field (Riese et al., 2005). The usual data range of $\delta^{18}O(H_2O)$ SMOW for meteoric water is 0‰ to -25‰.

Conclusions

It is noteworthy that $^{14}C/C$ values for the Vanderslice 101 #3AM and #3BM methane results (0.21 and 0.27 pMC) are in very close agreement with the corrected mean value of 0.21 pMC for Cretaceous coals. Thus, the maximum conventional age for the area of the Fruitland Formation where the sampled wells are located is 49,770 years.

I conclude that the FF#1A sample was contaminated in the processing at the AMS lab. That is shown by both the high $\delta^{18}O(H_2O)$ value and the high $^{14}C/C$ value, which are twice that of the FF#1B sample, which itself is quite high. Again, it is the same gas. Another reasonable conclusion is that the emplaced derivative CO_2 was subsequently slightly contaminated by somewhat younger dissolved CO_2 that was present in meteoric water that penetrated the coal bed formation shortly after its deposition, probably at the time of the Laramide uplift. Otherwise, the $^{14}C/C$ values for CO_2 and CH_4 should be identical, which they are not. On the other hand, if the coal bed had been penetrated by significant amounts of meteoric water in very recent geologic times as presumed in earlier hydrodynamic models of the San Juan Basin, then the $^{14}C/C$ values for CO_2 would have been substantially higher than those realized in this work.

Another primary finding is that there is indeed significant, detectable ^{14}C in both the CO_2 and CH_4; i.e., the fossil gas is not carbon-14 "dead." One could argue that the CH_4 was manufactured via methanogenesis from waterborne "contaminated" CO_2. However, the CO_2 is thought to be produced by the bacterial oxidative removal of C2+ hydrocarbons (alkanes), whose origin is contemporaneous with the coal. The fact that the $^{14}C/C$ values for CO_2 are consistently greater than those for CH_4 by only 0.95 pMC as shown in Figure 2 suggests that any such "contamination" is restricted to the CO_2 and is indeed slight.

The isotopic analysis presented in this paper, using $\delta^{18}O(H_2O)$ and $^{14}C/C(CO_2)$ values contained in the CBM gas, can be applied to other CBM fields to verify whether or not they do have a continuous flow of recent meteoric subsurface water throughout the formation. Such information is important to petroleum geologists in the prediction and modeling of the production potential of CBM fields.

Finally, the evidence presented in this paper strongly suggests that both gases had a common source (coal) thousands—not millions—of years ago, that was laid down in the aftermath (Cretaceous period) of the Genesis Flood.

Acknowledgements

I thank the Creation Research Society's Research Committee for the grant that financed this work. I also wish to thank Dr. Russ Humphreys for continual encouragement in the course of this research. Thanks are also in order to Mr. John Poore and Mr. Lee Murphy of Burlington Resources, Inc. of Farmington, New Mexico for their assistance in obtaining the gas samples. Finally, I thank my wife, Jeanette, for her encour-

agement and accompaniment throughout this work.

"Call to me and I will answer you and tell you great and unsearchable things you do not know." (Jeremiah 33:3)

References

Baumgardner, J.R., D.R. Humphreys, A.A. Snelling, and S.A. Austin. 2003. Measurable ^{14}C in fossilized organic materials: confirming the young earth creation-flood model. In Ivey, R.L. Jr. (editor), *Proceedings of the Fifth International Conference on Creationism*, pp.127–142. Creation Science Fellowship, Pittsburgh, PA.

Baumgardner, J.R. 2005. ^{14}C Evidence for a recent global flood and a young earth. In, Vardiman, L., A.A. Snelling and E.F. Chaffin (editors), *Radioisotopes and the Age of the Earth, Vol. II*, pp.587–630. Institute for Creation Research, Santee, CA and Creation Research Society, Chino Valley, AZ.

Doughty, J.R. 2005. CO_2 gas well effluent analysis. *Creation Research Society Quarterly* 42:95–103.

Fassett, J.E. 2000. Geology and coal resources of the Upper Cretaceous Fruitland Formation, San Juan Basin area, New Mexico and Colorado. In Kirschbaum, M.A., L.N.R. Roberts and L.R.H. Biewick (editors), *Geologic assessment of coal in the Colorado Plateau: Arizona, Colorado, New Mexico, and Utah.* U.S. Geological Survey Professional Paper 1625-B, Chapter Q.

Faure, G., and T. M. Mensing. 2005. *Isotopes: Principles and Applications* (3rd edition). John Wiley & Sons, Inc., Hoboken, NJ.

Riese, W.C.,W.L. Pelzmann, and G.T. Snyder. 2005. New Insights on the hydrocarbon system of the Fruitland Formation coal beds, northern San Juan Basin, Colorado and New Mexico, USA. In Warwick, P.D. (editor), *Coal Systems Analysis*, pp. 73–111. Geological Society of America Special Paper 387.

Schoell, M., K. Muehlenbachs, D.D. Coleman, S. Thibodeaux, L. Walters, and A. Martini. 2001. Natural sites of bioconversion of CO_2 and hydrocarbons in the subsurface: San Juan Basin and Michigan Basin. Americn Association of Petroleum Geologists paper 8867, AAPG Annual Meeting 2001.

Seewald, J., B.C. Benitez-Nelson, and J.K. Whelan. 1998. Laboratory and theoretical constraints on the generation and composition of natural gas. *Geochimica et Cosmochimica Acta*, 62(9): 1599–1617.

Snyder, G.T., W.C. Riese, S. Franks, U. Fehn, W.L. Pelzmann, A.W. Gorody, and J.E. Moran. 2003. Origin and history of waters associated with coalbed methane: ^{129}I, ^{36}Cl, and stable isotope results from the Fruitland Formation, CO and NM. *Geochimica et Cosmochimica Acta*, 67(23): 4529–4544.

Taylor, R.E., and J.R. Southon. 2005. Use of Natural Diamonds to Monitor ^{14}C AMS Instrument Backgrounds. Poster Paper presented at The 10th International Conference on Accelerator Mass Spectrometry (September 5–10, 2005), Berkeley, CA.