Deep Wells—Deep Time?

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Abstract

Radiocarbon is found throughout the geological record. The confirmation of this hypothesis in the cases investigated in this paper strengthens the young earth creationist paradigm. This research builds upon carbon isotope analyses done on diamonds, coal, carbon dioxide gas wells and coal bed methane (CBM) gas wells where significant amounts of radiocarbon were found, and extends it to the analysis of deep natural gas wells. The resulting radiocarbon data, given as percent of modern carbon (pMC), provide a strong indication that both the carbon dioxide (0.58 pMC) and methane (0.32 pMC) gases found in the Ordovician strata of two Valverde Basin natural gas fields are thousands, not hundreds of millions years old.

Introduction

This paper is the third in a series that show that significant detectable amounts of radiocarbon (^{14}C) can confidently be expected to be found in carbon dioxide and natural gas wells. The basis for such confidence stems from earlier experimental work by Baumgardner (2005) on diamonds and coal, and my recent experimental work on CO_2 and CBM gas wells (Doughty, 2005; 2006). This work experimentally verifies that carbon-14 is indeed present in the gases derived from very deep, Ordovician era, Ellenburger dolostone strata in two natural gas fields in the southwest Texas Valverde basin. Since carbon-14 has such a short half life of only 5,730 years, finding it in natural gas wells provides additional compelling evidence for the young earth position following a straightforward interpretation of the Holy Bible and in particular the Book of Genesis.

Background

A few years ago, Bernard Marty (2001) wrote an introductory article in *Nature* commenting on the work of Ballentine et al. (2001) regarding the age of CO_2 found in deep Valverde Basin natural gas wells. Marty noted that it appeared that gases such as CO_2 and CH_4 can be stored for much longer than has generally been assumed, specifically 280 to 300 million years. This is of particular interest to those concerned about global warming and the sequestration of carbon dioxide. Supposedly the CO_2 entered the Valverde Basin at the time of the Marathon Thrust uplift 300 million years ago. The hydrocarbon generation began 20 million years later and entered the fields at that time. If that is a correct conclusion, then there should not be any radiocarbon present in either the CO_2 or the CH_4. Also, if radiocarbon is found, the percent of modern carbon (pMC) value for CO_2 should be smaller (thereby older) than that for the CH_4 under the presumption that it preceded the methane. If the values are essentially the same, then one could conclude that they originated at about the same time and not too long ago.

Ballentine et al. (2001) conducted an extensive sampling (26 wells) of the Brown-Bassett and JM fields in southwest Texas. They noted that the gas temperature was uniform across the fields. Further, the values for the stable carbon-13 isotope for both CO_2 and CH_4 were within a narrow range varying primarily with the CO_2 concentration. Mean values for the 26 wells were $\delta^{13}C(CO_2) = -2.92‰$ pdb and $\delta^{13}C(CH_4) = -37.40‰$ pdb. The resulting fractionation factor, α, is 1.0358, which results in an equilibration temperature of 181°C (Faure

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and Mensing, 2005). However, Ballentine et al. (2001) wrote that "inorganic isotopic equilibrium between CO_2 and CH_4 does not occur on geologic timescales at temperatures less than 200ºC." They referenced the experimental work by Sackett and Chung (1979), which indicated no reaction between essentially dry inorganic CO_2 and CH_4 and therefore no isotopic carbon exchange at temperatures up to 500ºC. Therefore, Ballentine et al. (2001) logically concluded that the CO_2 and CH_4 found in the deep Valverde Basin wells had separate sources, the mantle for the CO_2 and the crust for the CH_4. While they did not mention the presence of water in the well gas in their paper, they did so in an earlier conference (Ballentine et al., 2000). Also, the *Atlas of Major Texas Gas Reservoirs* (Kosters et al., 1989) indicated that the Brown Bassett field had a water saturation of 35% and the JM field value was 20%. This is important because Seewald (2001, 2003) and Seewald et. al. (1998) have shown experimentally that the presence of water and catalytic minerals results in the rapid production of CO_2 from heavier hydrocarbons through decarboxylation (an organic reaction sequence). Long geologic time wasn't a factor in the kinetics, but rather there is a greater dependence on thermodynamic equilibrium constraints. Thus, the proper combination of pressure and temperature in the presence of water and minerals could rapidly produce the natural gas and organic alteration products (CO_2, etc.). If this was indeed the case for the Valverde Basin fields, then one would expect the carbon-14 values for CO_2 and CH_4 to be fairly close together, the primary hypothesis that motivated this work.

Figure 1: Sampling the Mitchell 5 #1 well.

Methods and Materials

The sampling apparatus and procedures used to sample and reduce the data are identical to that described previously (Doughty, 2006). The sampling apparatus can be seen in Figure 1, a photo taken at the Mitchell 5 #1 well site.

Results

As a result of a review of the work of Ballentine et al. (2001), three wells were selected to be sampled. The selection was based on sampling the wells with the highest, lowest, and an intermediate value for $\delta^{13}C(CO_2)$ and $\delta^{13}C(CH_4)$ as shown in Table I. Note that the production depth ranges from 2.5 to 2.8 miles

Table I. CO_2/CH_4 gas wells selected for sampling.

Well Sampled	Field	$\delta^{13}C(CO_2)$,‰ pdb	$\delta^{13}C(CH_4)$,‰ pdb	Production depth, ft.
Turk A No. 1	Brown-Bassett	-2.77	-37.68	13,718 to 14,697
Mitchell 5 No. 1	JM	-2.84	-37.57	13,736 to 14,490
Mitchell No. 3	JM	-3.06	-37.26	12,934 to 13,726

Notes:
1. Stable isotope data from Ballentine et al. (2001).
2. The mean value for $\delta^{13}C(CH_4)$ obtained earlier by Stahl and Carey (1975) was -38.14‰ pdb for gas wells penetrating the Ellenburger Formation across a major portion of the Permian Basin.

Table II. Well Gas Characteristics.

Field	Well sampled	Pressure psi	Temp. °F	CO_2, %	CH_4 %	N_2 %
Brown-Bassett	Turk A No.1	205	68	55.8	43.5	0.48
JM	Mitchell 5 No.1	200	96	53.1	46.3	0.36
JM	Mitchell No.3	202	100	21.5	77.7	0.54

Note: The data from the above fields are based on analyses performed in October and December 2005 by Manley Gas Testing, Inc. of Odessa, TX.

down. The well gas physical characteristics are shown in Table II. All wells had a water separator located upstream of the sampling port. Any residual traces of water were removed at the University of Arizona AMS lab. 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 III.

The stable isotope mean values are $\delta^{13}C(CO_2)$ = -2.69‰ pdb, $\delta^{13}C(CH_4)$ = -37.93‰ pdb, $\delta^{18}O(CO_2)$ = 25.74‰ 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 stable isotope ranges are shown in Figures 3 and 4 where they are compared with values for other sources.

The most important result is the radiocarbon data. The mean values for the carbon-14 results for the CO_2 are $^{14}C/C$(uncorrected) = 1.168 pMC and $^{14}C/C$(corrected) = 0.58 pMC and for the CH_4 $^{14}C/C$(uncorrected) = 0.578 pMC and $^{14}C/C$(corrected) = 0.32 pMC. Uncorrected values are given for future use and comparison since AMS labs do not have universally accepted procedures for the application of correction factors; i.e., the correction is lab specific. The corrected values for $^{14}C/C$ (CO_2) and $^{14}C/C$ (CH_4) are shown in histogram format in Figure 2.

Discussion

The JM and Brown-Bassett fields have a faulted anticline type of trap. The trap is supposed to be *tight*; i.e., no leakage into or out of the formation. The 300 million year date for the CO_2 emplacement was derived primarily by the best estimate of the geological community as to the timing of the Marathon uplift and secondarily from analysis of the CO_2 / ^3He ratio (Ballentine, Burgess, and Marty, 2002). The scenario is major faulting would allow juvenile magmatic CO_2 from the mantle to flow into the older Ordovician (440–500 million years) Ellenburger Formation. If that was truly the case, then the carbon-14 signature of the CO_2 flowing into the formation should have been in the range of 0.1 to 0.2 pMC, the same range as that for subsurface Precambrian diamonds (Baumgardner, 2005). Therefore, the carbon-14 CO_2 signature should have a lower value than the flood-deposited organics that produced the natural gas (primarily methane and ethane) found

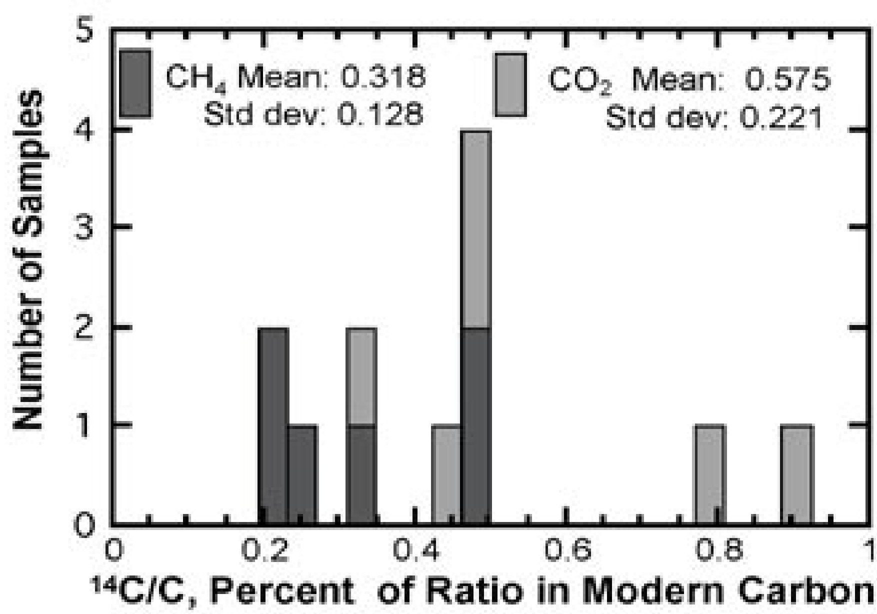

Figure 2. Distribution of 14C values for three Valverde Basin Natural Gas Wells.

Table III. Valverde Basin Ellenburger Formation Natural Gas Well Sample Isotope Values.

Well & Sample # *Suffix*: C=CO_2, M=CH_4	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
Turk A No.1, #1C	0.791	-2.548			32.714	0.73±0.03	0.34±0.13
Turk A No.1, #1M	0.605		-38.451	1.0373		0.97±0.08	0.48±0.12
Turk A No.1, #2C	0.801	-2.528			32.535	0.83±0.05	0.45±0.13
Turk A No.1, #2M	0.578		-39.348	1.0383		0.59±0.03	0.31±0.10
Mitchell No.3, #3C	0.282	-2.893			22.770	1.84±0.06	0.77±0.35
Mitchell No.3, #3M	1.10		-37.472	1.0359		0.27±0.02	<0.20
Mitchell No.3, #4C	0.277	-2.791			22.760	1.66±0.28	0.92±0.30
Mitchell No.3, #4M	0.937		-37.368	1.0355		0.34±0.03	<0.20
Mitchell 5 No.1, #5C	0.627	-2.583			21.851	0.98±0.05	0.49±0.17
Mitchell 5 No.1, #5M	0.514		-37.303	1.0361		0.76±0.04	0.47±0.11
Mitchell 5 No.1, #6C	0.628	-2.584			21.793	0.97±0.04	0.48±0.16
Mitchell 5 No.1, #6M	0.514		-37.627	1.0364		0.54±0.04	0.25±0.11

Notes:

1. Stable isotope mean values: $\delta^{13}C(CO_2)$ = -2.69‰ pdb, $\delta^{13}C(CH_4)$ = -37.93‰ pdb, $\delta^{18}O$ = 25.74‰ smow, fractionation factor: $\alpha(CO_2 \leftrightarrow CH_4)$ = 1.0366.

2. $^{14}C/C$ corrected mean values: $^{14}C/C(CO_2)$ = 0.58 pMC, $^{14}C/C(CH_4)$ = 0.32 pMC.

3. All wells were sampled on 2/28/06.

in today's wells. The data from this work show that such is not the case, but rather the opposite.

The most noteworthy result is that the *fossil* methane has significantly detectable carbon-14. Further, the magnitude is basically the same for methane and CO_2 within statistical bounds in both the Turk A #1 and the Mitchell 5 No.1 wells. That would suggest a common origin, most likely at the time of the Flood. Also notable is that the oldest (49,920 years) and youngest (37,660 years) conventional age for the two gases occurred in the same well, the Mitchell No. 3 well, suggesting some possible infiltration of groundwater containing some dissolved atmospheric CO_2 subsequent to the deposition of the Ellenburger Formation.

The data shown in Table III fit well within the previously reported range for carbon dioxide gas wells ($^{14}C/C$ mean value of 0.361 pMC) and coal bed methane gas wells ($^{14}C/C$ mean values from 0.53 to 1.48 pMC) as well as that from the overall Phanerozoic era ($^{14}C/C$ range from 0.2 to 0.65 pMC) as shown in Baumgardner (2005).

The stable isotopes, $\delta^{13}C(CO_2)$ and $\delta^{18}O(CO_2)$ fall in the range of sedimentary rocks and carbonates as shown in Figures 3 and 4 respectively, but they do not point to a physical age of material. I was unable to find any data in the literature concerning $\delta^{18}O$ for any Permian Basin fields. However, the data from this work fits well with CO_2 gas wells and sedimentary rock values. The two Mitchell wells compare closely with CO_2 gas wells ($\delta^{18}O$ data mean value of 23.44‰ smow).

From the data for $\delta^{13}C(CO_2)$ and $\delta^{13}C(CH_4)$, the mean value for the fractionation factor, α, is 1.03660. That results in an equilibration temperature of 175°C or about 6°C cooler since Ballentine et al. (2001) took their samples, the effect of six years or so of pumping.

Conclusions

Once again, fossil gas is not carbon-14 dead. Thus, the age of the gases is on the order of thousands, not millions of years. The mean value for the methane-derived carbon-14 is 0.32 pMC, which is in reasonable accord with the mean value for Pennsylvanian coals (0.27 pMC) reported by Baumgardner

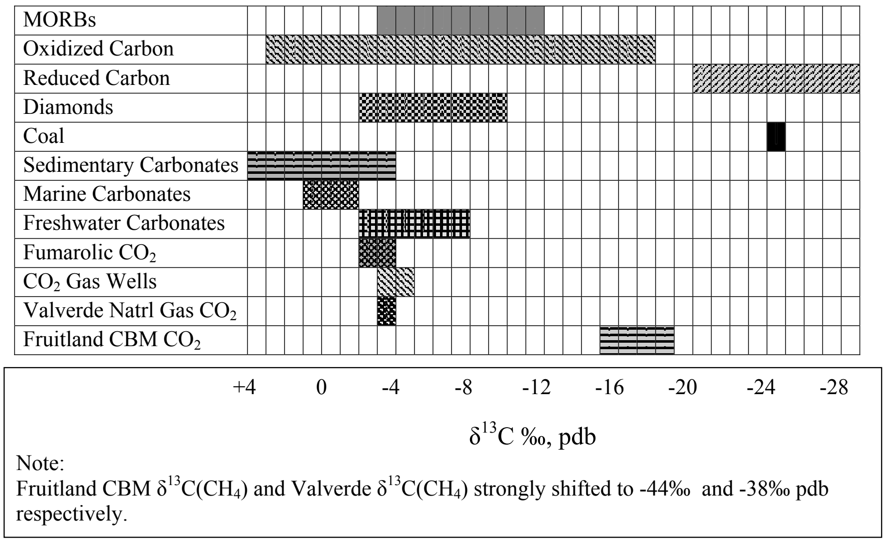

Figure 3. Range of Carbon-13 values for various rocks and gases.

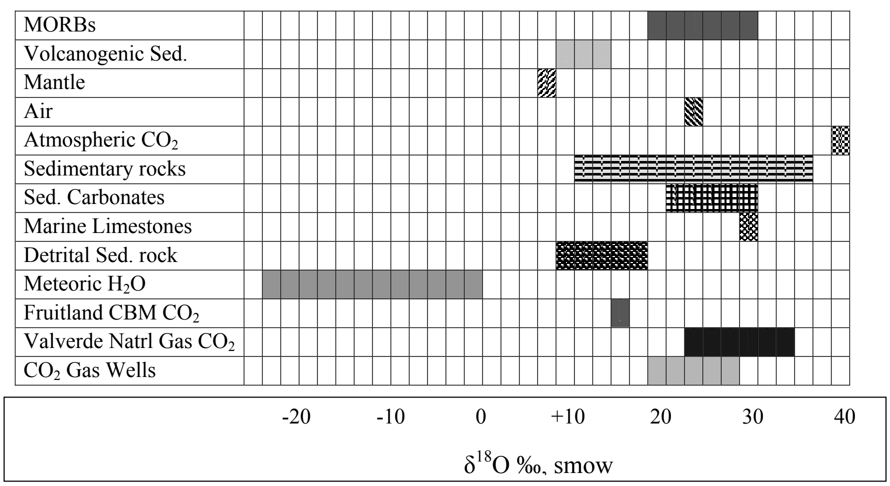

Figure 4. Range of Oxygen-18 values for various rocks and gases.

(2005). The $^{14}C/C$ mean value for CO_2, 0.58 pMC, is substantially less than that for coal bed methane (CBM) wells (Doughty, 2006), which have large amounts of water (mean value of 1.48 pMC). When compared to the relatively dry CO_2 gas well data (mean value 0.361 pMC) (Doughty, 2005), the deep well Valverde Basin gas shows only slight groundwater contamination influence. Carbon-14 can be a valuable diagnostic tool for isotopic analyses of other natural gas wells.

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Finally, I thank my wife, Jeanette, who accompanied me into the hinterlands. "*Far from where people dwell he cuts a shaft, in places forgotten by the foot of man*" (Job 28:4a).

References

Ballentine, C.J., R. Burgess, and B. Marty. 2002. Tracing fluid origin, transport and interaction in the crust. In Porcelli, D., C.J. Ballentine, and R. Weiler (editors), *Noble Gases in Geochemistry and Cosmochemistry*, Reviews in Mineralogy and Geochemistry, Vol. 47, pp. 573–576. Mineralogical Society of America, Washington, DC.

Ballentine, C.J., M. Schoell, D. Coleman, and B.A. Cain. 2000. Identifying the mechanism and character of magmatic CO_2 emplacement into sedimentary structures I: CO_2 / $^3He/\delta^{13}C(CO_2)$ variation in CO_2 rich Permian Basin natural gases. *Journal of Conference Abtracts* Vol. 5(2), 182. Goldschmidt 2000 Conference, September 3–8, 2000. Cambridge Publications, Oxford, UK.

Ballentine, C.J., M. Schoell, D. Coleman, and B.A. Cain. 2001. 300-Myr-old magmatic CO_2 in natural gas reservoirs of the west Texas Permian Basin. *Nature* 409:327–331.

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.

Doughty, J.R. 2005. CO_2 gas well effluent analysis. *CRSQ* 42:93–101.

Doughty, J.R. 2006. Isotopic analysis of Fruitland Formation coal bed carbon dioxide and methane. *CRSQ* 43:105–110.

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

Kosters, E.C., D.G. Bebout, S.J. Seni, C.M. Garrett Jr., L.F. Brown Jr., H.S. Hamlin, S.P. Dutton, S.C. Ruppel, R.J. Finley, and Noel Taylor. 1989. *Atlas of Major Texas Gas Reservoirs*. Bureau of Economic Geology, Publ. AT0001, Austin, TX.

Marty, B. 2001. New prospects for old gas. *Nature* 409:293–295.

Sackett,W.M., and H.M. Chung. 1979. Experimental confirmation of the lack of carbon isotope exchange between methane and carbon oxides at high temperatures. *Geochimica et Cosmochimica Acta* 43:273–276.

Seewald, J.S. 2001. Aqueous geochemistry of low molecular weight hydrocarbons at elevated temperatures and pressures: Constraints from mineral buffered laboratory experiments. *Geochimica et Cosmochimica Acta* 65(10):1641–1664.

Seewald, J.S. 2003. Organic-inorganic interactions in petroleum-producing sedimentary basins. *Nature* 426:327–333.

Seewald, J.S., 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.

Stahl, W.J., and B.D. Carey. 1975. Source-rock identification by isotope analyses of natural gases from fields in the Val-verde and Delaware Basins, West Texas. *Chemical Geology*, 16:257.

Book Review

Creation or Evolution—Does It Matter?

by Robert and Elizabeth Ridlon

Jordan Dill Associates, Bloomington, IN 2005, 195 pages, $12.00.

The Ridlons are part-time science faculty at Southwestern Illinois College. They frequently speak on creation science, and this book is a compilation of their seminar topics. The Ridlons present a very readable generalization of origins data, concentrating on biology and geology.

Little actually appears in the book concerning the title. This is unfortunate, since the many serious implications of evolution are rich areas to explore. The book instead ridicules evolution as the baseless story that we came from "slime" (p. 3). As an intricate, counterfeit theory of origins, evolution theory is not quite that simple.

The book has some embarrassing problems that can be corrected in future editions. The words *lightning* (p. 90) and *Becquerel* (p. 127) are misspelled. The authors state that new species do not arise, in conflict with observed speciation (p. 20). The authors describe a comet that struck Siberia in 1918 and doubled the carbon-14 content of the atmosphere. This event will be news to astronomers. Perhaps the authors are referring to the Tunguska Event of 1908, which may possibly have been a comet.

This book gives a clear presentation of the gospel. It would be a delight to hear the Ridlons speak while using this book as a guide.

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