



$\delta^{15}\text{N}$ and Non-Carbonate $\delta^{13}\text{C}$ Values for Two Petroleum Source Rock Reference Materials and a Marine Sediment Reference Material

Kristin O. Dennen¹, Craig A. Johnson², Marshall L. Otter³, Steven R. Silva⁴, and Gregory A. Wandless⁵

¹Eastern Energy Resources Team, U.S. Geological Survey, Reston, Virginia

²USGS Crustal Imaging and Characterization Team Stable Isotope Laboratory, Geology Discipline, Denver, Colorado

³Stable Isotope Laboratory, The Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts

⁴USGS Menlo Park Stable Isotope and Tritium Labs, Water Resources Discipline, Menlo Park, California

⁵USGS Reston Stable Isotope Laboratory, Geology Discipline, Reston, Virginia

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Open-File Report 2006-1071

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Suggested citation: Dennen, K. O., Johnson, C.A., Otter, M.A., Silva, S. R., Wandless, G.A, .2006, $\delta^{15}\text{N}$ and Non-carbonate $\delta^{13}\text{C}$ Values for Two Petroleum Source Rock Reference Materials and a Marine Sediment Reference Material: U. S. Geological Survey Open File Report 2006-1071.

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Contents

Abstract.....	1
Introduction	2
Methods	2
Terminology	2
Sample Preparation.....	2
Results	3
Statistical Analysis of Results	3
Discussion	4
Conclusions	5
References	6
Acknowledgements	7
Alphabetical list of contributing laboratories.....	7

List of Figures

1. Histograms and descriptive statistics for carbon analyses.
2. Histograms and descriptive statistics for nitrogen analyses.
3. Kolomogorov-Smirnov Comparison Cumulative Fraction Plots.

List of Tables

1. Reference materials used for isotopic and elemental calibrations.
2. Analytical results for individual laboratories.
3. Descriptive statistics.
4. Test for normality of data distribution for analyses from laboratories A and B.
5. Suggested isotopic and elemental values.

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³Stable Isotope Laboratory, The Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts

⁴USGS Menlo Park Stable Isotope and Tritium Labs, Water Resources Discipline, Menlo Park, California

⁵USGS Reston Stable Isotope Laboratory, Geology Discipline, Reston, Virginia

Abstract

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values have been determined for SDO-1, (Devonian Ohio Shale) and SGR-1 (Eocene Green River Shale), petroleum source rock reference materials and PACS-2, a modern marine sediment reference material. Analyses were performed after acid fumigation so that the data refer to non-carbonate carbon ($\delta^{13}\text{C}_{\text{ncc}}$ and $\text{Wt \% C}_{\text{ncc}}$). Acid fumigation had no apparent effect on nitrogen isotopic analyses. The results are averages of determinations from four analytical laboratories and are as follows:

Identification	$\delta^{13}\text{C}$ (‰)	Wt% C_{ncc}	$\delta^{15}\text{N}$ (‰)	Wt% N
SDO-1	-30.0 ± 0.1	9.64 ± 0.19	-0.8 ± 0.3	0.36 ± 0.01
SGR-1	-29.3 ± 0.1	24.01 ± 0.38	17.4 ± 0.4	0.81 ± 0.02
PACS-2	-23.3 ± 0.2	3.17 ± 0.06	4.9 ± 0.1	0.27 ± 0.01

Data are reported as Mean \pm the 95% confidence interval. Nitrogen isotope data are reported relative to atmospheric nitrogen. Carbon isotope data are reported relative to Vienna Peedee Belemnite (VPDB).

Introduction

Samples of United States Geological Survey (USGS) Certified Reference Materials USGS Devonian Ohio Shale (SDO-1), and USGS Eocene Green River Shale (SGR-1), and National Research Council Canada (NRCC) Certified Marine Sediment Reference Material (PACS-2), were sent for analysis to four separate analytical laboratories as blind controls for organic rich sedimentary rock samples being analyzed from the Red Dog mine area in Alaska. The samples were analyzed for stable isotopes of carbon ($\delta^{13}\text{C}_{\text{ncc}}$) and nitrogen ($\delta^{15}\text{N}$), percent non-carbonate carbon (Wt % C_{ncc}) and percent nitrogen (Wt % N).

SDO-1, collected from the Huron Member of the Ohio Shale, near Morehead, Kentucky (Kane and others, 1990), and SGR-1, collected from the Mahogany zone of the Green River Formation (Gladney and Roelandts, 1987) are petroleum source rocks used as reference materials for chemical analyses of sedimentary rocks. PACS-2 is modern marine sediment collected from the Esquimalt, British Columbia harbor (NRCC Institute for National Measurement Reference materials, 2000).

The results presented in this study are, with the exceptions noted below, the first published for these reference materials. There are published information values for the elemental concentrations of “organic” carbon (Wt % C_{org} measured range is 8.98 - 10.4) and nitrogen (Wt % N_{tot} 0.347 with SD 0.043) only for SDO-1. (Kane and others, 1990) The suggested values presented here should be considered “information values” as defined by the NRCC Institute for National Measurement Reference materials (2000) and should be useful for the analysis of ^{13}C , ^{15}N , C and N in organic material in sedimentary rocks.

Methods

Terminology

Isotope ratio measurements are calculated by the formula:

$$\delta \text{ (in } \text{‰}) = (R_x / R_s - 1) \times 1000$$

where R denotes the ratio of the heavy to light isotope (e.g., $^{15}\text{N}/^{14}\text{N}$), and R_x and R_s are the ratios in the sample and standard, respectively. Nitrogen isotope data are reported relative to atmospheric nitrogen. Carbon isotope data are reported relative to Vienna Peedee Belemnite (VPDB).

The term “non-carbonate carbon” (C_{ncc}), referring to carbon isotopic ($\delta^{13}\text{C}_{\text{ncc}}$) and elemental values (Wt. % C_{ncc}) determined on acid fumigated samples, is used in this paper because acid fumigation is assumed to remove carbonate carbon. Any carbon remaining in the sedimentary organic matter or samples after acid fumigation is assumed to be “non-carbonate”, that is, reduced forms of carbon, including graphite.

Sample Preparation

The laboratories participating in this study are designated Lab A, Lab B, Lab C, and Lab D. (An alphabetical list of the laboratories is provided after the

Acknowledgments section. However the letter designation does not correspond to a laboratory's position on the list.) Each laboratory analyzed the samples according to their own protocols. Information on reference materials used for calibration is shown in Table 1, according to the recommendations of Coplen (1996).

The author followed the acid fumigation procedure of Harris and others (2001) to prepare the samples at the USGS in Reston, Virginia. Before weighing, the samples were dried overnight in an oven at 60° C, stored in a desiccator and allowed to cool to room temperature. All samples for any particular reference material came from the same bottle, which was thoroughly mixed before each weighing. Samples were weighed on a micro-balance not to exceed 20 μ moles organic carbon in silver foil cups. While three of the four laboratories determined all analyses on one sample, Lab D requested separate samples for nitrogen and carbon analysis. These samples were weighed to provide 5 μ moles of nitrogen in tin foil cups and did not undergo HCl fumigation.

The samples (with the exception noted above) were fumigated with hydrochloric acid (HCl) to remove carbonate carbon. Numbered plastic trays holding the silver foil cups of weighed samples were seated in glass chambers with approximately 100 ml of concentrated (12.1 N) HCl contained in beakers at the bottom. The chambers were sealed and samples were exposed to the acid fumes for 48 hours. After fumigation, the sample trays were removed and dried overnight at 60° C. The foil cups were then sealed and crushed to a spherical shape for analysis.

The author also prepared working calibration reference materials at the USGS in Reston, Virginia, from International Reference Materials (IRM) USGS40 and USGS41 (Qi and others, 2003), for Lab A and Lab B. Samples of 600 - 750 μ g were weighed on a micro-balance into silver foil cups and fumigated as described above. The laboratories were provided with reference material volumes and calculated estimates of elemental carbon and nitrogen content.

Results

Analytical results from the four laboratories are shown in Table 2. The data were combined and spreadsheet functions were used to describe basic statistics and determine confidence intervals. The distributions of $\delta^{13}\text{C}_{\text{ncc}}$, $\delta^{15}\text{N}$, Wt % C_{ncc} , Wt. % N are shown as histograms with descriptive statistics in Figures 1 and 2. Lab D's contributions to the combined data sets for $\delta^{15}\text{N}$ and Wt. % N are labeled on Figure 2 in order to determine the effect of acid fumigation on nitrogen values. Descriptive statistics for the combined data are summarized in Table 4. Suggested values are shown in Table 5.

Statistical Analysis of Results

Differences in laboratory analytical procedures can be a problem in comparing light stable isotope ratio measurements from several laboratories (Coplen and others, 1983). In an attempt to identify any source of variability in the results among the laboratories, the distributions of the results were analyzed statistically. Lab A and Lab B used the same calibration reference materials, IRM USGS40 and IRM USGS41 (See Table 1) prepared in the same way, as described above. Also, results from Lab A and Lab

B had enough numbers (≥ 10) for statistical tests (Lab C and D received and reported on only one set of duplicate samples), so these two sets of analyses were considered good candidates for statistical examination and comparison. The results for a test for normality of the distributions are shown in Table 3.

Because most of the data sets were not normally distributed, the Kolmogorov-Smirnoff (K-S) test was chosen to compare the sets of data from Lab A and Lab B. This test determines whether or not two sets of data belong to the same population. (Davis, 1973) It requires neither large numbers of data nor normally distributed data, but it also gives no information about the sources of variation among and between data sets (compared to analysis of variance techniques which require large numbers of values and normal distributions). The College of St. Benedict/St. John's University, Minnesota on-line calculator was used to do calculations for the tests¹. The results are shown in Figure 3.

Discussion

Except for the $\delta^{13}\text{C}$ values for SDO-1 in the K-S comparison test between Labs A and B (See Figure 3), the results from the two laboratories are considered to be statistically different. Lab A's sets of values are normally distributed except for $\delta^{15}\text{N}$ (Table 3). Lab A did not report $\delta^{15}\text{N}$ values for SDO-1 and SGR-1, nor did they report enough Wt % N values for a statistical test for these two materials. The fact that Lab A's reported $\delta^{15}\text{N}$ values are not normally distributed and that there are no reported $\delta^{15}\text{N}$ values for two of the reference materials or enough Wt% N values for these reference materials for a statistical analysis indicates bias in the analysis for isotopic and elemental nitrogen from Lab A. According to Lab A, the amount of nitrogen in the aliquots of SDO-1 and SGR-1 was too small to give reliable $\delta^{15}\text{N}$ values. This could easily account for the bias in the analysis for $\delta^{15}\text{N}$, but it does not account for the differences in the carbon values between Lab A and Lab B.

None of Lab B's sets of analyses are normally distributed except for $\delta^{15}\text{N}$. (Table 3) During the year in which the samples were analyzed, Lab B replaced the detector on their mass spectrometer with one much more sensitive to carbon. This may be a factor in the biased distribution of Lab B's analyses for carbon and can account for some of the differences between the two laboratories' carbon analyses.

Lab A randomized the order in which the samples were run. Lab B ran triplicate samples one after the other, with standard reference materials inserted after every five unknowns. The difference in sample order protocol would require different drift correction procedures. Some of the variation is probably due to differences in correction procedures for drift and blanks like those described for nitrogen by Böhlke and Coplen (1995).

Another factor in the range of values, illustrated in Figures 1 and 2, and Table 2, could be sample inhomogeneity. SGR-1, SDO-1 and PACS-2 are all complex, naturally occurring materials with varying ranges of elemental carbon and nitrogen. They are not

¹ http://www.physics.csbsju.edu/stats/KS-test.n.plot_form.html (accessed 3/22/2006)

as homogeneous as chemically simple, synthetic reference materials, constructed to have ideal analytical ranges for several analytes. Maximum sample volume for isotopic analysis is limited by the size of the entrance into the combustion chamber of the analytical instrument. Getting a representative sample of heterogeneous material in the limited volume required can be very difficult. This can be remedied in part, by analyzing multiple samples, which has the effect of broadening the range of values, and narrowing the confidence limits.

Analyzing separately for carbon and nitrogen eliminates difficulties encountered when there are large differences in the concentrations of carbon and nitrogen in one sample. Sample volumes can be calculated and weighed specifically for either carbon or nitrogen and the calibration range can be simplified.

According to Harris and others (2001), fumigating sedimentary organic material in acid can change the nitrogen isotopic value, but not significantly. Because samples for both Lab A and Lab B were fumigated, fumigation can not explain the difference in these sets of data. Lab D analyzed $\delta^{15}\text{N}$ and elemental nitrogen separately from carbon on samples that were not acid fumigated. There is no discernable pattern in the placement of Lab D's contributions on the histograms for $\delta^{15}\text{N}$ and elemental nitrogen (Figure 2), which implies that bias in acid fumigation had no effect on $\delta^{15}\text{N}$ and Wt. %N determinations for SDO-1, SGR-1 and PACS-2.

The confidence intervals for the $\delta^{13}\text{C}$ values reported in Table 5 are close to the range of those reported in other interlaboratory comparisons, for example, in Stichler (1995) where the 95% confidence intervals for $\delta^{13}\text{C}$ range from 0.025 to 0.150. The 95 % confidence intervals for $\delta^{15}\text{N}$ reported here are similar to the range (0.186 to 0.473) for reference materials in Gonfiantini and others (1995). The elemental values for SDO-1 compare favorably to the published information values for nitrogen and "organic" carbon.

Conclusions

This report establishes SDO-1, (Devonian Ohio Shale) and SGR-1 (Eocene Green River Shale), petroleum source rock reference materials and PACS-2, a modern marine sediment reference material as a set of reference materials useful for analysis of ^{13}C , ^{15}N , C and N in organic material in sedimentary rocks.

Acid fumigation of samples to remove carbonate carbon affected neither $\delta^{15}\text{N}$ values nor Wt. %N for these reference materials. Thus although some change in $\delta^{15}\text{N}$ values has been shown for soil samples, such shifts are not characteristic of all rock types.

Stichler and others (1995) recommend adopting and documenting common data reduction procedures to increase the precision of interlaboratory comparison of materials. Obtaining formal certified values for these and other geologic reference materials will require standardization of analytical protocols, analytical blank determinations and data reduction procedures among participating laboratories. This should probably include separate analysis for carbon and nitrogen isotopes and elemental concentrations.

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Acknowledgements

Haiping Qi of the USGS Reston Stable Isotope Laboratory provided samples of the new International Reference Materials USGS40 and USGS41 and as a reviewer, greatly improved the manuscript with her suggestions. Reviewer Steve Wilson of the USGS Central Mineral Resources Team also provided helpful comments. Tyler Coplen of the USGS Reston Stable Isotope Laboratory provided guidance on isotopic procedures and reporting guidelines. Lawrence Drew of the USGS Eastern Mineral Resources Team made sure that the use of statistical tests was appropriate.

Alphabetical list of contributing laboratories

Stable Isotope Laboratory, The Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts, <http://ecosystems.mbl.edu/silab>

USGS Crustal Imaging and Characterization Team Stable Isotope Laboratory, Geology Discipline, Denver, Colorado

USGS Menlo Park Stable Isotope and Tritium Labs, Water Resources Discipline, Menlo Park, California

USGS Reston Stable Isotope Laboratory, Geology Discipline, Reston, Virginia.
<http://isotopes.usgs.gov>

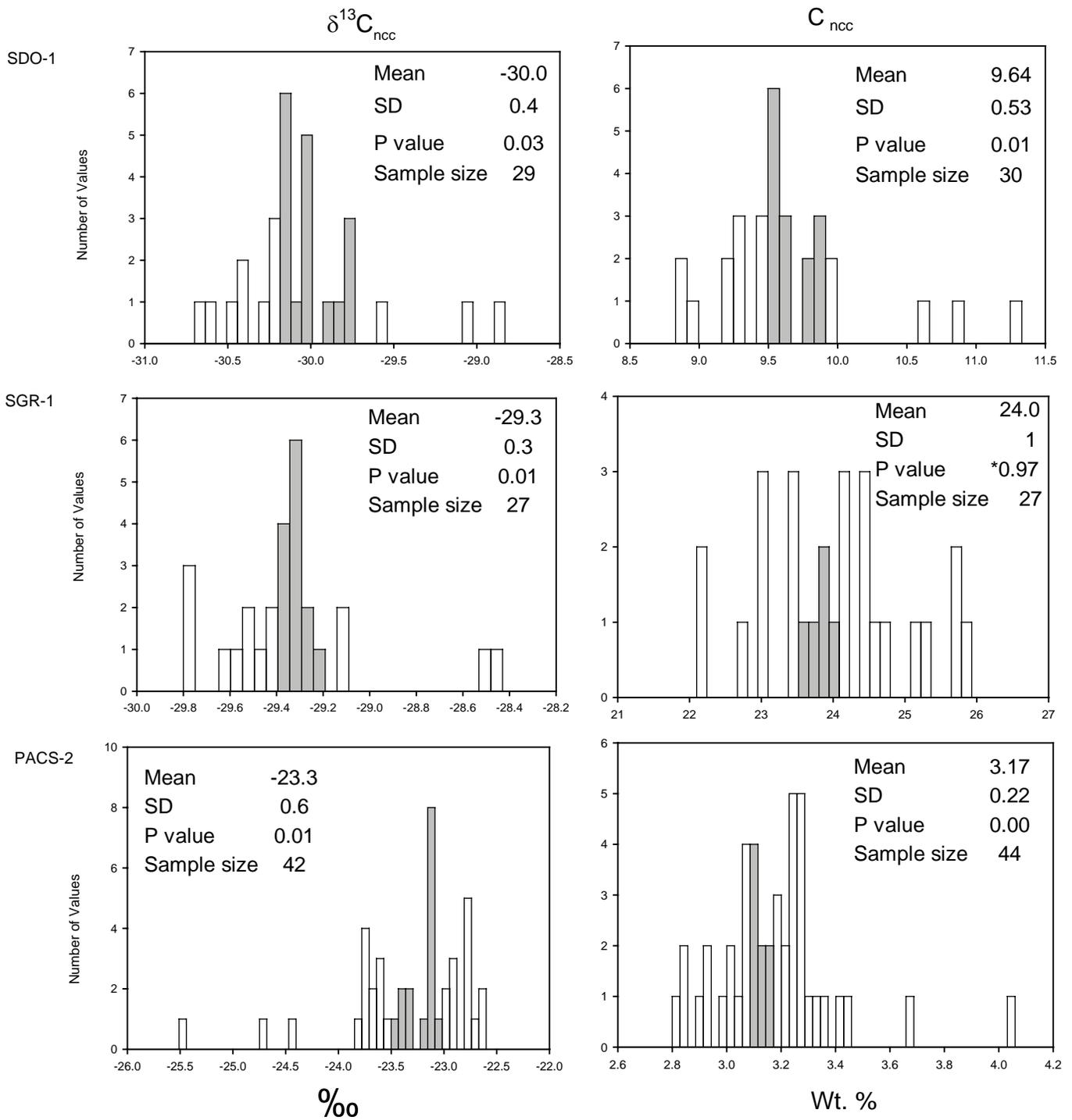


Figure 1. Histograms and descriptive statistics for carbon isotopic and elemental results of combined data sets. The 95% confidence interval about the mean is shown in shaded bars. *P value is large enough to consider the distribution to be normal. SD is standard deviation. Sample size is the number of results used to calculate the mean.

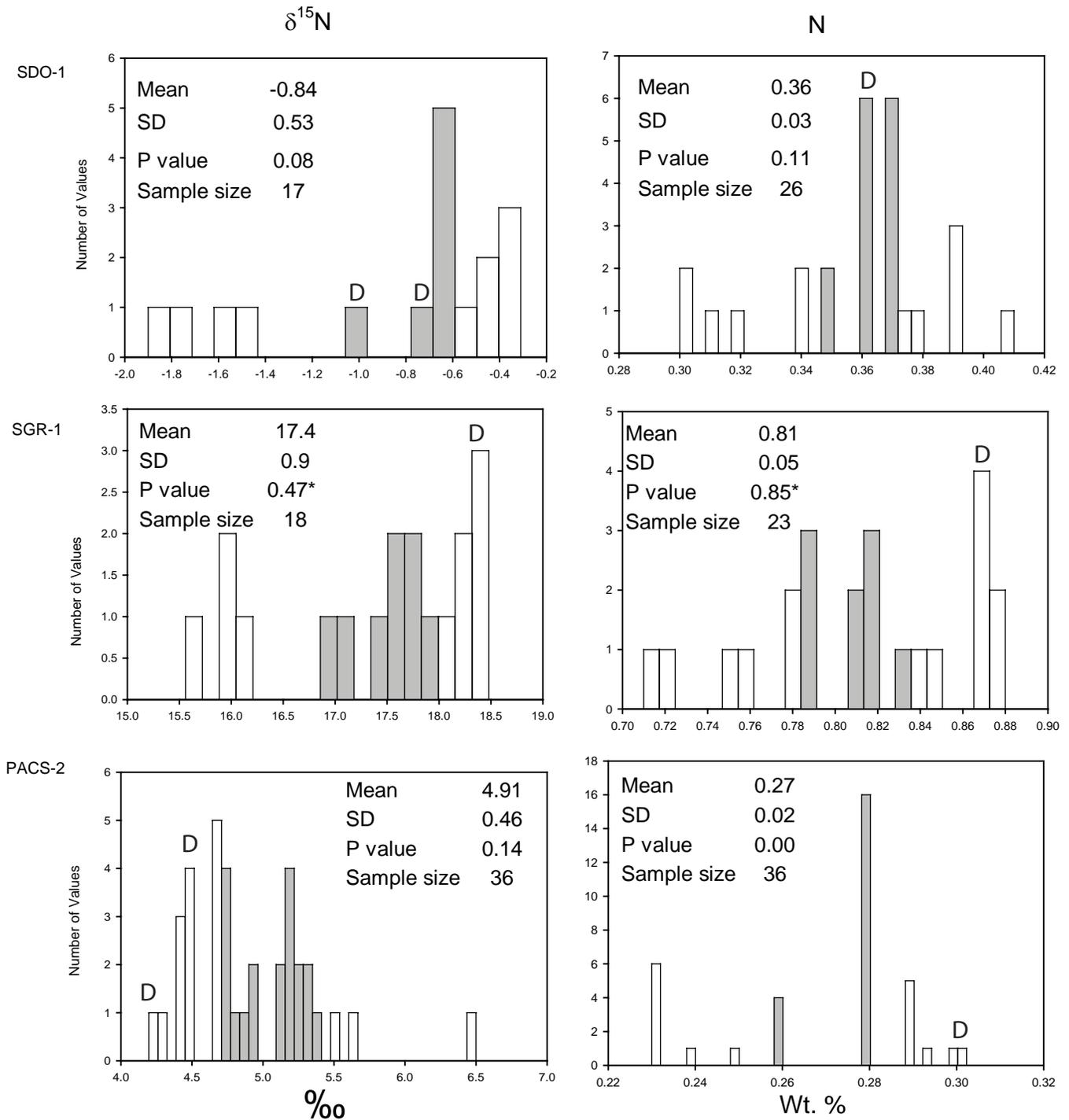


Figure 2. Histograms and descriptive statistics of combined data sets for nitrogen analyses. The 95% confidence interval about the mean is shown in shaded bars. *P value is large enough to consider the distribution to be normal. SD is standard deviation. Sample size is the number of analyses used to calculate the mean. The positions of Lab D's results are labelled and the lack of a pattern of Lab D's results within the group suggests that acid fumigation had no effect on nitrogen isotopic and elemental analyses. (Lab D analyzed duplicate samples.)

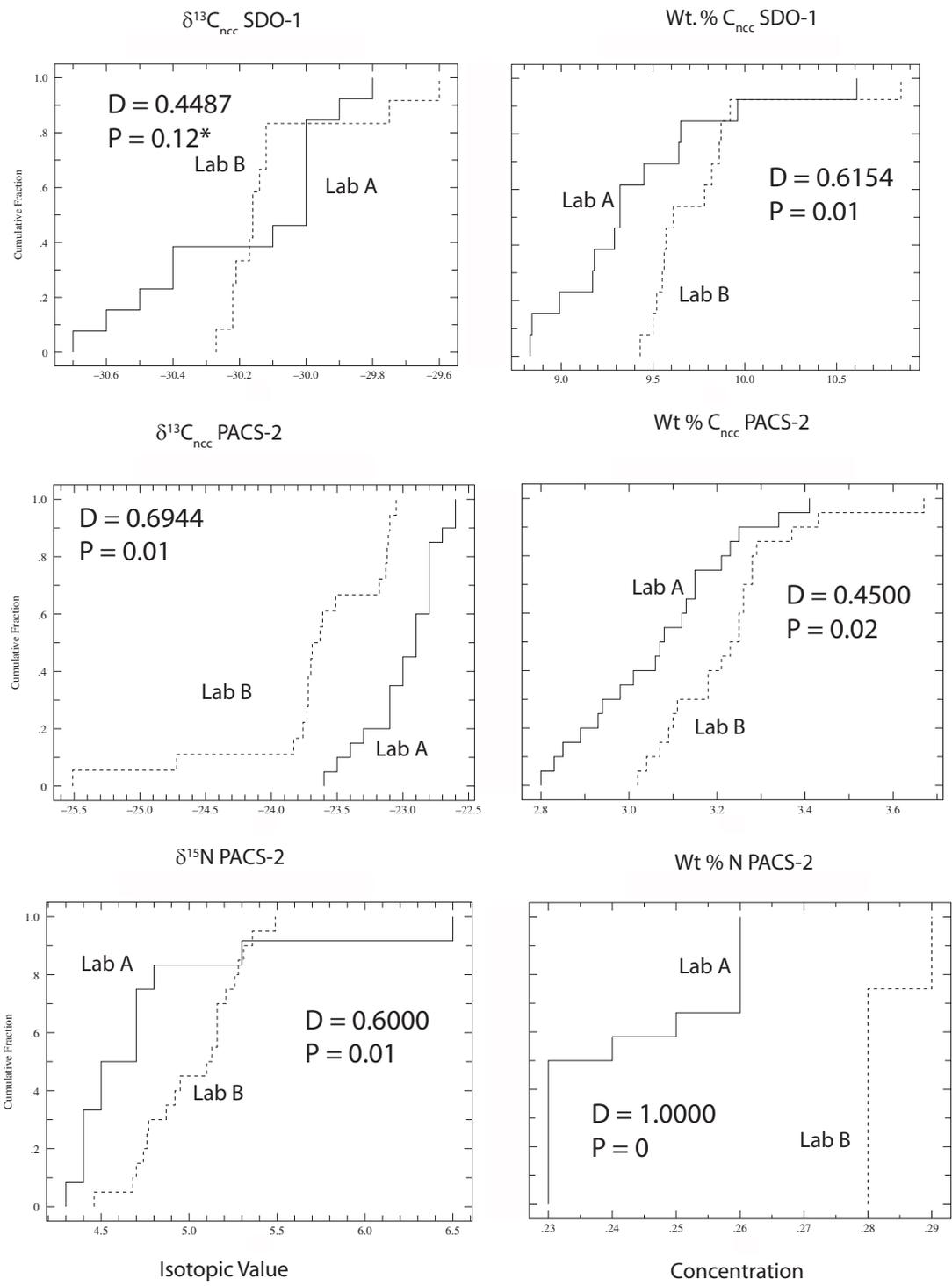


Figure 3. Kolmogorov-Smirnov (K-S) Comparison Cumulative Fraction Plots. Steps are data points on the X axis. The Y axis represents the cumulative fraction of the data smaller than the data point. The K-S test compares the difference between the plots (D value) and computes a P value for the probability of the analytical results being from different populations. To say the results are from different populations with 95% confidence, the P value must be ≤ 0.05 . *In this case, the P value is too large to assume the results are from different populations. Therefore they are considered to be similar.

Table 1. Reference materials used for isotopic and elemental calibrations

Lab A	Lab B	Lab C	Lab D
Working Reference Materials used for Isotopic Analysis (values are those used by the laboratories)			
USGS40:	USGS40:	EDTA:	In-house working reference materials
$\delta^{13}\text{C}$ -26.24 ‰	$\delta^{13}\text{C}$ -26.24 ‰	$\delta^{13}\text{C}$ -32.24 ‰	
$\delta^{15}\text{N}$ - 4.52 ‰	$\delta^{15}\text{N}$ - 4.52 ‰	$\delta^{15}\text{N}$ +0.72 ‰	
USGS41:	USGS41:		
$\delta^{13}\text{C}$ +37.76 ‰	$\delta^{13}\text{C}$ +37.76 ‰		
$\delta^{15}\text{N}$ +47.57 ‰	$\delta^{15}\text{N}$ +47.57 ‰		
(Qi and others, 2003).	(Qi and others, 2003).		
Reference Materials used for calibrating Working Reference Materials (values are those used by the laboratories)			
Same as above	Same as above	$\delta^{13}\text{C}$:	$\delta^{13}\text{C}$:
		NBS 18 carbonatite -5.0 ‰	NBS 21
		NBS 19 limestone +1.95 ‰	graphite -28.1 ‰
		NBS 22 oil -29.7 ‰	$\delta^{15}\text{N}$:
		IAEA CH 6 sucrose -10.4 ‰	IAEA N1 ammonium
		$\delta^{15}\text{N}$:	sulfate +0.4 ‰
		IAEA N1 ammonium	IAEA N2 ammonium
		sulfate +0.4 ‰	sulfate +20.3 ‰
		IAEA N2 ammonium	
		sulfate +20.3 ‰	
		USGS 25 ammonium	
		sulfate -30.2 ‰ (provisional)	
		USGS 26 ammonium	
		sulfate +53.6 ‰ (provisional)	
Working Reference Materials for Elemental Concentrations			
Atropine	USGS40	EDTA	In-house working reference materials
	USGS41		

EDTA-Ethylenediaminetetraacetic acid NBS-National Institute of Standards and Technology (NIST) Reference Material

Most of the Standard Reference Materials listed here are distributed by NIST on behalf of the International Atomic Energy Agency (IAEA).

Descriptions of the materials may be found at: <https://srmors.nist.gov/tables/104-10.htm> (accessed 3/22/2006).

Table 2. Analytical results for individual laboratories

	$\delta^{13}\text{C}_{\text{ncc}}$				Wt% C_{ncc}				$\delta^{15}\text{N}$				Wt% N				
	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D	Lab A	Lab B	Lab C	Lab D	
SDO-1	-30.40	-30.14	-28.83	-29.7	8.83	9.92	11.33	9.48		-1.51	-0.31	-1.0	0.30	0.39	0.37	0.37	
	-30.00	-30.27	-29.03	-29.8	8.84	9.86	9.83	9.52		-1.8	-0.38	-0.7	0.30	0.39	0.35	0.37	
	-29.90	-30.12			9.64	9.61				-0.74			0.38	0.36			
	-29.80	-30.16			9.96	9.5			No	-0.58			0.36	0.36			
	-30.00	-30.17			9.18	9.56			values	-0.67			0.34	0.36			
	-30.00	-30.22			8.99	9.57			reported	-0.62			0.34	0.36			
	-30.10	-30.22			9.45	9.78				-0.67			0.32	0.37			
	-30.00	-30.21			9.29	9.82				-0.47			0.31	0.37			
	-30.00	-30.16			10.61	9.43				-0.61			0.35	0.37			
	-30.60	-30.12			9.65	9.52				-0.44				0.36			
	-30.70	-29.60			9.32	9.55				-0.31				0.37			
	-30.50	-29.75			9.32	10.85				-1.90				0.41			
	-30.40				9.17	9.87				-1.6				0.39			
	SGR-1	-29.50	-29.31	-28.43	-29.2	23.05	25.36	25.74	25.10		15.56	16.92	18.3	0.71	0.88	0.78	0.87
		-29.40	-29.28	-28.51	-29.6	22.14	23.75	25.65	24.42		15.98	17.13	18.4	0.75	0.87	0.78	0.88
-29.30		-29.37			23.51	23.09				18.39			0.79	0.79			
-29.60		-29.28			23.85	22.98			No	17.90			0.72	0.79			
-29.50		-29.31			25.93	23.54			values	17.82			0.81	0.81			
-29.80		-29.34			24.16	22.10			reported	18.02				0.76			
-29.80		-29.30			24.15	24.00				17.51				0.82			
-29.40		-29.48			22.67	24.69				17.40				0.85			
-29.80		-29.36			24.56	24.46				18.48				0.82			
		-29.36				23.43				17.80				0.82			
		-29.32				23.47				17.51				0.83			
		-29.35				23.94				18.20				0.84			
		-29.12				24.44				16.08				0.87			
		-29.12				24.16				16.00				0.87			
PACS-2		-23.00	-24.72	-23.11	-23.4	2.83	3.43	3.20	3.29	4.70	4.70	4.75	4.2	0.23	0.28	0.28	0.30
	-22.90	-25.51	-24.46	-23.3	2.80	3.67	4.06	3.09	4.80	4.68	5.62	4.5	0.23	0.28	0.30	0.29	
	-23.10	-23.61			3.01	3.21			6.50	5.49			0.24	0.28			
	-22.80	-23.72			2.85	3.25			4.40	5.31			0.23	0.28			
	-22.60	-23.70			3.06	3.25			4.40	5.16			0.26	0.28			
	-22.80	-23.73			3.08	3.26			4.50	5.28			0.26	0.28			
	-22.60	-23.83			2.98	3.28			4.40	5.10			0.26	0.28			
	-22.80	-23.63			2.94	3.26			4.50	5.13			0.23	0.29			
	-22.70	-23.72			2.93	3.18			4.70	5.36			0.23	0.28			
	-22.80	-23.76			2.89	3.29			5.30	4.92			0.23	0.29			
	-22.90	-23.69			3.25	3.28			4.70	5.16			0.26	0.28			
	-23.10	-23.11			3.41	3.23			4.30	5.26			0.25	0.29			
	-23.40	-23.12			3.15	3.18				5.16				0.29			
	-23.60	-23.10			3.15	3.02				5.21				0.28			
	-23.00	-23.13			3.07	3.11				4.95				0.28			
	-23.50	-23.51			3.23	3.04				4.74				0.28			
	-23.30	-23.18			3.34	3.07				4.87				0.28			
	-22.90	-23.05			3.13	3.37				4.77				0.29			
	-22.80				3.12	3.1				4.46				0.28			
	-23.10				3.21	3.09				4.76				0.28			

Table 3. Test for normality of data distribution for analyses from laboratories A and B

SDO-1	Data Set	Mean	SD	P value
$\delta^{13}\text{C} \text{ ‰}$	Lab A	-30.2	0.3	0.32
$\delta^{13}\text{C} \text{ ‰}$	Lab B	-30.1	0.2	*0.01
Wt % C_{ncc}	Lab A	9.40	0.49	0.44
Wt % C_{ncc}	Lab B	9.76	0.37	*0.03
PACS-2				
$\delta^{13}\text{C} \text{ ‰}$	Lab A	-23.0	0.3	0.40
$\delta^{13}\text{C} \text{ ‰}$	Lab B	-23.7	0.6	*0.03
Wt % C_{ncc}	Lab A	3.07	0.17	0.99
Wt % C_{ncc}	Lab B	3.23	0.15	*0.01
$\delta^{15}\text{N} \text{ ‰}$	Lab A	4.77	0.61	*0.02
$\delta^{15}\text{N} \text{ ‰}$	Lab B	5.02	0.28	0.66
Wt % N	Lab A	0.24	0.01	0.14
Wt % N	Lab B	0.28	0.00	*0

SD is the standard deviation. The P value is the probability of wrongly rejecting the hypothesis that the data from each lab is normally distributed. To reject the hypothesis that the data sets are normally distributed with a 95% probability of being correct, the P value must be ≤ 0.05 . *These data sets are not normally distributed.

Table 4. Descriptive statistics

Identification	$\delta^{13}\text{C}$ (‰)	Wt% C_{ncc}	$\delta^{15}\text{N}$ (‰)	Wt% N
	As Reported			
SDO-1	-30.0 (0.4) (n=29)	9.64 (0.53) (n=30)	-0.8 (0.6) (n=18)	0.36 (0.03) (n=26)
SGR-1	-29.3 (0.3) (n=27)	24.01 (1.01) (n=27)	17.4 (0.9) (n=18)	0.81 (0.05) (n=23)
PACS-2	-23.3 (0.6) (n=42)	3.17 (0.22) (n=44)	4.9 (0.5) (n=36)	0.27 (0.02) (n=36)

Data are reported as Mean (Standard Deviation)

(n = number of values used to calculate the mean)

Carbon isotope data are reported relative to Vienna Peedee Belemnite (VPDB).

Nitrogen isotope data are reported relative to atmospheric nitrogen.

Table 5. Suggested isotopic and elemental values

Identification	$\delta^{13}\text{C}$ (‰)	Wt% C_{ncc}	$\delta^{15}\text{N}$ (‰)	Wt% N
SDO-1	-30.0 ± 0.1	9.64 ± 0.19	- 0.8 ± 0.3	0.36 ± 0.01
SGR-1	-29.3 ± 0.1	24.01 ± 0.38	17.4 ± 0.4	0.81 ± 0.02
PACS-2	-23.3 ± 0.2	3.17 ± 0.06	4.9 ± 0.1	0.27 ± 0.01

Data are reported as Mean ± the 95% confidence interval.

Carbon isotope data are reported relative to Vienna Peedee Belemnite (VPDB).

Nitrogen isotope data are reported relative to atmospheric nitrogen.