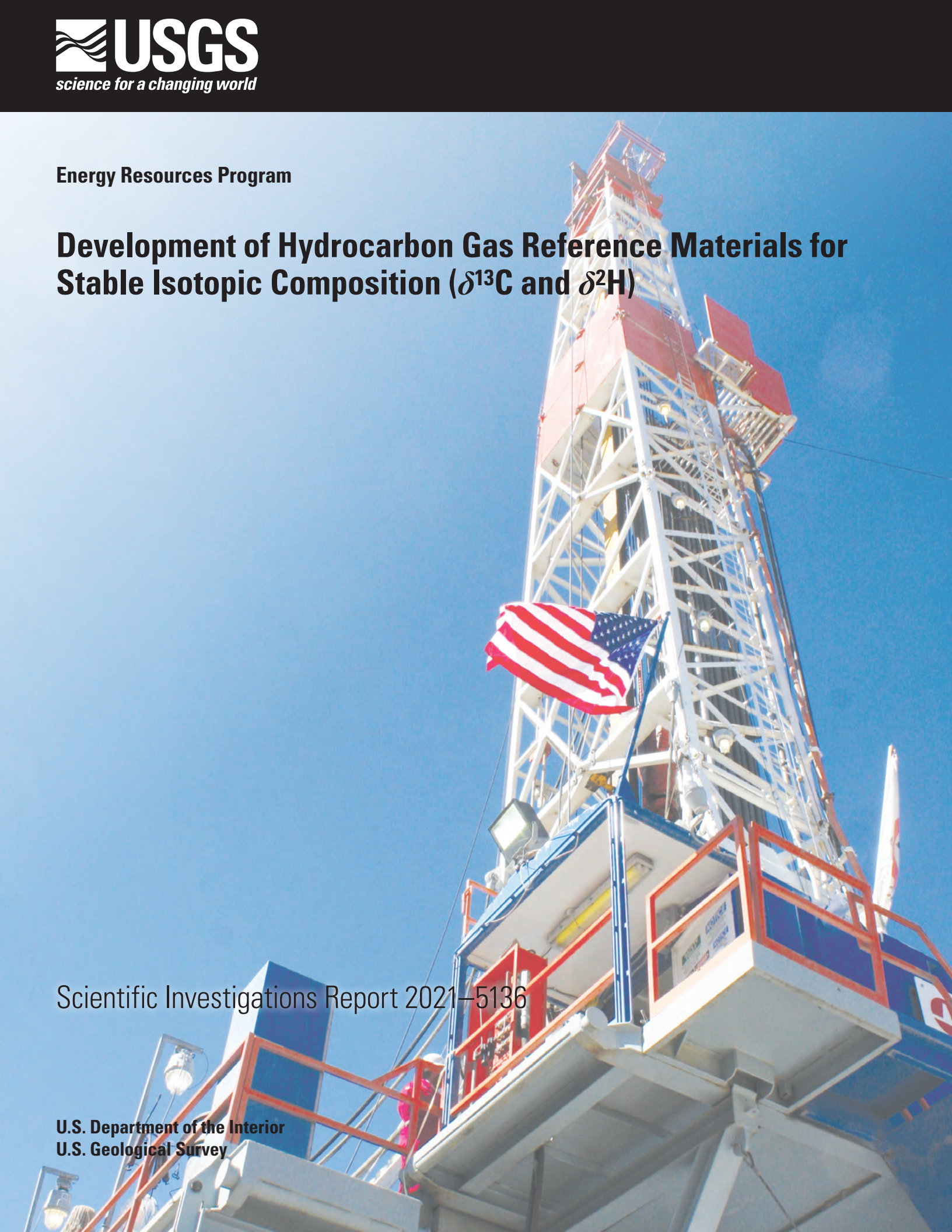


Energy Resources Program

Development of Hydrocarbon Gas Reference Materials for Stable Isotopic Composition ($\delta^{13}\text{C}$ and $\delta^2\text{H}$)

Scientific Investigations Report 2021–5136

U.S. Department of the Interior
U.S. Geological Survey



Covers. Front cover. Energy drilling rig [Photograph by Jessica K. Robertson, U.S. Geological Survey multimedia gallery in the public domain.] Back cover. Gas cylinders and mass spectrometer. [Photographs by Geoffrey S. Ellis, U.S. Geological Survey].

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By Geoffrey S. Ellis and Robert F. Dias

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**U.S. Department of the Interior
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Conversion Factors

International System of Units to U.S. customary units

| Multiply | By | To obtain |
|------------------|----------|---|
| Length | | |
| kilometer (km) | 0.6214 | mile (mi) |
| Volume | | |
| liter (L) | 33.81402 | ounce, fluid (fl. oz) |
| Pressure | | |
| kilopascal (kPa) | 0.1450 | pound per square inch (lb/in ²) |

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:
 $^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8.$

Abbreviations

| | |
|---------|--|
| AGIP | Azienda Generale Italiana Petroli |
| COFRC | Chevron Oil Field Research Company |
| ERP | Energy Resources Program |
| GC-IRMS | Gas chromatography isotope-ratio mass spectrometry |
| IAEA | International Atomic Energy Agency |
| MPa | Megapascal |
| NIST | National Institute of Standards and Technology |
| RM | Reference material |
| SLAP | Standard light Antarctic precipitation |
| USGS | U.S. Geological Survey |
| VPDB | Vienna Peedee belemnite |
| VSMOW | Vienna standard mean ocean water |

Isotope Unit Explanation

Relative difference of isotope ratios: The ratio of stable isotopic abundance of an element in a sample to the abundance of the same element in a standard material. Values are reported using the delta notation (δ) expressed in per mil units (parts per thousand) and computed as follows (Coplen, 2011):

$$\delta^nX = (R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}$$

where

- δ is the “delta” notation,
- n is the heavier stable isotope,
- X is the element, and
- R is the ratio of the heavier, less abundant isotope to the lighter, stable isotope in a sample or standard.

The δ values for stable isotope ratios discussed in this report are referenced to the following standard materials:

| Element | Stable isotopic ratio | Standard identity and reference |
|----------|---|---|
| Carbon | Carbon-13/carbon-12 ($\delta^{13}\text{C}$) | Vienna Peedee belemnite [VPDB], (Hut, 1987; Coplen and others, 2006a; Coplen and others, 2006b; Brand and others, 2014) |
| Hydrogen | Hydrogen-2/hydrogen-1 ($\delta^2\text{H}$) | Vienna Standard Mean Ocean Water [VSMOW], (Gonfiantini, 1978) |

Stable isotope ratios of carbon ($^{13}\text{C}/^{12}\text{C}$) and hydrogen (^2H [deuterium]/ ^1H) are shown in delta (δ) notation as $\delta^{13}\text{C}$ and $\delta^2\text{H}$, in per mil (parts per thousand).

Development of Hydrocarbon Gas Reference Materials for Stable Isotopic Composition ($\delta^{13}\text{C}$ and $\delta^2\text{H}$)

By Geoffrey S. Ellis and Robert F. Dias

Abstract

A suite of gas standards was developed to serve as international secondary reference materials (RMs) for the determination of the compound-specific carbon-13/carbon-12 ($\delta^{13}\text{C}$) and hydrogen-2/hydrogen-1 ($\delta^2\text{H}$) values of hydrocarbon gases. This report provides background information on the project, the methods used to produce and analyze the gases, as well as the data analysis and recommended stable isotopic values. Additionally, samples of older hydrocarbon gas RMs no longer available were analyzed along with the new RMs to allow for traceability to historical data. These secondary RMs are intended for interlaboratory standardization and traceability to primary RMs. The gaseous RMs are currently (at time of publication) available for purchase from the U.S. Geological Survey Energy Resources Program.

Introduction

The use of reference materials (RMs) is of fundamental importance in analytical chemistry and essential for ensuring proper instrument calibration, standardization, and traceability. Appropriate RMs are critical for stable isotopic measurements in particular because these analyses are typically made relative to one or more internationally recognized standards rather than on an absolute scale (Gröning, 2004). For the stable isotopic composition of hydrogen ($\delta^2\text{H}$), the scale is defined by the primary RMs Vienna Standard Mean Ocean Water (VSMOW) with a δ value of 0 and Standard Light Antarctic Precipitation (SLAP) with a δ value of -428 per mil (‰) (Gonfiantini, 1978). Carbon stable isotopic measurements ($\delta^{13}\text{C}$) are reported on the Vienna Pee Dee belemnite (VPDB) scale, which is defined by the carbonate standards NBS 19 (natural calcite) and LVSEC (lithium carbonate) with assigned δ values of $+1.95$ and -46.6 ‰, respectively (Hut, 1987; Coplen and others, 2006a; Coplen and others, 2006b; Brand and others, 2014). The highest quality stable isotopic analyses are achieved by employing RMs having chemical and physical properties (including isotopic compositions) similar to those of the samples. Additionally, RMs should be processed in a similar manner to the sample analyte—termed the principle of

identical treatment (Werner and Brand, 2001). Because of the limited supply of primary RMs and the desire to match RMs to the sample, stable isotope analysts generally rely on secondary standards to ensure measured isotopic values are accurately reported on the appropriate scale. The stable isotopic values assigned to these secondary RMs are typically based on consensus values from interlaboratory studies of direct comparisons with primary standards (Brand and others, 2014).

The measurement of the stable carbon and hydrogen isotopic compositions of individual hydrocarbon gases dates back as far as the 1930s (Snow and Johnston, 1934; Nier, 1939). However, over the ensuing decades, only a limited number of analyses of the isotopic composition of individual hydrocarbon gases were performed because the methods available to isolate and analyze these compounds were labor intensive, required large amounts of sample, and were difficult to perform with great precision. In the late 1970s, gas chromatographs were interfaced with magnetic-sector mass spectrometers to allow for stable isotopic analysis of individual compounds in a gas-phase matrix in a single continuous process (Sano and others, 1976; Matthews and Hayes, 1978). This approach was termed “continuous-flow” or “online” analysis to distinguish it from the earlier manual “offline” or “dual-inlet” techniques. This development ushered in a new era of compound-specific isotopic analysis as the technique was adapted to a variety of different sample types and analytes (see for example, Baylis and others, 1994; Tobias and Brenna, 1996, 1997; Burgoyne and Hayes, 1998). With the adoption of continuous-flow analysis of the stable isotopic composition of individual hydrocarbon gases came the recognition of the need for secondary RMs for these analyses.

In 1984, the Chevron Oil Field Research Company (COFRC, La Habra, California) initiated a collaboration with Azienda Generale Italiana Petroli (AGIP, S.p.A., Milano, Italy), the University of Groningen (Netherlands), and the International Atomic Energy Agency (IAEA) to develop a suite of natural gas materials for interlaboratory comparison of stable isotopic composition (Verkouteren, 2004). These RMs included a coal-related gas (NGS-1), an oil-related gas (NGS-2), and a biogenic gas (NGS-3). NGS-1 was collected by G. Hut (University of Groningen, Netherlands) and consisted of more than 80 percent methane with a $\delta^{13}\text{C}$ value of approximately -29 ‰ (VPDB). NGS-2 was collected by T. Ricchiuto (AGIP) and contained more than 50 percent

acquired by the California Institute of Technology and then subsequently transferred to a private research institution (Power, Environmental, and Energy Research Institute in Covina, Calif.). As of the date of the publication of this report, the NGS gases are no longer being distributed and reside with the Energy Resources Program (ERP) at the U.S. Geological Survey (USGS) in Denver, Colorado.

In the late 2000s, an interlaboratory study of a suite of produced natural gases from China involving 10 laboratories from the United States, Europe, and China was conducted with the purported aim of replacing the discontinued NIST gas standards (Dai and others, 2012). However, following this study, the gases were not made available for general use as RMs outside of China. In response to this situation, the ERP (USGS) initiated a project to develop a new suite of gas standards to replace the now retired NGS gases. This project was a collaborative effort by researchers from academic, governmental, and industrial organizations from around the world. USGS personnel took the lead to coordinate the work related to the development of these standards including collection of gas samples, distribution of aliquots of the gases for calibration, compilation and statistical analysis of the calibration data, preparation of this final report, and storage and distribution of the new standards.

The main objective of this project was to develop a suite of light hydrocarbon (methane, ethane, and propane) gaseous RMs to replace the NGS gases formerly distributed by NIST. Three new gas mixtures were developed as secondary carbon and hydrogen isotopic RMs in consultation with an international advisory committee. The standards produced by this project were primarily designed to address the analytical needs related to natural gas as an energy resource. Where feasible, the interests of other applications (for example, atmospheric and environmental sciences) were accommodated; however, priority was placed on energy-related considerations.

Methods

Advisory Committee

An important component of this project was the technical advice provided throughout the duration of the project by an international committee of experts in the field of natural gas geochemistry (table 3). All aspects of this project were subject to review by the advisory committee, and members were encouraged to actively participate by providing objective and constructive suggestions. There were several key areas where the counsel of the advisory committee was critical. These included:

- The determination of the number and the molecular and isotopic composition of the gases used as RMs.
- The selection of the analytical methods used for the calibration of the gases.
- The choice of subsampling and sample distribution methods.

In instances where various individuals or constituencies within the committee had different priorities or concerns, a consensus position was adopted. The USGS gave due consideration to all serious recommendations, and in no instances was a course of action taken against the advice of the committee. Although the committee provided valuable oversight throughout the development of the standards, ultimately, the USGS is solely responsible for the scientific integrity of the standard gases and the process leading to their development.

Selection of Reference Materials

After extensive consultation with the technical advisory committee, the ideal molecular and stable isotopic compositions of the new standard RMs were identified. The targeted compositions and $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values (table 4) represent a series of compromises among selection of specific compounds, identification of the most useful isotopic ranges, and the amount of work required to provide a proper calibration. The inclusion of nonhydrocarbon gases (particularly nitrogen and carbon dioxide) was considered and determined not to be a priority given the availability of other RMs for these compounds. Furthermore, heavier hydrocarbon homologues (specifically iso- and normal butanes and pentanes) were discussed as additional potential compounds of interest for inclusion in these standards. Although RMs for the stable carbon and hydrogen isotopic composition of butane and pentane gases do not currently exist, the consensus view of the committee was that the potential negatives associated with inclusion of these compounds outweighed the benefits. In particular, the heavier hydrocarbon components present a risk of phase separation under certain pressure and temperature conditions, which complicates the storage, handling, and distribution of the standards. Moreover, it was difficult to justify the significant increase in the amount of analytical work required to calibrate these additional components when most analytical methods used to determine their stable isotopic composition are directly tied to methane, ethane, or propane. The molecular compositions of the three mixtures were selected such that the gas components were equimolar on a carbon basis to facilitate the stable isotopic analysis of the RMs by modern continuous-flow gas chromatography isotope-ratio mass spectrometry (GC-IRMS) methods.

The NGS gases (RM8559, RM8560 and RM8561) are natural gases of thermogenic oil-associated, non-associated, and microbial origins and provided a reasonable spread along both the carbon and hydrogen isotope δ scales. However, there is no reason gas samples used as RMs must be of completely natural origin. Locating and acquiring samples of naturally occurring gases covering the full range of stable isotopic compositions desired for this project proved to be quite difficult. Moreover, produced natural gases from geologic reservoirs are likely to contain additional undesirable components (for example, hydrocarbons heavier than propane and nonhydrocarbons, such as carbon dioxide) (Tissot and Welte, 1984). In consultation with the technical committee, a hybrid approach was

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Table 3. Natural gas reference material technical advisory committee.

| Name | Institution | Organization type | Geographic region |
|-------------------------------|---|-------------------|-------------------|
| Robert Dias ¹ | U.S. Geological Survey | Government | North America |
| Geoffrey Ellis ¹ | U.S. Geological Survey | Government | North America |
| Alexandre de Andrade Ferreira | Petrobras | Industry | South America |
| Andrew Bishop | Shell Oil | Industry | North America |
| Junhong Chen | Geoscience Australia | Government | Asia |
| Dennis Coleman ² | Isotech Laboratories, Inc. | Industry | North America |
| Tyler Coplen | U.S. Geological Survey | Government | North America |
| Jingxing Dai | PetroChina | Industry | Asia |
| Giuseppe Etiope | Instituto Nazionale di Geofisica e Vulcanologia | Government | Europe |
| Brian Giebel ² | National Institute of Standards and Technology | Government | North America |
| Maciej Kotarba | AGH University of Science and Technology | Academia | Europe |
| Michael Lawson | ExxonMobil | Industry | North America |
| Christy Legner ² | Isotech Laboratories, Inc. | Industry | North America |
| Fang Lin | Chevron | Industry | North America |
| Steve Pelphrey | Isotech Laboratories, Inc. | Industry | North America |
| Alain Prinzhofer | IPEX Inc. | Industry | South America |
| Elin Rein | StatOil (now Equinor) | Industry | Europe |
| Karyne Rogers | GNS Science | Government | Asia |
| Arndt Schimmelmann | Indiana University | Academia | North America |
| Stefan Schloemer | GeoForschungsZentrum | Government | Europe |
| Martin Schoell | Gas Consult International | Industry | North America |
| Stephen Sestak | CSIRO | Government | Asia |
| Barbara Sherwood Lollar | University of Toronto | Academia | North America |
| Yongchun Tang | Power, Environment, and Energy Research Institute | Industry | North America |
| Bruce Vaughn | University of Colorado | Academia | North America |
| Andrea Vieth-Hillebrand | GeoForschungsZentrum | Government | Europe |
| Michael Whiticar | University of Victoria | Academia | North America |
| John Zumberge | Geomark Research | Industry | North America |

¹Committee cochair.

²Left the committee before the completion of the project.

selected involving a combination of synthesized gas mixtures made from commercially available individual hydrocarbon gases and isotopically labeled individual hydrocarbon gases and a produced natural gas from a biogenic gas field. The individual hydrocarbon gases were blended in various proportions to achieve gas mixtures approximating the ideal molecular and isotopic compositions listed in table 4. The methods used for preparing these mixtures are discussed below.

Reference Material Preparation

Because most commercially available compressed hydrocarbon gases are derived from thermogenic natural gas sources, they typically have $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values similar to average thermogenic natural gases. Large cylinders of pure methane, ethane, and propane were acquired from a local supplier (Air Products, Trexlertown, Pennsylvania); their $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values were measured and were confirmed to be in the range of typical thermogenic gases (Milkov and Etiope, 2018). Individual cylinders of methane, ethane, and propane were selected that most closely matched the ideal δ values shown

Table 4. Target molecular and isotopic compositions for the reference materials.

[$\delta^{13}\text{C}$, carbon-13/carbon-12; ‰_{VPDB}, per mil Vienna Pee Dee Belemnite; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; ‰_{VSMOW}, per mil Vienna Standard Mean Ocean Water; %, percent; ^{13}C , carbon-13; ^2H , hydrogen-2]

| Analyte | $\delta^{13}\text{C}$ (‰ _{VPDB}) | $\delta^2\text{H}$ (‰ _{VSMOW}) | Mole fraction (%) |
|--|--|--|-------------------|
| ^{13}C - and ^2H -depleted methane | -85 | -350 | 55 |
| Intermediate methane | -45 | -200 | 55 |
| ^{13}C - and ^2H -enriched methane | -15 | -50 | 55 |
| ^{13}C - and ^2H -depleted ethane | -50 | -250 | 27 |
| Intermediate ethane | -35 | -175 | 27 |
| ^{13}C - and ^2H -enriched ethane | -15 | -100 | 27 |
| ^{13}C - and ^2H -depleted propane | -50 | -250 | 18 |
| Intermediate propane | -35 | -175 | 18 |
| ^{13}C - and ^2H -enriched propane | -15 | -100 | 18 |

in table 4 for use in the intermediate isotopic-composition mixture. These gases were then blended together in proportions approximating the molar concentrations shown in table 4 (fig. 1).

To produce the compound-specific δ values desired for the isotopically enriched mixture, small aliquots of ^{13}C -(carbon-13) and ^2H -(hydrogen-2) enriched methane, ethane, and propane (Cambridge Isotopes, Tewksbury, Massachusetts) were separately mixed with additional cylinders of methane, ethane, and propane of intermediate isotopic compositions to produce three additional gases each enriched in both ^{13}C and ^2H . The cylinders of spiked gases were mixed using a combination of thermal (that is, heating jackets) and physical (that is, rollers) techniques over a period of several months. The cylinders were periodically subsampled, and the isotopic compositions were measured to evaluate the effectiveness of the mixing process. The gases were considered to have reached isotopic homogeneity when repeated analyses (following an additional mixing interval) produced stable isotopic values within the analytical precision of the continuous-flow technique used (less than [$<$] 0.2 ‰ for $\delta^{13}\text{C}$ and $<$ 4.0 ‰ for $\delta^2\text{H}$). Once the individual gases were homogenized, they were blended at approximately the molar ratios shown in table 4 (fig. 1). The validity of this approach has been confirmed by subsequent analyses of aliquots of these gases measured throughout the final stages of the development and the initial distribution of the gas RMs showing no significant deviation from the initial homogenized δ values.

The addition of ^{13}C - and ^2H -depleted gases to the stock (intermediate isotopic composition) gases was considered as a possible method to produce the gas components for the RMs with more negative δ values (table 4). However, it was determined that this would require hundreds of liters of ^{13}C - and ^2H -depleted gas mixed with the initial stock gases to produce gases having marginally lower ^{13}C and ^2H abundances. Moreover, the commercial availability of methane, ethane, and propane depleted in ^{13}C and ^2H was quite limited, and the purchase of sufficient volumes of these gases to produce the

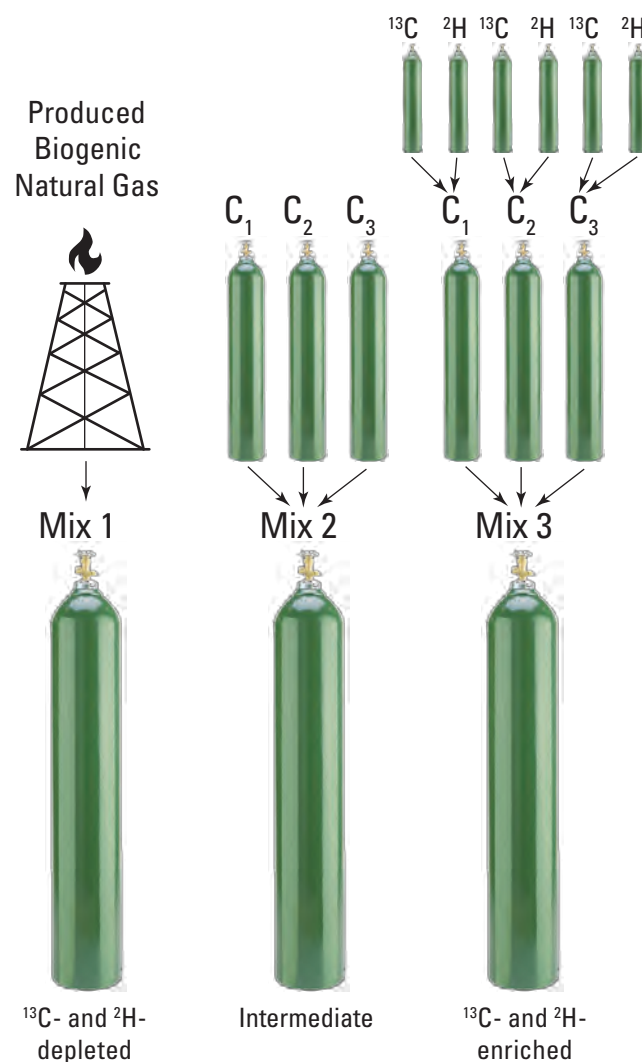


Figure 1. Schematic representation of process used to develop the gas reference materials. [^{13}C , carbon-13; ^2H , hydrogen-2; C_1 , methane; C_2 , ethane; C_3 , propane]

desired isotopic compositions would have been cost prohibitive. Consequently, a natural microbial gas was chosen to serve as the isotopically ^{13}C - and ^2H -depleted gas RM (fig. 1). Three large cylinders were collected from the Beecher Island gas field by Mark Dreier (USGS) and Owen Sherwood (Dolan Integration Group) on June 19, 2013, for use as the gaseous hydrocarbon RM depleted in ^{13}C and ^2H (HCG-3). Because the wellhead pressures in this field were rather low, the gases were collected from the North Beecher Island compressor located approximately 8 kilometers (5 miles) south of Wray, Colo., at a pressure of 5.2 megapascals (750 pounds per square inch). The gases were collected upstream of any gas cleanup (for example, nonhydrocarbon or water removal). Natural gas in Beecher Island field is produced from chalk beds of the Upper Cretaceous Niobrara Formation located at shallow depths (approximately 500 meters) on the gently sloping eastern flank of the Denver Basin in northeastern Colorado. Based on the low thermal maturity of the source rock, the high methane content, and the ^{13}C -depleted methane isotopic composition, this gas accumulation has been reported to be microbially sourced (Rice, 1984).

Isotopic Determination

A total of 16 cylinders of compressed gas were subsampled and analyzed for this project. These included two cylinders of the ^{13}C - and ^2H -enriched isotopic composition gas mixture (HCG-1), two cylinders of the intermediate isotopic composition gas mixture (HCG-2), one cylinder of the isotopically ^{13}C - and ^2H -depleted gas mixture (HCG-3), eight cylinders of the individual hydrocarbon components used to make the enriched (HCG-1) and intermediate (HCG-2) mixtures (two cylinders of intermediate methane, two cylinders of ^{13}C - and ^2H -enriched methane, one cylinder of intermediate ethane, one cylinder of ^{13}C - and ^2H -enriched ethane, one cylinder of intermediate propane, and one cylinder of ^{13}C - and ^2H -enriched propane), and three cylinders of the NGS gases (RM8559, RM8560 and RM8561). The subsampling, preparation, and analyses of these gases are summarized in table 5.

The recommended compound-specific δ values for the new RMs were derived from analytical work performed at the USGS Petroleum Geochemistry Research Laboratory in Denver, Colorado, and Isotech Laboratories, Inc. (Isotech) in Champaign, Illinois. The hydrocarbon gases were directly measured against the inorganic carbonate RMs NBS 19 and LSVEC for carbon (VPDB scale) and the water RMs VSMOW2 and SLAP2 (VSMOW scale) for hydrogen.

Both laboratories were provided with pressurized stainless steel cylinders of the individual components (methane, ethane, and propane) comprising the mixtures named USGS HCG-1 and HCG-2. Four cylinders of methane (two for each of HCG-1 and HCG-2) and two cylinders of ethane and propane (one for each of HCG-1 and HCG-2) were subsampled for a total of eight individual gas samples sent to each laboratory (table 5). These gases were prepared for

dual-inlet isotopic analyses on a manual vacuum line. Briefly, this involved the combustion of the individual hydrocarbons to carbon dioxide and water and the subsequent reduction of water to hydrogen by zinc reduction (400 degrees Celsius [$^{\circ}\text{C}$], 60 minutes). All dual-inlet methods followed in this work are derivatives of methods found in Horita and Kendall (2004) and de Groot (2009).

The RM containing ^{13}C - and ^2H -depleted components (USGS HCG-3) is a produced natural gas from a biogenic gas field (Beecher Island) in northern Colorado. As such, it contains a mixture of methane, ethane, and propane and required splitting into the component hydrocarbon gases prior to offline combustion and analysis. The component isolation from this gas mixture was done at Isotech (Champaign, Ill.) by means of a preparatory GC system. The additional gas blends (HCG-1 and HCG-2) were also split into their individual hydrocarbon gases, combusted to carbon dioxide and water, and distributed to the USGS laboratory for analysis. Glass ampoules (one carbon dioxide and one water sample for pure methane, ethane, and propane, each in triplicate) were distributed to the USGS laboratory for $\delta^{13}\text{C}$ analysis of the carbon dioxide and reduction of the water to hydrogen gas for $\delta^2\text{H}$ analysis of the hydrogen. Similar sample preparation (that is, water reduction to hydrogen) and isotopic analysis was performed at Isotech.

Additionally, samples of the NGS gases (NIST RM8559, RM8560, and RM8561) were prepared and analyzed by the same methods as the USGS RM gases. This allows for the new gaseous RMs to be directly tied to the NIST RM gases previously in circulation.

The carbon and hydrogen stable isotopic compositions of the carbon dioxide and hydrogen derived from the combustion of the hydrocarbon gases and subsequent reduction of water were measured by dual-inlet magnetic-sector isotope-ratio mass spectrometer (MAT253, ThermoFisher Scientific, Waltham, Massachusetts). The carbon dioxide was analyzed directly against isolated, purified carbon dioxide produced from phosphoric acid (H_3PO_4) digestion (30 $^{\circ}\text{C}$, 24 hours) of NBS 19 and LSVEC under vacuum. The hydrogen gases were analyzed against hydrogen prepared from VSMOW2 and SLAP2 by zinc reduction. Each sample and primary RM was analyzed in replicate to establish the statistical significance of each result. All the carbon and hydrogen isotopic data used for the determination of the recommended δ values are included in appendix 1. Except for the $\delta^{13}\text{C}$ and $\delta^2\text{H}$ of methane in HCG-1, the recommended δ values for HCG-1 and HCG-2 include the measured δ values from the pure components combined with those from the gases split from the mixtures. The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values of the ^{13}C - and ^2H -enriched pure methane used to make the HCG-1 mixture are significantly higher (approximately 4 ‰) than those of the methane in the mixed gas (app. 1 and 2). The most likely explanation for this is that the ^{13}C - and ^2H -enriched methane added to the stock cylinder of methane had not fully equilibrated at the time this methane was used to make the HCG-1 mixture.

Table 5. Summary of the sample preparation, analysis, and starting materials used in this study.

[Blanks indicate work not performed on a sample. X, indicates a preparation process or analytical procedure conducted on a sample; Prep GC, preparatory gas chromatography; GC/FID, gas chromatography flame ionization detection; $\delta^{13}\text{C}$, carbon-13/carbon-12; ‰, per mil; VPDB, Vienna Pee Dee Belemnite; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; VSMOW, Vienna Standard Mean Ocean Water; %, percent; ^{13}C -, carbon-13; ^2H , hydrogen-2; RM, reference material]

| Gas cylinder | Subsample | Prep GC | Prep GC | Offline | Dual-inlet analysis | | GC/FID |
|--|-----------|------------|--|----------------------|----------------------------------|--------------------------------|----------------------|
| | | Separation | Product | Combustion/reduction | $\delta^{13}\text{C}$ (‰VPDB) | $\delta^2\text{H}$ (‰VSMOW) | Mole fraction (%) |
| ^{13}C - and ^2H -enriched gases | | | | | | | |
| HCG-1: Cylinder A | | X | | | | | X |
| | | | ^{13}C - and ^2H -enriched methane | X | X | X | |
| | | | ^{13}C - and ^2H -enriched ethane | X | X | X | |
| | | | ^{13}C - and ^2H -enriched propane | X | X | X | |
| HCG-1: Cylinder B | | X | | | | | X |
| | | | ^{13}C - and ^2H -enriched methane | X | X | X | |
| | | | ^{13}C - and ^2H -enriched ethane | X | X | X | |
| | | | ^{13}C - and ^2H -enriched propane | X | X | X | |
| Methane (HCG-1): Cylinder A | Aliquot A | | | X | X | X | |
| | Aliquot B | | | X | X | X | |
| Methane (HCG-1): Cylinder B | Aliquot A | | | X | X | X | |
| | Aliquot B | | | X | X | X | |
| Ethane (HCG-1) | Aliquot A | | | X | X | X | |
| | Aliquot B | | | X | X | X | |
| Propane (HCG-1) | Aliquot A | | | X | X | X | |
| | Aliquot B | | | X | X | X | |
| Intermediate gases | | | | | | | |
| HCG-2: Cylinder A | | X | | | | | X |
| | | | Intermediate methane | X | X | X | |
| | | | Intermediate ethane | X | X | X | |
| | | | Intermediate propane | X | X | X | |
| HCG-2: Cylinder B | | X | | | | | X |
| | | | Intermediate methane | X | X | X | |
| | | | Intermediate ethane | X | X | X | |
| | | | Intermediate propane | X | X | X | |
| Methane (HCG-2): Cylinder A | Aliquot A | | | X | X | X | |

Table 5. Summary of the sample preparation, analysis, and starting materials used in this study.—Continued

[Blanks indicate work not performed on a sample. X, indicates a preparation process or analytical procedure conducted on a sample; Prep GC, preparatory gas chromatography; GC/FID, gas chromatography flame ionization detection; $\delta^{13}\text{C}$, carbon-13/carbon-12; ‰, per mil; VPDB, Vienna Pee Dee Belemnite; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; VSMOW, Vienna Standard Mean Ocean Water; %, percent; ^{13}C -, carbon-13; ^2H , hydrogen-2; RM, reference material]

| Gas cylinder | Subsample | Prep GC | Prep GC | Offline | Dual-inlet analysis | | GC/FID |
|--|-----------|------------|--|----------------------|----------------------------------|--------------------------------|----------------------|
| | | Separation | Product | Combustion/reduction | $\delta^{13}\text{C}$ (‰VPDB) | $\delta^2\text{H}$ (‰VSMOW) | Mole fraction (%) |
| Intermediate gases—Continued | | | | | | | |
| Methane (HCG-2): Cylinder B | Aliquot B | | | X | X | X | |
| | Aliquot A | | | X | X | X | |
| Ethane (HCG-2) | Aliquot B | | | X | X | X | |
| | Aliquot A | | | X | X | X | |
| Propane (HCG-2) | Aliquot B | | | X | X | X | |
| | Aliquot A | | | X | X | X | |
| | Aliquot B | | | X | X | X | |
| ^{13}C - and ^2H -depleted gases | | | | | | | |
| HCG-3 | | X | | | | | X |
| | | | ^{13}C - and ^2H -depleted methane | X | X | X | |
| | | | ^{13}C - and ^2H -depleted ethane | X | X | X | |
| | | | ^{13}C - and ^2H -depleted propane | X | X | X | |
| NGS gas RMs | | | | | | | |
| NGS-1 (RM8559) | | X | | | | | |
| | | | ^{13}C - and ^2H -enriched methane | X | X | X | |
| | | | ^{13}C - and ^2H -enriched ethane | X | X | X | |
| | | | ^{13}C - and ^2H -enriched propane | X | X | X | |
| NGS-2 (RM8560) | | X | | | | | |
| | | | Intermediate methane | X | X | X | |
| | | | Intermediate ethane | X | X | X | |
| | | | Intermediate propane | X | X | X | |
| NGS-3 (RM8561) | | X | | | | | |
| | | | ^{13}C - and ^2H -depleted methane | X | X | X | |
| | | | ^{13}C - and ^2H -depleted ethane | X | X | X | |
| | | | ^{13}C - and ^2H -depleted propane | X | X | X | |

In conjunction with the offline calibration work described above, a round-robin study of the new gas hydrocarbon RM mixtures was conducted by nine U.S.-based laboratories using standard continuous-flow methodologies for carbon and hydrogen isotopic analysis. The purpose of this study was to evaluate the interlaboratory variability of $\delta^{13}\text{C}$ and $\delta^2\text{H}$ analyses of hydrocarbon gases by the most commonly employed methods. A rigorous quantitative comparison of methodologies is beyond the scope of this work, and these results are not presented in this report.

Statistical Analysis

The arithmetic mean of the replicate analyses of each individual component is taken as the recommended δ value for the RM gases as reported in table 6. Because the number of laboratories involved in this study is small ($n=2$), we use a Type B model of bias (often abbreviated BOB) approach for the calculation of the uncertainty associated with the recommended values as described by Levenson and others (2000). The approach is briefly described below.

The standard uncertainty $u(X)$ of a sample mean from the random variation in the measurements can be expressed as:

$$u(X) = \frac{s(X)}{\sqrt{n}}, \quad (1)$$

where

$s(X)$ is the standard deviation of multiple measurements; and

n is the number of measurements.

The associated degrees of freedom (v_s) for the standard uncertainty is $n - 1$. The between-laboratory uncertainty $u(B)$ can be expressed as:

$$u(B) = \frac{|\bar{X}_1 - \bar{X}_2|}{2\sqrt{3}}, \quad (2)$$

where

\bar{X}_n is the arithmetic mean of the measurements from laboratory n .

This assumes a hypothetical bias distribution model (1) centered at the average of the mean values of the two laboratories; (2) bounded by the range of the two mean values; and (3) equally likely to be anywhere within this range. The degrees of freedom for the between-laboratory uncertainty (v_B) is:

$$v_B = \left(\frac{1}{2}\right) \frac{(\bar{X}_1 - \bar{X}_2)^2}{u^2(X_1) + u^2(X_2)}, \quad (3)$$

where

$u^2(X_n)$ is the standard uncertainty of the mean of the measurements from laboratory n .

The combined uncertainty $u(C)$ for analytical data from two laboratories can be determined from the expression:

$$u(C) = \sqrt{\left(\frac{1}{2}\right)^2 u^2(X_1) + \left(\frac{1}{2}\right)^2 u^2(X_2)}, \quad (4)$$

The degrees of freedom associated with the combined uncertainty (v_c) as calculated from the Welch-Satterthwaite formula is:

$$v_c = \frac{u^4(C)}{\left(\frac{1}{2}\right)^4 \frac{u^4(X_1)}{v_{x_1}} + \left(\frac{1}{2}\right)^4 \frac{u^4(X_2)}{v_{x_2}}}, \quad (5)$$

where

v_{x_n} is the degrees of freedom for the standard uncertainty for the measurements from laboratory n .

The between-laboratory and combined-laboratory uncertainties can be summed as follows:

$$u(S) = \sqrt{u^2(B) + u^2(C)}, \quad (6)$$

with the corresponding degrees of freedom (v_s) determined by:

$$v_s = \frac{u^4(S)}{u^4(B) \frac{1}{v_B} + u^4(C) \frac{1}{v_c}}, \quad (7)$$

The total uncertainty $u(T)$ is derived by combining the sum of the analytical uncertainties ($u(S)$) with the uncertainties of the RMs ($u(\text{RM}_x)$) used to define the isotopic scales, as follows:

$$u(T) = \sqrt{u^2(S) + u^2(\text{RM}_1) + u^2(\text{RM}_2)}, \quad (8)$$

with the total degrees of freedom (v_T) determined as:

$$v_T = \frac{U_T^4}{u^4(S) \frac{1}{v_s} + u^4(\text{RM}_1) \frac{1}{v_{\text{RM}_1}} + u^4(\text{RM}_2) \frac{1}{v_{\text{RM}_2}}}, \quad (9)$$

Specifically, the RMs NBS 19 and LVSEC were used for the carbon scale (VPDB), and VSMOW2 and SLAP2 were used for the hydrogen scale (VSMOW). The values of $u(\text{RM}_x)$ are determined by summing the uncertainties associated with the assigned values with those of the analytical measurements. There is no uncertainty on the $\delta^{13}\text{C}$ values originally assigned to NBS 19 and LSVEC, and an uncertainty of 0.3 ‰ for the assigned hydrogen isotopic compositions of VSMOW2 and SLAP2 (IAEA, 2017).

After the analytical work for this study was completed, it was recognized that the carbon isotopic composition of LSVEC could shift by as much as 0.3–0.5 ‰ if aliquots were not properly stored (Assonov and others, 2015; Qi and others, 2020). Given the observed reproducibility of the replicate analyses of LSVEC and the excellent agreement between the measured and accepted δ values for the NGS gases (fig. 2), it was concluded the aliquots of LSVEC used in this study had retained their original isotopic composition. Consequently, the uncertainty on the assigned δ value on LSVEC was taken to be zero.

The expanded uncertainty (U_e) can be obtained by multiplying the total uncertainty $u(T)$ by the coverage factor k .

$$U_e = k \cdot u(T), \quad (10)$$

Coverage factors for a 95 percent level of confidence interval based on the total degrees of freedom ν_T were obtained from Taylor and Kuyatt (1994, table B1). Calculated values used to determine the uncertainties on the recommended compound-specific carbon and hydrogen δ values for the HCG gases are included in appendix 1.

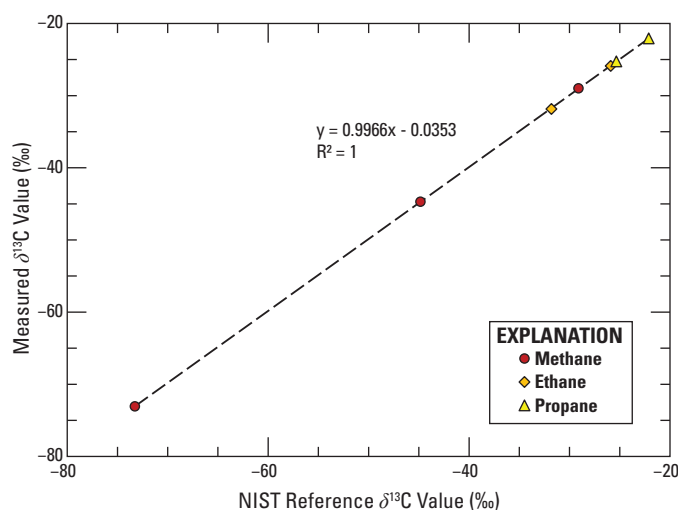


Figure 2. Graph showing stable carbon isotopic composition (VPDB) of the methane, ethane, and propane in the NGS reference materials (RM8559, RM8560, and RM8561) measured for this study compared to the reference carbon-13/carbon-12 ($\delta^{13}\text{C}$) values reported by National Institute of Standards and Technology (NIST; Wise and Watters, 2007) in units of per mil (‰). Error bars for the measured $\delta^{13}\text{C}$ values are smaller than the data symbols.

Results

The recommended carbon and hydrogen δ values and the approximate molecular compositions of the three new gas RMs (HCG-1, HCG-2, and HCG-3) are shown in table 6. The $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values are the result of offline preparation methods and dual-inlet isotope-ratio mass spectrometry (IRMS) analyses performed at the USGS and Isotech and include both the mixed-gas samples and the individual component gases where available. The recommended δ values shown are the arithmetic means of all δ values reported by the USGS and Isotech, the total number of analyses (n) used to determine the mean δ value, and the uncertainty (U) associated with the data. All data produced by the USGS and Isotech are provided in appendixes 1 and 2 and are available in digital form in Dias and others (2022). Appendix 1 contains all carbon and hydrogen isotope data used to determine the recommended δ values and the associated uncertainties. Appendix 2 contains carbon and hydrogen isotopic data for (1) the NGS RMs, (2) the primary RMs analyzed as part of this study, and (3) additional analyses of the pure components used to make the HCG gas mixtures but not used for the calculation of the recommended δ values.

The use of the combined offline, dual-inlet and continuous-flow datasets was considered for the determination of the recommended δ values. Although this composes a larger dataset involving multiple different analytical methods, data produced by continuous-flow methods are generally less accurate and precise compared to those generated by offline, dual-inlet methods (Hayes and others, 1990; Baylis and others, 1994). Moreover, the dual-inlet analyses performed for this study were conducted directly against the primary RMs NBS 19 and LSVEC for carbon (VPDB scale) and VSMOW2 and SLAP2 (VSMOW scale) for hydrogen, whereas all continuous-flow methods rely on secondary or tertiary RMs, which increases the uncertainty of the measurements. The

Table 6. Recommended isotopic compositions and approximate molar compositions of the reference materials HCG-1, HCG-2, and HCG-3.

[$\delta^{13}\text{C}$, carbon-13/carbon-12; ‰_{VPDB}, per mil Vienna Pee Dee Belemnite; U , Uncertainty; n , number of analyses; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; ‰_{VSMOW}, per mil Vienna Standard Mean Ocean Water; %, percent]

| Value type | HCG-1 | | | HCG-2 | | | HCG-3 | | |
|--|---------|--------|---------|---------|--------|---------|---------|--------|---------|
| | Methane | Ethane | Propane | Methane | Ethane | Propane | Methane | Ethane | Propane |
| $\delta^{13}\text{C}$ (‰ _{VPDB}) | | | | | | | | | |
| Recommended value | -1.51 | -10.22 | -15.43 | -43.09 | -29.80 | -19.35 | -61.39 | -45.31 | -36.80 |
| U | 0.10 | 0.09 | 0.11 | 0.14 | 0.09 | 0.10 | 0.15 | 0.11 | 0.11 |
| n | 12 | 21 | 21 | 30 | 21 | 21 | 6 | 6 | 6 |
| $\delta^2\text{H}$ (‰ _{VSMOW}) | | | | | | | | | |
| Recommended value | -64.0 | +54.3 | +74.6 | -183.2 | -125.6 | -171.0 | -224.3 | -262.2 | -245.2 |
| U | 4.0 | 4.9 | 6.5 | 5.5 | 2.2 | 2.7 | 4.0 | 3.7 | 3.4 |
| n | 12 | 21 | 18 | 28 | 21 | 20 | 6 | 5 | 6 |
| Approximate molecular composition | | | | | | | | | |
| Mole fraction (%) | 46 | 43 | 11 | 59 | 33 | 8 | 93.5 | 1.2 | 0.4 |

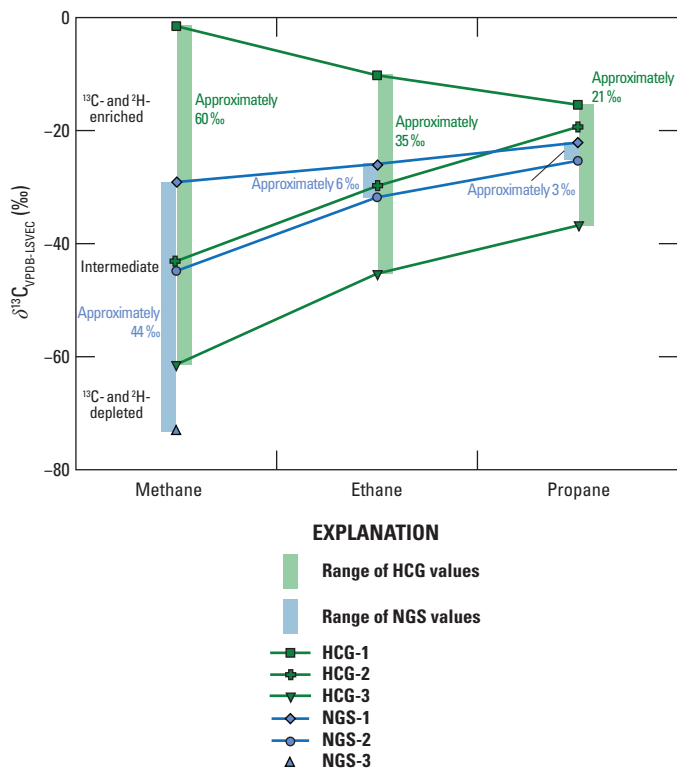


Figure 3. Graph showing comparison of the stable carbon isotopic composition (VPDB) of the U.S. Geological Survey HCG and the NGS reference materials (RM8559, RM8560, and RM8561). Data for the NGS gases are from Wise and Watters (2007). Green and blue bars represent the approximate ranges of isotopic values covered by the HCG and NGS RMs, respectively. [^{13}C , carbon-13; ^2H , hydrogen-2; ‰, per mil; $\delta^{13}\text{C}$, carbon-13/carbon-12]

Summary

The U.S. Geological Survey and Isotech Laboratories, Inc., collaborated to produce a new suite of hydrocarbon reference materials (RMs). Stable carbon and hydrogen isotopic values ($\delta^{13}\text{C}$ and $\delta^2\text{H}$, respectively) were determined by traditional offline, dual-inlet methods. Stable carbon δ values are anchored to the VPDB-LSVEC (Vienna Pee Dee Belemnite-lithium carbonate standard) scale through direct measurement of the primary carbonate RMs NBS 19 and LSVEC. Stable hydrogen δ values are anchored to the VSMOW-SLAP (Vienna Standard Mean Ocean Water-Standard Light Antarctic Precipitation) scale through direct measurement of the primary water RMs VSMOW2 and SLAP2. The previous NGS RM gases (RM8559, RM8560, and RM8561) were analyzed concurrently to directly tie the new RM gases to historical RMs. Compared to the discontinued NGS RMs, the new HCG RMs provide expanded ranges of stable carbon and hydrogen δ values for hydrocarbon gas analysis. The HCG RMs are now available for purchase by the public.

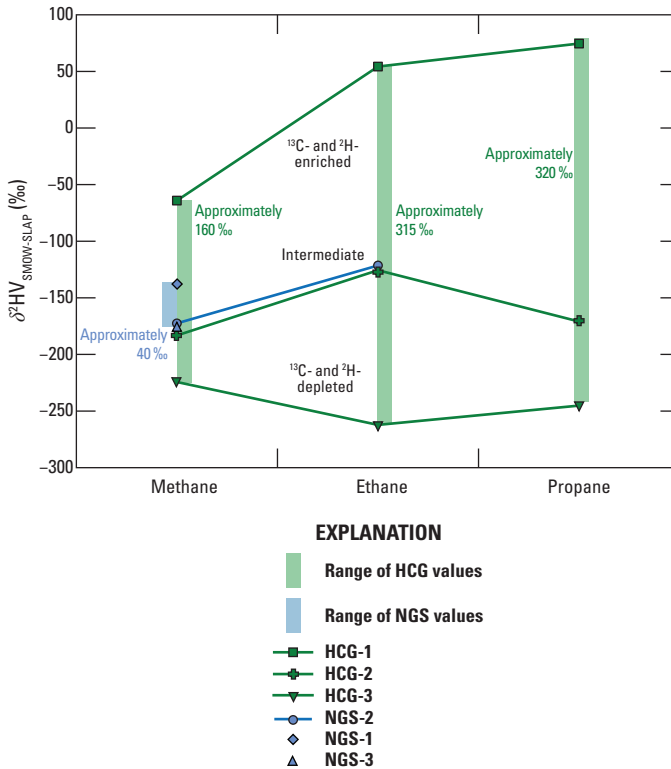


Figure 4. Graph showing comparison of the stable hydrogen isotopic composition (VSMOW) of the U.S. Geological Survey HCG and the NGS reference materials (RM8559, RM8560, and RM8561). Data for the NGS gases are from Hut (1987). Note no reference hydrogen-2/hydrogen-1 ($\delta^2\text{H}$) values were provided by National Institute of Standards and Technology (NIST; Wise and Watters, 2007). Green and blue bars represent the approximate ranges of isotopic values covered by the HCG and NGS RMs, respectively. [^{13}C , carbon-13; ^2H , hydrogen-2; ‰, per mil; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; VSMOW, Vienna Standard Mean Ocean Water; SLAP, Standard Light Antarctic Precipitation]

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Appendix 1. Stable Isotopic Data Used to Determine Recommended Values

Table 1.1. Stable carbon isotope data from offline preparation and dual-inlet mass spectrometric analysis by U.S. Geological Survey and Isotech Laboratories, Inc., used in the determination of the recommended $\delta^{13}\text{C}$ values for HCG reference materials.[Values reported in units of ‰_{V-PDB} (per mil, Vienna Pee Dee Belemnite). $\delta^{13}\text{C}$, carbon-13/carbon-12; na, not available; SD, standard deviation; n, number of analyses; U_{std} , standard uncertainty; DoF (v), degrees of freedom; %, percent]

| Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder | Methane | Ethane | Propane |
|----------------------------|---------|--------|---------|---------------------------|---------|--------|---------|------------------|---------|--------|---------|
| Isotech Laboratories, Inc. | | | | | | | | | | | |
| HCG-1 Mix (d) | -1.62 | -10.25 | -15.57 | HCG-2 Mix (f) | -43.19 | -29.85 | -19.48 | HCG-3 Mix | -61.51 | -45.28 | -36.70 |
| HCG-1 Mix (d) | -1.55 | -10.20 | -15.48 | HCG-2 Mix (f) | -43.19 | -29.82 | -19.42 | HCG-3 Mix | -61.47 | -45.35 | -36.80 |
| HCG-1 Mix (d) | -1.54 | -10.20 | -15.49 | HCG-2 Mix (f) | -43.16 | -29.81 | -19.39 | HCG-3 Mix | -61.51 | -45.41 | -36.89 |
| HCG-1 Mix (e) | -1.46 | -10.26 | -15.58 | HCG-2 Mix (g) | -43.19 | -29.86 | -19.45 | na | na | na | na |
| HCG-1 Mix (e) | -1.41 | -10.24 | -15.54 | HCG-2 Mix (g) | -43.17 | -29.82 | -19.4 | na | na | na | na |
| HCG-1 Mix (e) | -1.41 | -10.21 | -15.50 | HCG-2 Mix (g) | -43.17 | -29.83 | -19.41 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.24 | -15.48 | HCG-2 Pure (a) | -43.28 | -29.86 | -19.34 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.22 | -15.36 | HCG-2 Pure (a) | -43.25 | -29.81 | -19.19 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.16 | -15.31 | HCG-2 Pure (a) | -43.24 | -29.82 | -19.12 | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.24 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.24 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.20 | na | na | na | na | na | na |
| Average | -1.50 | -10.22 | -15.48 | Average | -43.21 | -29.83 | -19.36 | Average | -61.50 | -45.35 | -36.80 |
| SD | 0.09 | 0.03 | 0.09 | SD | 0.04 | 0.02 | 0.12 | SD | 0.02 | 0.07 | 0.1 |
| <i>n</i> | 6 | 9 | 9 | <i>n</i> | 12 | 9 | 9 | <i>n</i> | 3 | 3 | 3 |
| U_{std} | 0.035 | 0.010 | 0.03 | U_{std} | 0.011 | 0.007 | 0.040 | U_{std} | 0.013 | 0.038 | 0.055 |
| DoF (v) | 5 | 8 | 8 | DoF (v) | 11 | 8 | 8 | DoF (v) | 2 | 2 | 2 |
| U.S. Geological Survey | | | | | | | | | | | |
| HCG-1 Mix (d) | -1.57 | -10.18 | -15.42 | HCG-2 Mix (f) | -43.00 | -29.74 | -19.38 | HCG-3 Mix | -61.26 | -45.27 | -36.78 |
| HCG-1 Mix (d) | -1.59 | -10.22 | -15.48 | HCG-2 Mix (f) | -43.05 | -29.74 | -19.40 | HCG-3 Mix | -61.32 | -45.28 | -36.80 |
| HCG-1 Mix (d) | -1.61 | -10.22 | -15.42 | HCG-2 Mix (f) | -43.06 | -29.75 | -19.43 | HCG-3 Mix | -61.26 | -45.24 | -36.81 |
| HCG-1 Mix (e) | -1.48 | -10.24 | -15.47 | HCG-2 Mix (e) | -43.03 | -29.75 | -19.34 | na | na | na | na |
| HCG-1 Mix (e) | -1.44 | -10.19 | -15.49 | HCG-2 Mix (e) | -43.03 | -29.73 | -19.39 | na | na | na | na |
| HCG-1 Mix (e) | -1.48 | -10.22 | -15.46 | HCG-2 Mix (e) | -43.01 | -29.72 | -19.39 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.21 | -15.29 | HCG-2 Pure (a) | -42.95 | -29.80 | -19.25 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.27 | -15.28 | HCG-2 Pure (a) | -42.97 | -29.80 | -19.30 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.22 | -15.29 | HCG-2 Pure (a) | -43.00 | -29.85 | -19.32 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.21 | -15.31 | HCG-2 Pure (a) | -43.04 | -29.81 | -19.29 | na | na | na | na |
| HCG-1 Pure (a) | na | -10.22 | -15.35 | HCG-2 Pure (a) | -43.05 | -29.83 | -19.33 | na | na | na | na |

Table 1.1. Stable carbon isotope data from offline preparation and dual-inlet mass spectrometric analysis by U.S. Geological Survey and Isotech Laboratories, Inc., used in the determination of the recommended $\delta^{13}\text{C}$ values for HCG reference materials.—Continued[Values reported in units of ‰_{V-PDB} (per mil, Vienna Pee Dee Belemnite). $\delta^{13}\text{C}$, carbon-13/carbon-12; na, not available; SD, standard deviation; n, number of analyses; U_{std} , standard uncertainty; DoF (ν), degrees of freedom; ‰, percent]

| Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder | Methane | Ethane | Propane |
|--|---------|--------|---------|---------------------------|---------|--------|---------|------------------|---------|--------|---------|
| U.S. Geological Survey—Continued | | | | | | | | | | | |
| HCG-1 Pure (a) | na | -10.20 | -15.39 | HCG-2 Pure (a) | -43.01 | -29.83 | -19.30 | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.02 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.01 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -42.99 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.01 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.04 | na | na | na | na | na | na |
| na | na | na | na | HCG-2 Pure (b) | -43.05 | na | na | na | na | na | na |
| Average | -1.53 | -10.22 | -15.39 | Average | -43.02 | -29.78 | -19.34 | Average | -61.28 | -45.26 | -36.80 |
| SD | 0.07 | 0.02 | 0.08 | SD | 0.03 | 0.05 | 0.05 | SD | 0.03 | 0.02 | 0.02 |
| <i>n</i> | 6 | 12 | 12 | <i>n</i> | 18 | 12 | 12 | <i>n</i> | 3 | 3 | 3 |
| U_{std} | 0.028 | 0.007 | 0.023 | U_{std} | 0.007 | 0.013 | 0.015 | U_{std} | 0.018 | 0.012 | 0.010 |
| DoF (ν) | 5 | 11 | 11 | DoF (ν) | 17 | 11 | 11 | DoF (ν) | 2 | 2 | 2 |
| Between method uncertainty | | | | | | | | | | | |
| <i>u</i> (B) | 0.0091 | 0.0011 | 0.0264 | <i>u</i> (B) | 0.0554 | 0.0148 | 0.0036 | <i>u</i> (B) | 0.0624 | 0.0238 | 0.0004 |
| ν_{B} | 1 | 6 | 1 | ν_{B} | 130 | 20 | 0 | ν_{B} | 53 | 2 | 0 |
| Combined uncertainties | | | | | | | | | | | |
| <i>u</i> (C) | 0.022 | 0.006 | 0.019 | <i>u</i> (C) | 0.006 | 0.007 | 0.022 | <i>u</i> (C) | 0.011 | 0.020 | 0.028 |
| ν_{C} | 10 | 15 | 16 | ν_{C} | 19 | 16 | 10 | ν_{C} | 4 | 2 | 2 |
| Sum of uncertainties | | | | | | | | | | | |
| <i>u</i> (S) | 0.024 | 0.006 | 0.033 | <i>u</i> (S) | 0.056 | 0.017 | 0.022 | <i>u</i> (S) | 0.063 | 0.031 | 0.028 |
| ν_{S} | 11 | 15 | 2 | ν_{S} | 134 | 30 | 11 | ν_{S} | 55 | 4 | 2 |
| Total uncertainty | | | | | | | | | | | |
| <i>u</i> (T) | 0.044 | 0.038 | 0.050 | <i>u</i> (T) | 0.067 | 0.041 | 0.043 | <i>u</i> (T) | 0.074 | 0.049 | 0.047 |
| ν_{T} | 11 | 7 | 8 | ν_{T} | 53 | 9 | 11 | ν_{T} | 49 | 10 | 8 |
| Coverage factor <i>k</i> (95% confidence level) ² | | | | | | | | | | | |
| <i>k</i> | 2.20 | 2.36 | 2.31 | <i>k</i> | 2.01 | 2.26 | 2.20 | <i>k</i> | 2.01 | 2.23 | 2.31 |
| Expanded uncertainty | | | | | | | | | | | |
| U_{e} | 0.10 | 0.09 | 0.11 | U_{e} | 0.14 | 0.09 | 0.10 | U_{e} | 0.15 | 0.11 | 0.11 |

¹Letters in parentheses indicate the gas cylinder identifier.²Coverage factors obtained from Taylor and Kuyatt, 1994, table B1.

Table 1.2. Stable hydrogen isotope data from offline preparation and dual-inlet mass spectrometric analysis by U.S. Geological Survey and Isotech Laboratories, Inc., used in the determination of the recommended $\delta^2\text{H}$ values for HCG reference materials.

[Values are reported in units of ‰_{VSMOW} (per mil, Vienna Standard Mean Ocean Water). $\delta^2\text{H}$, hydrogen-2/hydrogen-1; na, not available; SD, standard deviation; n, number of analyses; U_{std} , standard uncertainty; DoF (v), degrees of freedom; %, percent]

| Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder | Methane | Ethane | Propane |
|----------------------------|---------|--------|---------|---------------------------|---------|---------|---------|------------------|---------|---------|---------|
| Isotech Laboratories, Inc. | | | | | | | | | | | |
| HCG-1 Mix (d) | -61.2 | +56.9 | +70.1 | HCG-2 Mix (f) | -189.4 | -127.4 | -169.1 | HCG-3 Mix | -226.8 | -263.8 | -243.4 |
| HCG-1 Mix (d) | -62.9 | +57.8 | +77.0 | HCG-2 Mix (f) | -187.7 | -127.1 | -170.8 | HCG-3 Mix | -227.8 | -264.5 | -245.8 |
| HCG-1 Mix (d) | -59.1 | +61.6 | +72.9 | HCG-2 Mix (f) | -188.1 | -125.8 | -170.6 | HCG-3 Mix | -226.6 | -264.8 | -249.3 |
| HCG-1 Mix (e) | -63.1 | +57.0 | +76.3 | HCG-2 Mix (g) | -186.2 | -125.9 | -169.2 | na | na | na | na |
| HCG-1 Mix (e) | -60.4 | +59.9 | +84.2 | HCG-2 Mix (g) | -188.3 | -127.2 | -171.7 | na | na | na | na |
| HCG-1 Mix (e) | -61.7 | +59.2 | +81.8 | HCG-2 Mix (g) | -189.3 | -126.5 | -171.7 | na | na | na | na |
| HCG-1 Pure (a) | na | +58.9 | +77.4 | HCG-2 Pure (a) | -186.6 | -121.9 | -174.3 | na | na | na | na |
| HCG-1 Pure (a) | na | +55.2 | +81.5 | HCG-2 Pure (a) | -185.8 | -124.4 | -173.3 | na | na | na | na |
| HCG-1 Pure (a) | na | +59.5 | +81.8 | HCG-2 Pure (a) | -188.6 | -124.4 | -174.2 | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -187.8 | na | na | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -187.8 | na | na | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -190.1 | na | na | na | na | na | na |
| Average | -61.40 | +58.44 | +78.11 | Average | -187.98 | -125.62 | -171.66 | Average | -227.07 | -264.37 | -246.17 |
| SD | 1.52 | 1.92 | 4.64 | SD | 1.30 | 1.79 | 1.96 | SD | 0.64 | 0.51 | 2.97 |
| <i>n</i> | 6 | 9 | 9 | <i>n</i> | 12 | 9 | 9 | <i>n</i> | 3 | 3 | 3 |
| U_{std} | 0.621 | 0.639 | 1.546 | U_{std} | 0.377 | 0.596 | 0.652 | U_{std} | 0.371 | 0.296 | 1.713 |
| <i>DoF</i> | 5 | 8 | 8 | <i>DoF</i> | 11 | 8 | 8 | <i>DoF</i> | 2 | 2 | 2 |
| U.S. Geological Survey | | | | | | | | | | | |
| HCG-1 Mix (d) | -67.4 | +48.0 | +65.5 | HCG-2 Mix (f) | -187.2 | -129.3 | -172.1 | HCG-3 Mix | -220.1 | -259.6 | -242.7 |
| HCG-1 Mix (d) | -66.3 | +48.7 | +61.2 | HCG-2 Mix (f) | -188.0 | -128.3 | -170.2 | HCG-3 Mix | -223.4 | -258.4 | -245.1 |
| HCG-1 Mix (d) | -66.6 | +49.0 | +61.1 | HCG-2 Mix (f) | na | -128.1 | -173.0 | HCG-3 Mix | -221.4 | na | -244.8 |
| HCG-1 Mix (e) | -66.7 | +47.2 | +68.0 | HCG-2 Mix (e) | -186.1 | -126.9 | -172.5 | na | na | na | na |
| HCG-1 Mix (e) | -68.8 | +47.7 | +64.6 | HCG-2 Mix (e) | -188.3 | -126.3 | -170.4 | na | na | na | na |
| HCG-1 Mix (e) | -64.3 | +48.5 | na | HCG-2 Mix (e) | -183.4 | -123.9 | -171.3 | na | na | na | na |
| HCG-1 Pure (a) | na | +51.4 | na | HCG-2 Pure (a) | -175.4 | -125.5 | na | na | na | na | na |
| HCG-1 Pure (a) | na | +52.6 | +78.7 | HCG-2 Pure (a) | -177.0 | -123.8 | -166.4 | na | na | na | na |
| HCG-1 Pure (a) | na | +53.6 | +79.6 | HCG-2 Pure (a) | -175.1 | -123.9 | -170.1 | na | na | na | na |
| HCG-1 Pure (a) | na | +56.3 | na | HCG-2 Pure (a) | -175.8 | -124.2 | -168.1 | na | na | na | na |
| HCG-1 Pure (a) | na | +55.9 | +80.8 | HCG-2 Pure (a) | -178.1 | -123.4 | -171.1 | na | na | na | na |

Table 1.2. Stable hydrogen isotope data from offline preparation and dual-inlet mass spectrometric analysis by U.S. Geological Survey and Isotech Laboratories, Inc., used in the determination of the recommended $\delta^2\text{H}$ values for HCG reference materials.—Continued

[Values are reported in units of ‰_{VSMOW} (per mil, Vienna Standard Mean Ocean Water). $\delta^2\text{H}$, hydrogen-2/hydrogen-1; na, not available; SD, standard deviation; n, number of analyses; U_{std} , standard uncertainty; DoF (ν), degrees of freedom; %, percent]

| Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder ¹ | Methane | Ethane | Propane | Gas cylinder | Methane | Ethane | Propane |
|---|---------|--------|---------|---------------------------|---------|---------|---------|------------------|---------|---------|---------|
| U.S. Geological Survey—Continued | | | | | | | | | | | |
| HCG-1 Pure (a) | na | +55.3 | +80.6 | HCG-2 Pure (a) | -177.0 | -123.7 | -169.3 | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -175.7 | na | na | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -176.4 | na | na | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -177.0 | na | na | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -176.8 | na | na | na | na | na | na |
| HCG-1 Pure (b) | na | na | na | HCG-2 Pure (b) | -176.1 | na | na | na | na | na | na |
| Average | -66.69 | +51.17 | +71.11 | Average | -179.59 | -125.60 | -170.42 | Average | -221.60 | -258.97 | -244.18 |
| SD | 1.46 | 3.44 | 8.63 | SD | 5.05 | 2.11 | 1.94 | SD | 1.65 | 0.86 | 1.33 |
| <i>n</i> | 6 | 12 | 9 | <i>n</i> | 16 | 12 | 11 | <i>n</i> | 3 | 2 | 3 |
| U_{std} | 0.595 | 0.993 | 2.878 | U_{std} | 1.262 | 0.608 | 0.585 | U_{std} | 0.955 | 0.607 | 0.769 |
| <i>DoF</i> | 5 | 11 | 8 | <i>DoF</i> | 15 | 11 | 10 | <i>DoF</i> | 2 | 1 | 2 |
| Between method uncertainty | | | | | | | | | | | |
| $u(\text{B})$ | 1.5261 | 2.0988 | 2.0199 | $u(\text{B})$ | 2.4195 | 0.0050 | 0.3579 | $u(\text{B})$ | 1.5770 | 1.5572 | 0.5741 |
| ν_{B} | 19 | 19 | 2 | ν_{B} | 20 | 0 | 1 | ν_{B} | 14 | 32 | 1 |
| Combined uncertainties | | | | | | | | | | | |
| $u(\text{C})$ | 0.430 | 0.590 | 1.634 | $u(\text{C})$ | 0.659 | 0.426 | 0.438 | $u(\text{C})$ | 0.512 | 0.338 | 0.939 |
| ν_{C} | 10 | 18 | 12 | ν_{C} | 18 | 19 | 17 | ν_{C} | 3 | 1 | 3 |
| Sum of uncertainties | | | | | | | | | | | |
| $u(\text{S})$ | 1.586 | 2.180 | 2.598 | $u(\text{S})$ | 2.508 | 0.426 | 0.565 | $u(\text{S})$ | 1.658 | 1.593 | 1.100 |
| ν_{S} | 22 | 22 | 6 | ν_{S} | 23 | 19 | 6 | ν_{S} | 16 | 33 | 3 |
| Total uncertainty | | | | | | | | | | | |
| $u(\text{T})$ | 1.847 | 2.377 | 2.765 | $u(\text{T})$ | 2.681 | 1.039 | 1.104 | $u(\text{T})$ | 1.910 | 1.854 | 1.452 |
| ν_{T} | 31 | 29 | 7 | ν_{T} | 29 | 14 | 15 | ν_{T} | 24 | 43 | 8 |
| Coverage factor k (95% confidence level) ² | | | | | | | | | | | |
| k | 2.14 | 2.05 | 2.36 | k | 2.05 | 2.14 | 2.45 | k | 2.07 | 2.02 | 2.31 |
| Expanded uncertainty | | | | | | | | | | | |
| U_e | 4.0 | 4.9 | 6.5 | U_e | 5.5 | 2.2 | 2.7 | U_e | 4.0 | 3.7 | 3.4 |

¹Letters in parentheses indicate the gas cylinder identifier.

²Coverage factors obtained from Taylor and Kuyatt, 1994, table B1.

Appendix 2. Additional Data

Table 2.1. Results of the analysis of the reference materials NGS-1, NGS-2, and NGS-3 (RM8559, RM8560, and RM8561).

[nd, not determined; NGS-3 was not analyzed for ethane or propane, because the concentrations were too low. $\delta^{13}\text{C}$, carbon-13/carbon-12; ‰_{VPDB-LSVEC}, per mil Vienna Peedee Belemnite LSVEC; Isotech, Isotech Laboratories, Inc.; USGS, U.S. Geological Survey; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; ‰_{VSMOW-SLAP}, per mil Vienna Standard Mean Ocean Water Standard Light Antarctic Precipitation]

| Laboratory | NGS-1 | | | NGS-2 | | | NGS-3 | | |
|--|---------|--------|---------|---------|--------|---------|---------|--------|---------|
| | Methane | Ethane | Propane | Methane | Ethane | Propane | Methane | Ethane | Propane |
| $\delta^{13}\text{C}$ (‰ _{VPDB-LSVEC}) | | | | | | | | | |
| Isotech | -29.03 | -25.93 | -22.18 | -44.79 | -31.89 | -25.31 | -73.23 | nd | nd |
| Isotech | -29.03 | -25.93 | -22.12 | -44.80 | -31.91 | -25.29 | -73.21 | nd | nd |
| Isotech | -29.02 | -25.92 | -22.09 | -44.80 | -31.93 | -25.28 | -73.19 | nd | nd |
| USGS | -28.93 | -25.86 | -21.98 | -44.58 | -31.77 | -25.20 | -72.89 | nd | nd |
| USGS | -28.92 | -25.82 | -22.01 | -44.61 | -31.80 | -25.23 | -72.90 | nd | nd |
| USGS | -28.93 | -25.81 | -22.00 | -44.59 | -31.80 | -25.20 | -72.92 | nd | nd |
| $\delta^2\text{H}$ (‰ _{VSMOW-SLAP}) | | | | | | | | | |
| Isotech | -141.3 | -109.9 | -76.9 | -180.0 | -124.6 | -110.6 | -177.5 | nd | nd |
| Isotech | -141.8 | -112.1 | -74.9 | -182.3 | -124.0 | -110.9 | -179.1 | nd | nd |
| Isotech | -142.9 | -113.7 | -73.3 | -181.7 | -123.5 | -107.8 | -181.6 | nd | nd |
| USGS | -141.0 | -113.5 | -73.2 | -179.9 | -126.7 | -111.6 | -179.3 | nd | nd |
| USGS | -142.4 | -117.2 | -75.0 | -177.3 | -126.3 | -112.3 | -177.6 | nd | nd |
| USGS | -145.8 | -115.1 | -77.1 | -178.1 | -124.5 | -113.2 | -177.8 | nd | nd |

22 Development of Hydrocarbon Gas Reference Materials for Stable Isotopic Composition ($\delta^{13}\text{C}$ and $\delta^2\text{H}$)

Table 2.2. Raw (that is, unscaled) $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values for the analyses of the primary reference materials LSVEC, NBS 19, VSMOW2, and SLAP2.

[nd, not determined due to limited number of replicate analyses. $\delta^{13}\text{C}$, carbon-13/carbon-12; ‰, per mil; $\delta^2\text{H}$, hydrogen-2/hydrogen-1; USGS, U.S. Geological Survey; SD, standard deviation; n , number of analyses; U_{std} , standard uncertainty; DoF (ν), degrees of freedom; U , uncertainty; v , variance; $u(C)$, combined uncertainty; ν_C , variance on combined uncertainty; na, not applicable]

| Laboratory | Reference materials | | | |
|----------------|---------------------------|--------|------------------------|---------|
| | $\delta^{13}\text{C}$ (‰) | | $\delta^2\text{H}$ (‰) | |
| | LSVEC | NBS 19 | VSMOW2 | SLAP2 |
| USGS | -47.070 | 1.880 | 0.82 | -415.87 |
| USGS | -47.069 | 1.907 | 0.79 | -412.19 |
| USGS | -47.040 | 1.868 | -0.27 | -415.87 |
| USGS | -46.961 | 1.895 | -0.35 | -414.93 |
| USGS | -46.891 | 1.886 | 1.69 | -418.09 |
| USGS | -46.865 | 1.921 | 0.53 | -416.37 |
| USGS | -46.844 | 1.853 | -0.29 | nd |
| USGS | nd | 1.865 | -0.75 | nd |
| USGS | nd | 1.887 | nd | nd |
| USGS | nd | 1.889 | nd | nd |
| USGS | nd | 1.855 | nd | nd |
| USGS | nd | 1.889 | nd | nd |
| USGS | nd | 1.900 | nd | nd |
| Average | -46.963 | 1.884 | 0.27 | -415.55 |
| SD | 0.098 | 0.020 | 0.82 | 1.95 |
| n | 7 | 13 | 8 | 6 |
| U_{std} | 0.037 | 0.006 | 0.29 | 0.80 |
| DoF (ν) | 6 | 12 | 7 | 5 |
| Assigned U | 0 | 0 | 0.3 | 0.3 |
| Assigned ν | na | na | 100 | 100 |
| $u(C)$ | na | na | 0.42 | 0.85 |
| ν_C | na | na | 28 | 7 |

Table 2.3. Results of analyses of pure methane that was used in the preparation of HCG-1. The data were not used in the determination of the recommended $\delta^{13}\text{C}$ values.

[$\delta^{13}\text{C}$, (carbon-13/carbon-12); ‰, per mil; $\delta^2\text{H}$, (hydrogen-2/hydrogen-1); Isotech, Isotech Laboratories, Inc.; USGS, U.S. Geological Survey]

| Laboratory | Pure methane (a) | | Pure methane (b) | |
|------------|---------------------------|------------------------|---------------------------|------------------------|
| | $\delta^{13}\text{C}$ (‰) | $\delta^2\text{H}$ (‰) | $\delta^{13}\text{C}$ (‰) | $\delta^2\text{H}$ (‰) |
| Isotech | 2.35 | -64.6 | 2.40 | -66.5 |
| Isotech | 2.38 | -64.8 | 2.47 | -63.8 |
| Isotech | 2.41 | -64.2 | 2.47 | -65.1 |
| USGS | 2.43 | -60.2 | 2.46 | -56.1 |
| USGS | 2.43 | -58.8 | 2.53 | -58.0 |
| USGS | 2.40 | -57.4 | 2.52 | -58.9 |
| USGS | 2.45 | -59.2 | 2.47 | -58.0 |
| USGS | 2.46 | -57.7 | 2.51 | -55.9 |
| USGS | 2.46 | -58.2 | 2.50 | -51.5 |

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