

# Navigating Challenges for Isotope Ratio Measurements of Greenhouse Gases



Michelle M.G. Chartrand

Research Officer, Metrology Research Centre  
National Research Council Canada  
Ottawa, ON, K1A 0R6, Canada

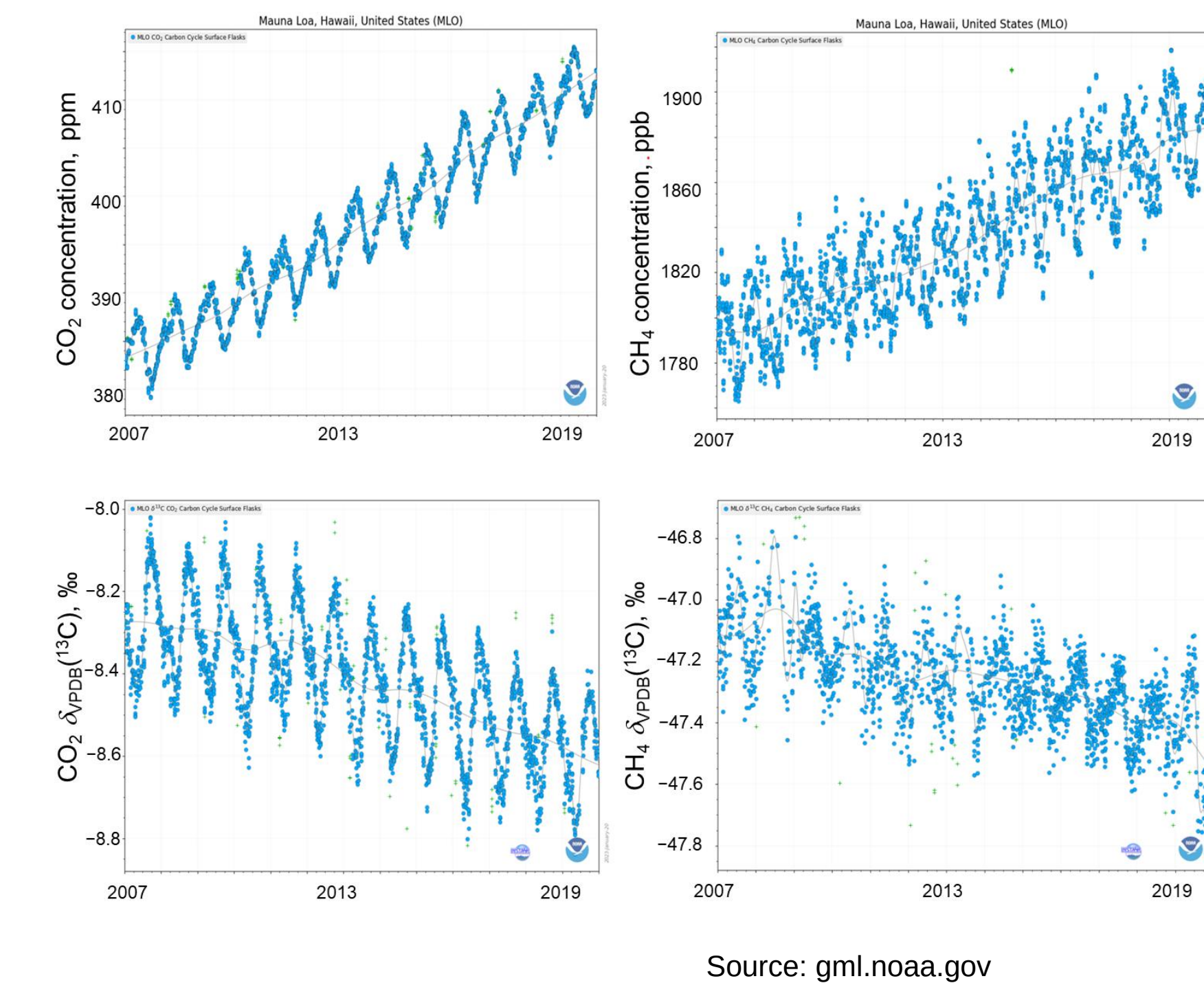
## Introduction

The potential for human activities to affect the climate was first mentioned at the United Nations Scientific Conference in 1972. More recently, climate change, defined as long-term changes in temperature and weather patterns, has emerged as an urgent global issue. Atmospheric studies have identified increasing concentrations of greenhouse gases as the primary driver of climate change. This led to the 2005 Kyoto Protocol, which aimed to reduce anthropogenic greenhouse gas emissions in industrialized countries, and the 2016 Paris Agreement, with the main goal of restricting the increase in global temperature to no more than 1.5 °C above pre-industrial levels.

Before we can reduce anthropogenic greenhouse gas emissions, we need to first identify the sources of these emissions, a challenging task given the complexity of the global atmospheric cycle. Carbon isotope ratio ( $^{13}\text{C}/^{12}\text{C}$ ) analysis is an important measurement used to distinguish between the different sources of these gases. This technique is based on small, but measurable, differences in the isotopic signatures of both anthropogenic and natural sources of these gases, and require measurements of the highest precision. Metrology has an important role in climate studies, as reliable measurements are required for good policy decisions. The World Meteorological Organization (WMO) identified several challenges for isotopic measurements, and the reliability of reference materials (RMs) is considered to be a main priority. To ensure comparability of measurements obtained from different laboratories, the WMO has established the rigorous inter-laboratory data comparability goals, which laboratories providing atmospheric measurements is striving to achieve.

## Greenhouse gas measurements

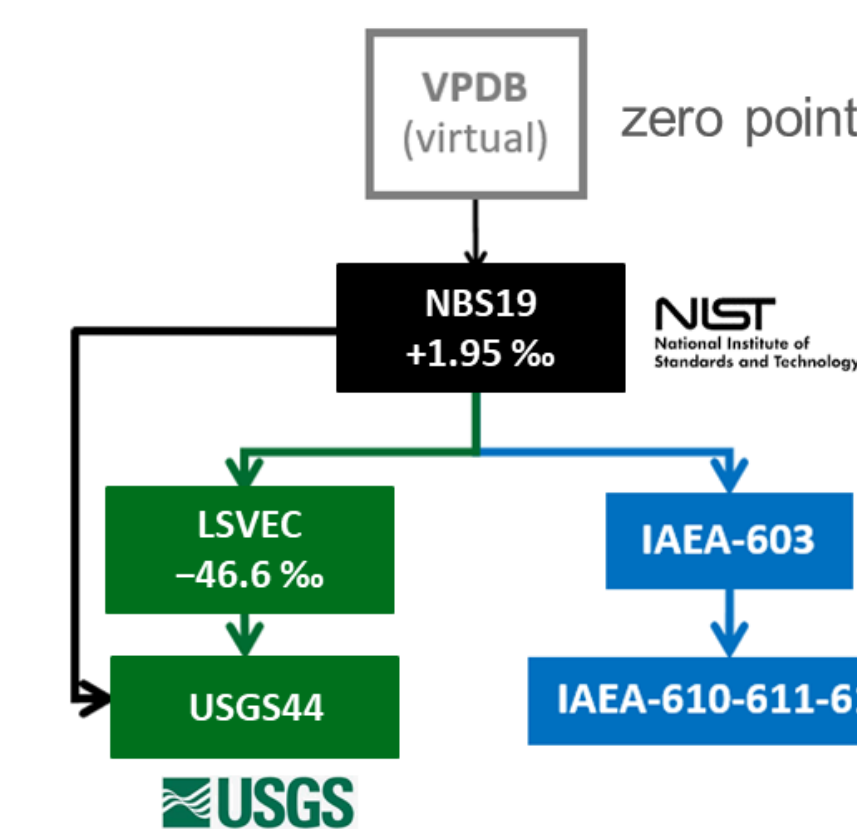
Most climate change research has focused on carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ), and their concentrations and carbon isotope ratios have been monitored for decades. Evaluation of the long-term trends in carbon isotope ratios of these gases can help monitor changes in anthropogenic emissions, and contribute to science-based policy and decision-making.



**Figure 1.** As concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  increase, the carbon isotope ratio values of these gases shift to more negative values. For  $\text{CO}_2$ , this is primarily due to increased burning of fossil fuels. The relative contribution of  $\text{CH}_4$  from natural sources such as microbial production from wetlands, as well as anthropogenic sources such as oil and natural gas production, agriculture, and decomposing waste, are less understood.

## Carbon isotope delta scale definition

Carbon isotope ratios, which is the relative difference in the carbon isotope ratio between the sample and a reference material, are expressed as carbon isotope-delta values, denoted as  $\delta^{13}\text{C}$ . These delta values are reported on an internationally agreed-upon scale relative to the Vienna Pee Dee Belemnite (VPDB), which serves as the zero-point of the scale. VPDB is a virtual material and cannot be directly measured. As such, the VPDB scale is defined by assigning an exact value of +1.95 ‰ to the carbonate RM NBS19. To improve inter-laboratory comparability, a second anchor point, LSVEC, also a carbonate RM, with an exact value of -46.6 ‰, was introduced to the VPDB scale definition in 2006.

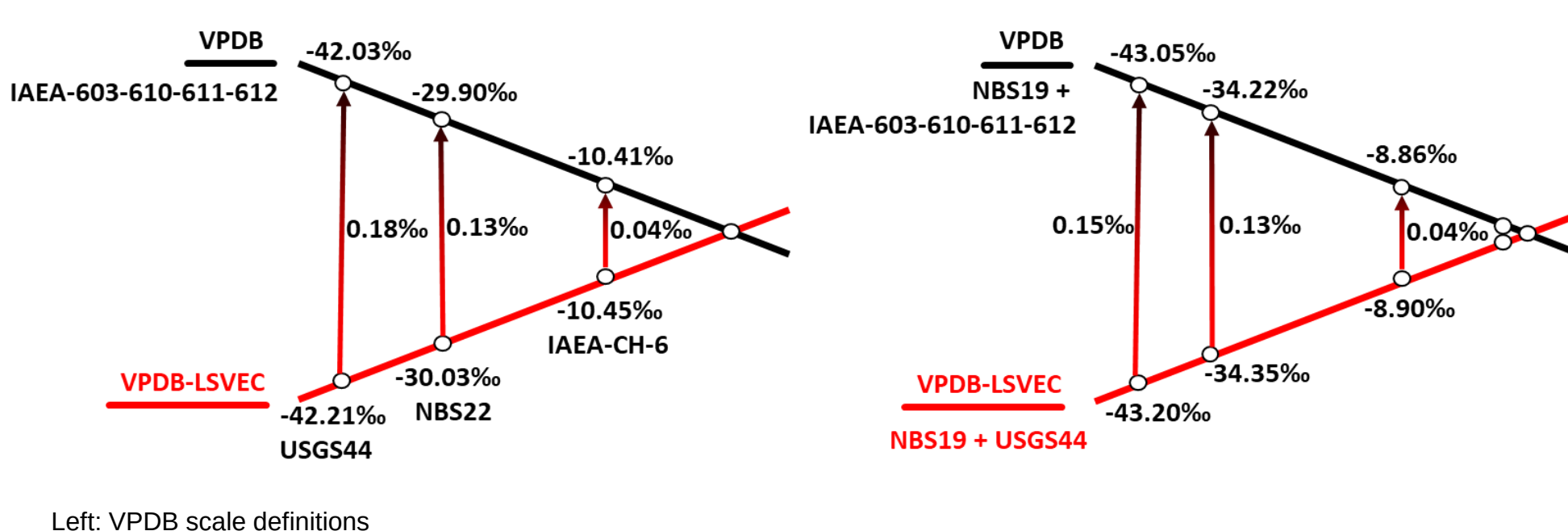


**Figure 2.** Traceability of select RMs to the VPDB. Since 2006, many organic RMs were calibrated using NBS19 and LSVEC. Due to the near exhaustion of NBS19, the IAEA released the RM IAEA-603, a similar carbonate material to replace NBS19, as well as a suite of carbonate materials, IAEA-610, IAEA-611 and IAEA-612, all traceable to NBS19 alone. The USGS also released its own carbonate RM, USGS44, is traceable to both NBS19 and LSVEC.

Beginning in 2016, researchers reported inconsistencies in the measured carbon isotope delta value of LSVEC, which called into question the reliability of the VPDB scale.

## Systematic bias between scale definitions

The suite of RMs released by the International Atomic Energy Agency (IAEA) allows for more than one realization of the VPDB carbon isotope delta scale: one using RMs traceable to NBS19 and LSVEC, and a second traceable to NBS19 only. In collaboration with NRC, Hélie *et al* measured several international RMs using an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS), and calibrated them to the two different scale realizations. The systematic bias observed between the two scale realizations (Fig. 3) is amplified at increasingly negative carbon isotope delta values.



**Figure 3.** Results from two studies reporting the differences in carbon isotope delta values between the VPDB scale realization including LSVEC (red line), and one not including LSVEC (black line). A systematic bias is observed in both studies, with more pronounced differences with increasingly negative carbon isotope delta values. Fig. 3 left: Study using EA-IRMS to calibrate RMs using two VPDB scale definition. Fig. 3 right: Study showing a similar bias in four  $\text{CO}_2$  samples analyzed by DI-IRMS.

The NRC participated in the CCQM-P204 study, measuring the carbon isotope delta values in four pure  $\text{CO}_2$  samples via dual inlet (DI)-IRMS (Fig. 3 right). The  $\text{CO}_2$  samples were reported on both VPDB scale realizations, and a nearly identical bias to the Hélie *et al* study was observed. This study provided further conformation of the discontinuity between the two VPDB scale realizations.

## Two carbon isotope delta scales

In 2018, the International Union of Pure and Applied Chemistry (IUPAC) recommended the discontinuation of LSVEC as a scale defining RM. Multiple studies have suggested that the original carbon isotope delta value was incorrect, and -46.4 ‰ may be closer to the true value. The re-assignment of the carbon isotope delta values of RMs to the VPDB scale realized by NBS19 only, and the dissemination of this change to the isotope the isotope community, would be a challenging task. After much discussion, an outcome of the 2024 IAEA Experts Meeting was the acknowledgement of two carbon isotope delta scales:

VPDB:  $\delta^{13}\text{C}$  value of NBS19 is exactly +1.95 ‰

VPDB-LSVEC:  $\delta^{13}\text{C}$  value of NBS19 is exactly +1.95 ‰ and  $\delta^{13}\text{C}$  value of LSVEC is exactly -46.6 ‰

The Hélie *et al* study provided an equation to convert carbon isotope delta values between the VPDB and VPDB-LSVEC scales.

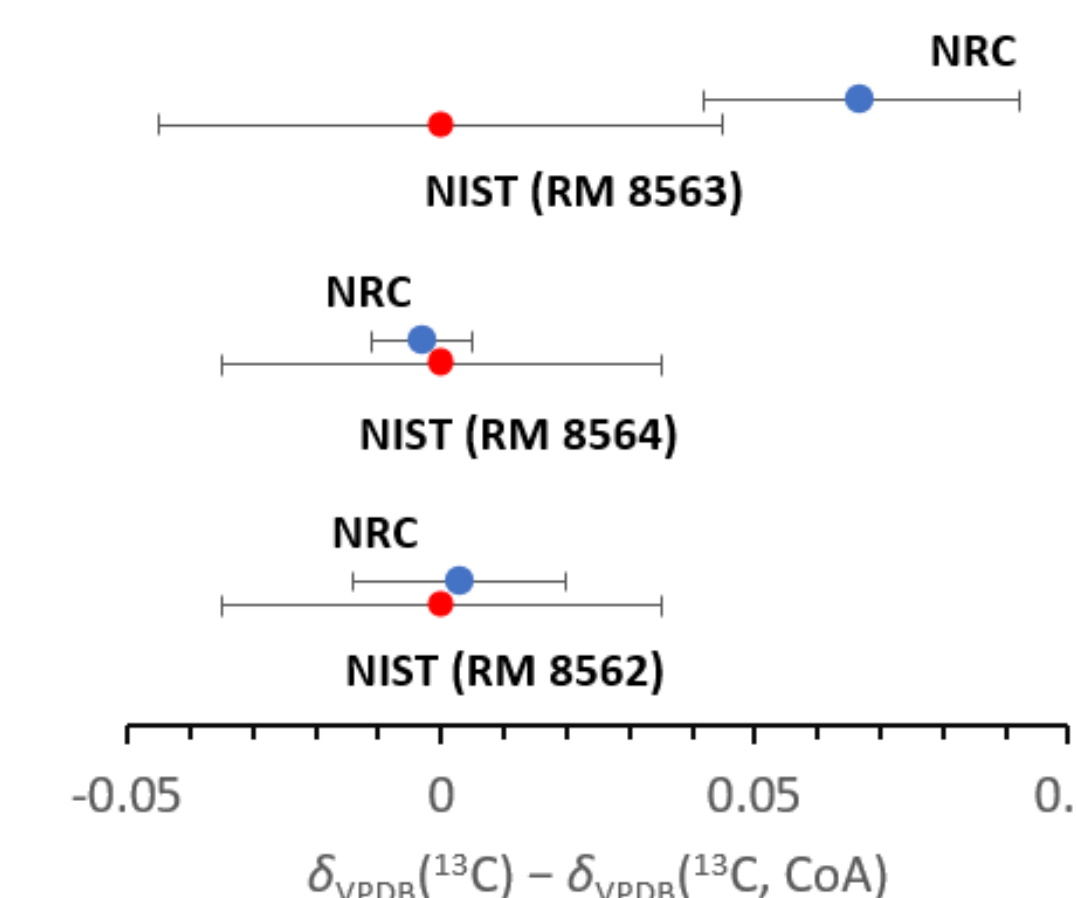
## Impact of two scales in atmospheric science

The WMO has established an extended inter-laboratory data comparability goal of  $\pm 0.02$  ‰ for carbon isotope delta measurements. A main reason why this goal has not been met for atmospheric  $\text{CO}_2$  measurements is the reliability of RMs.

## $\text{CO}_2$ measurements

While the use of optical spectroscopic methods are gaining traction, most isotopic measurements of atmospheric  $\text{CO}_2$  samples are analyzed using DI-IRMS, a technique that requires the calibrating RMs to be  $\text{CO}_2$  gas. The only suitable RM available at the time atmospheric monitoring programs began was NBS19, and  $\text{CO}_2$  was evolved from this carbonate material via acid reaction. The atmospheric monitoring community did not use LSVEC traceable RMs, presumably for continued calibration continuity. The current average carbon isotope delta value of atmospheric  $\text{CO}_2$  is approx. -8.7 ‰. Had they made the switch, it may have introduced a bias of approx. 0.04 ‰ (Fig. 3).

Recently, several high-quality reference materials traceable to NBS19 or IAEA-603 have been prepared. However, there is a lack of independent measurements of these materials, prompting NRC to analyze the set of three NIST pure  $\text{CO}_2$  RMs 8562, 8564 and 8563. These RMs were calibrated against in-house  $\text{CO}_2$  reference gases traceable to NBS19 only. Figure 4 plots the difference in  $\delta_{\text{VPDB}}^{13}\text{C}$  values between those reported on the most recent NIST Certificate of Analysis (CoA), and the values measured at IAEA and NRC, for the three pure  $\text{CO}_2$  gases. All measurements are in excellent agreement within their stated uncertainties, and NRC provided independent corroboration of the  $\delta_{\text{VPDB}}^{13}\text{C}$  values reported by NIST.



**Figure 4.** The differences between  $\delta_{\text{VPDB}}^{13}\text{C}$  values reported on the NIST CoA (red) to measurements from NRC (blue) for NIST  $\text{CO}_2$  RMs 8562, 8564 and 8563. All measurements are reported on the VPDB scale, and error bars are  $k = 1$ .

## $\text{CH}_4$ measurements

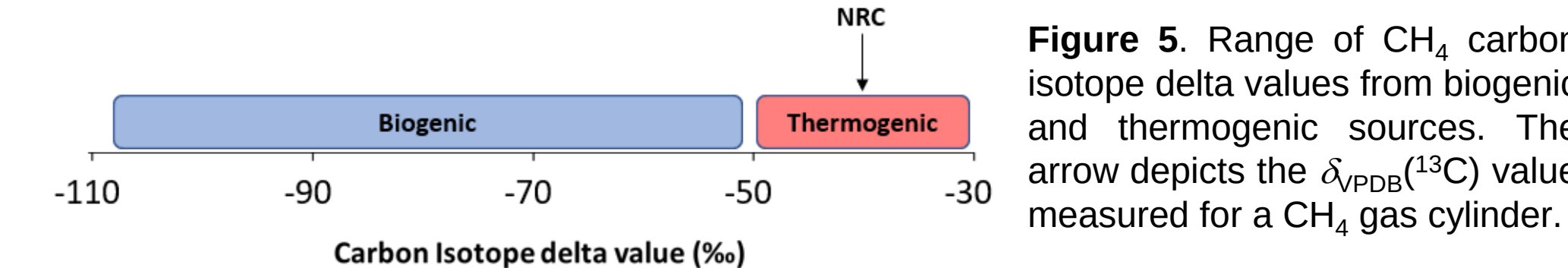
Both the carbon and the hydrogen isotope ratios are important to distinguish between sources of  $\text{CH}_4$ . Carbon isotopic analysis of atmospheric samples using IRMS can be challenging due to the low concentration of  $\text{CH}_4$  in air (1.8 ppm). Additionally,  $\text{CH}_4$  cannot be directly measured and requires conversion to  $\text{CO}_2$ .

A popular alternative to IRMS is optical spectroscopy which is capable of directly measuring  $\text{CH}_4$  at low concentrations. However, IRMS is still needed to provide high-precision isotope delta values for  $\text{CH}_4$  reference gases.

The NRC is a member of a task group to determine the needs and challenges associated with  $\text{CH}_4$  isotope ratio measurements, and several priorities have been identified.

### 1) More diverse $\text{CH}_4$ reference gases are needed

Methane can be formed from several sources, including biogenic and thermogenic processes. Obtaining  $\text{CH}_4$  from these sources would provide the desired range of isotope delta values, however, it remains challenging to locate  $\text{CH}_4$  from biogenic sources.



**Figure 5.** Range of  $\text{CH}_4$  carbon isotope delta values from biogenic and thermogenic sources. The arrow depicts the  $\delta_{\text{VPDB}}^{13}\text{C}$  value measured for a  $\text{CH}_4$  gas cylinder.

The NRC has measured a  $\text{CH}_4$  gas cylinder, with a preliminary  $\delta_{\text{VPDB}}^{13}\text{C}$  of  $-39.67 \pm 0.09$  ‰ (Fig.5). Regrettably, this  $\text{CH}_4$  is from the most commonly available source, thermogenic.

### 2) Unclear traceability for carbon isotope delta measurements

Methane measurements with absent or incomplete information about the traceability to either of the carbon isotope delta scales can often be found in the literature, highlighting the widespread lack of attention paid to measurement scales. With an atmospheric  $\text{CH}_4$  carbon isotope delta value of -47.5 ‰, the bias between the carbon isotope delta scales is approx. 0.2 ‰ (Fig. 3), a whopping ten times larger than the comparability goal set by the WMO.

The  $\text{CH}_4$  gas measurements at NRC provides independent evidence of this bias. The in-house  $\text{CO}_2$  reference gases were calibrated to both the VPDB and VPDB-LSVEC scales, allowing for a direct comparison. The measured difference between the two scales was 0.15 ‰, in agreement with the predicted difference of 0.17 ‰ using the equation from Hélie *et al*.

$$\delta_{\text{VPDB}}^{13}\text{C} = -39.67 \pm 0.09 \text{ ‰}$$

$$\delta_{\text{VPDB-LSVEC}}^{13}\text{C} = -39.82 \pm 0.09 \text{ ‰}$$

## Concluding thoughts

As  $\text{CH}_4$  reference gases are being developed, adopting a single measurement scale could help circumvent the challenges associated with  $\text{CO}_2$  carbon isotope ratio measurements. The task group has advocated to use the VPDB scale, which is used for  $\text{CO}_2$  measurements, thus promoting consistency in atmospheric isotopic measurements. Finally, laboratories are encouraged to evaluate their measurements to verify which carbon isotope delta scale their with  $\text{CH}_4$  reference gases are reported on.

## References

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