United States Geological Survey

Reston Stable Isotope Laboratory

Report of Stable Isotopic Composition

Reference Materials USGS106, USGS107, and USGS108

(Carbon Isotopes in Calcium Formate)

These reference materials (RMs) are intended for normalization [1] of stable carbon ($\delta^{13}C$) measurements of unknown calcium formates [$Ca(HCO_2)_2$] and similarly-behaving carbon-bearing substances. A unit consists of 0.5 g in a glass container. There is no limit on distribution. USGS106, USGS107, and USGS108 calcium formate RMs were developed through a collaboration among David W. Hoffman (University of Texas at Austin), Arndt Schimmelmann (Indiana University, Bloomington), and the U.S. Geological Survey. The preparation of the RMs was carried out by Arndt Schimmelmann.

Recommended values: Stable carbon isotopic compositions are expressed herein as delta values [2] relative to VPDB (Vienna Peedee belemnite) on a scale normalized such that the $\delta^{13}C$ values of NBS 19 limestone and LSVEC lithium carbonate are +1.95 ‰ and –46.6 ‰, respectively [3,4]. The $\delta^{13}C_{VPDB}$ values and the $R(^{13}C/^{12}C)$ ratios are available [5]. The stable carbon-isotope delta values of USGS106, USGS107, and USGS108 calcium formates with combined standard uncertainties ($k = 1$) are:

Reference	$\delta^{13}C_{VPDB\text{-}LSVEC}$	Data source
USGS106	–28.54 ± 0.05 ‰	[5]
USGS107	–10.13 ± 0.03 ‰	[5]
USGS108	+13.84 ± 0.03 ‰	[5]

Technical coordination for these RMs was provided by Arndt Schimmelmann of Indiana University and Haiping Qi of the U.S. Geological Survey Reston Stable Isotope Laboratory (RSIL).

Reston, Virginia 20192
July 2, 2026

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Expiration of Reference Value: The reference values for the isotopic compositions of USGS106, USGS107, and USGS108 are valid until December 31, 2033, provided the RMs are handled in accordance with the instructions given in this Report of Stable Isotopic Composition (see "Instructions for Use"). A reference value is nullified if the RM is damaged, contaminated, or otherwise modified.

Sources of the RM: The following description is taken from Hoffman and others [5]. Three kilograms of BioUltra grade calcium formate $Ca(HCOO)_2$ were obtained from Sigma Aldrich, and formic acid [$R(^{13}C/^{12}C)$ = 0.99 mol/mol] was obtained from Cambridge Isotope Laboratories (Manchester, New Hampshire). The calcium formate was divided into three fractions. Using the validated method described by Schimmelmann et al. [6] for producing isotopically homogeneous materials, calcium formate was dissolved in ultrapure water. One fraction remained unspiked (USGS106). The other two calcium formate solutions were spiked with small amounts of ^{13}C-enriched calcium formate that had been prepared from the ^{13}C-enriched formic acid *via* reaction with pure calcium hydroxide to pH 5.02. The isotopic spikes maintained the calcium/formate molar ratio and produced calcium formate solutions that were enriched in ^{13}C by approximately 18.4 ‰ and 42.4 ‰, compared to the –28.54 ± 0.05 ‰ unspiked solution, resulting in $\delta^{13}C_{VPDB\text{-}LSVEC}$ values of −10.13 ± 0.03 ‰ (USGS107) and +13.84 ± 0.03 ‰ (USGS108). The spiked and unspiked calcium formate solutions were then individually fed through Teflon capillaries into liquid nitrogen to generate small icy droplets that were freeze dried to generate isotopically homogeneous fine-grained powders. The solid calcium formates were analyzed by isotope-ratio mass spectrometry to determine their $\delta^{13}C$ values relative to the VPDB-LSVEC scale. Users will receive aliquots of 0.5 g in glass containers as RMs for $\delta^{13}C$ normalization.

Maintenance of RM Report of Isotopic Composition: The U.S. Geological Survey RSIL will monitor these RMs and will notify the purchaser if substantive technical changes occur that affect their isotopic compositions.

Distribution and Stability: A distribution unit of each RM is available in amounts of 0.5 g in a glass container that is vacuum sealed in a plastic pouch. USGS106, USGS107, and USGS108 are stable at normal room temperatures when stored under dry conditions. To minimize the potential for contamination, it is recommended that USGS106, USGS107, and USGS108 be stored in the containers in which they were was supplied. Storing in a dark and cool place is preferred.

Instructions for Use: USGS106, USGS107, and USGS108 can be interspersed among every 10–15 unknowns. They can be used with other carbon isotopic RMs. To prevent USGS106, USGS107, and USGS108 from degrading over time, after they are opened, it is recommended that users always close the cap tightly after usage and store in a dry desiccator or in a refrigerator. A glass container from a refrigerator or freezer should be gently warmed to room temperature before opening to avoid condensation of moisture.

Reporting of stable-isotope-delta values: The following recommendations are provided for reporting stable carbon isotope-delta values. It is recommended that:

- The $\delta^{13}C$ values of all carbon-bearing substances be expressed relative to VPDB-LSVEC on a scale such that the $\delta^{13}C$ values of the primary isotopic reference materials [7] NBS 19 calcium carbonate and LSVEC lithium carbonate are +1.95 ‰ and –46.6 ‰, respectively [3,4].

- Authors report delta values of international distributed (secondary [7]) isotopic reference materials as though they had been interspersed among and used for normalization of unknowns, as appropriate for the measurement method [8]. In this manner, measurement results can be adjusted in the future as analytical methods improve and consensus values of internationally distributed isotopic reference materials change.
- Reporting of delta values relative to PDB (Peedee belemnite) be discontinued [9].

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