USGS44, a new high purity calcium carbonate reference material for $\delta^{13}C$ measurements

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ABSTRACT

RATIONALE: The stable carbon isotopic (δ¹³C) reference material (RM) LSVEC Li₂CO₃ has been found to be unsuitable for δ¹³C standardization work because its δ¹³C value increases with exposure to atmospheric CO₂. A new CaCO₃ RM, USGS44, has been prepared to alleviate this situation.

METHODS: USGS44 was prepared from 8 kg of Merck high purity CaCO₃. Two sets of δ¹³C values of USGS44 were determined. The first set of values was determined by on-line combustion, continuous-flow (CF) isotope-ratio mass spectrometry (IRMS) of NBS 19 CaCO₃ (δ¹³Cvpdb = +1.95 milliurey (mUr) exactly, where mUr = 0.001 = 1 ‰), and LSVEC Li₂CO₃ (δ¹³Cvpdb = −46.6 mUr exactly), and normalized to the two-anchor δ¹³Cvpdb-LSVEC isotope-delta scale. The second set of values was obtained by dual-inlet (DI) IRMS of CO₂ evolved by reaction of H₃PO₄ with carbonates, corrected for cross contamination, and normalized to the single anchor δ¹³Cvpdb scale.

RESULTS: USGS44 is stable and isotopically homogeneous to within 0.02 mUr in 100-µg amounts. It has a δ¹³Cvpdb-LSVEC value of −42.21 ± 0.05 mUr. Single-anchor δ¹³Cvpdb values of −42.08 ± 0.01 and −41.99 ± 0.02 mUr were determined by DI-IRMS with corrections for cross contamination.

CONCLUSIONS: The new high-purity, well homogenized calcium carbonate isotopic reference material USGS44 is stable and has a δ¹³Cvpdb-LSVEC value of −42.21 ± 0.05 mUr for both EA-IRMS and DI-IRMS measurements. As a carbonate relatively depleted in ¹³C, it is intended for daily use as a secondary isotopic reference material to normalize stable carbon isotope-delta measurements to the δ¹³Cvpdb-LSVEC scale. It is useful in quantifying drift with time, determining mass-dependent isotopic fractionation (linearity correction), and adjusting isotope-ratio-scale contraction. Due to its fine grain size (smaller than 63 µm), it is not suitable as a δ¹⁸O reference material. A δ¹³Cvpdb-LSVEC value of −29.99 ± 0.05 mUr was determined for NBS 22 oil.