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Interlaboratory compatibility of $\delta^{13}C$-VPDB scale realisation

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Importance of $\delta^{13}C$-CO_2 value assignment

$\delta^{13}C$-CO_2 VPDB scale realizations directly impact the GAW-WMO compatibility goals for measurements of atmospheric CO_2 and CH_4.

Where do we stand on laboratory compatibility when analysing international standards?

Where are the constraints on laboratory intercomparability?

Component	*Network compatibility goal[1]*	*Extended network compatibility goal[2]*
$\delta^{13}C$-CO_2	0.01‰	0.1‰
$\delta^{13}C$-CH_4	0.02‰	0.2‰

GAW-WMO (2020)

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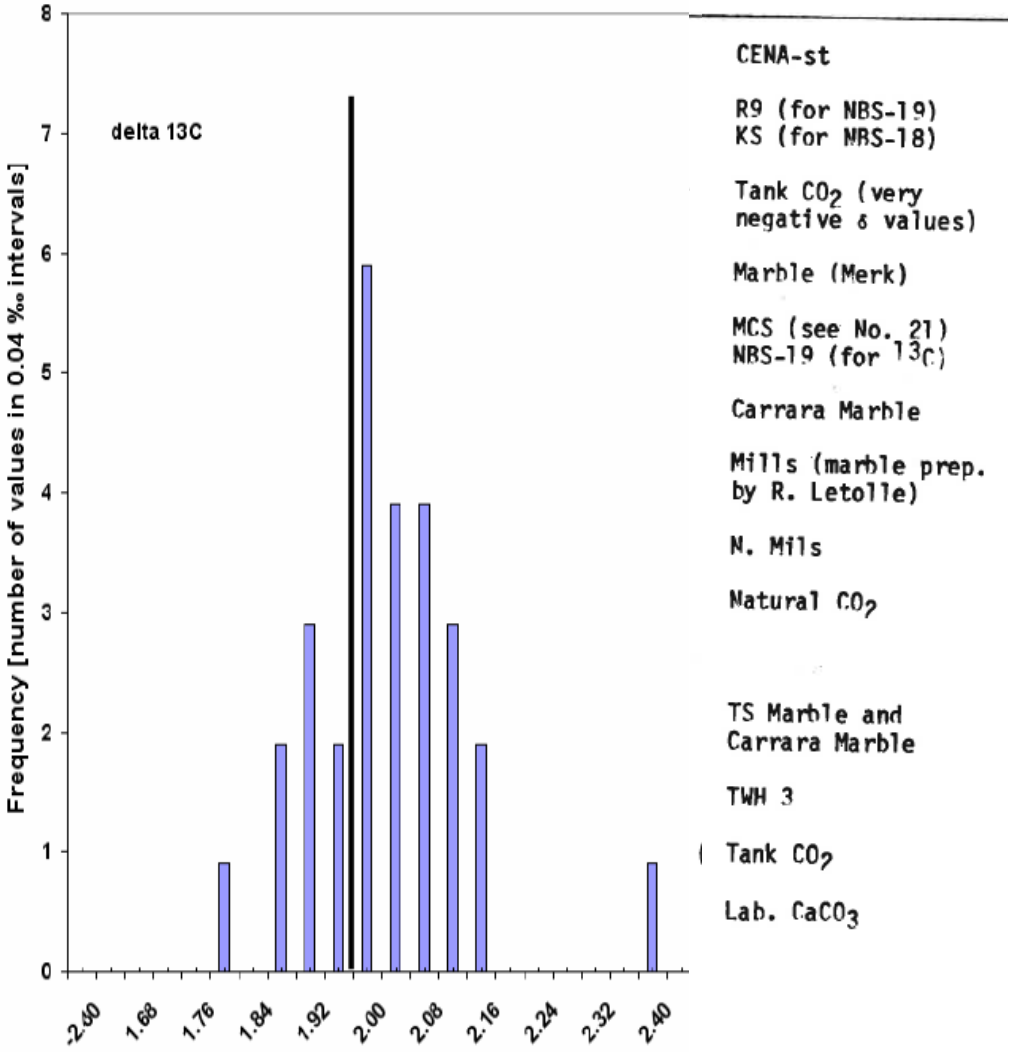
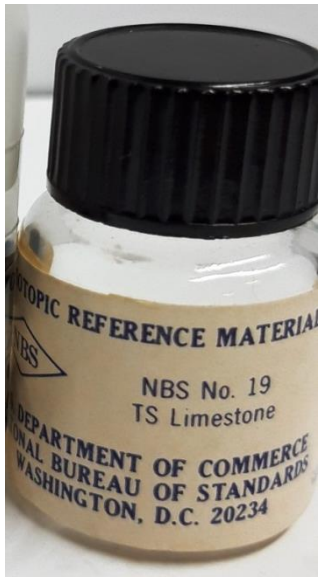
Interlab comparability of $\delta^{13}C$-CO_2 values



$\delta^{13}C$ value assignment constraint:

- different standards



$\delta^{13}C$: +1.95‰ (VPDB)

$\delta^{18}O$: -2.20 ‰ (VPDB)

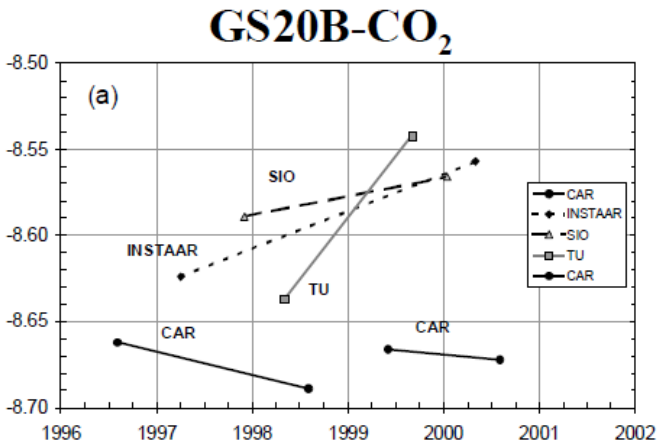
Data from IAEA “Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigation” R. Gofiantini, 1984; Graphs made by Willi Brand

Interlab comparability of $\delta^{13}C$-CO_2 values

$\delta^{13}C_{VPDB\text{-}CO2}$ value assignment comparability is constrained by:

- phosphoric acid reaction
- scale contraction

CLASSIC Project, WMO-GAW Report 148, **2003**



Reported isotopic composition of the pure CO_2 gas in canister GS20B: (a) $\delta^{13}C_{VPDB\text{-}CO2}$, (b) $\delta^{18}O_{VPDB\text{-}CO2}$.

$\delta^{13}C$

Verkouteren & Klinedinst, NIST special publication **2004**

Average of 6 laboratories

	Average (std dev)
$\delta^{13}C$(RM8562)	-3.72 (0.04)
$\delta^{13}C$(RM8563)	-41.57 (0.09)
$\delta^{13}C$(RM8564)	-10.45 (0.03)
$\delta^{13}C$(NBS18)	-5.01 (0.02)
$\delta^{13}C$(IAEA-CO9)	-47.38 (0.14)
$\delta^{13}C$(LSVEC)	-46.57 (0.12)

Interlab comparability of $\delta^{13}C$-CO_2 values

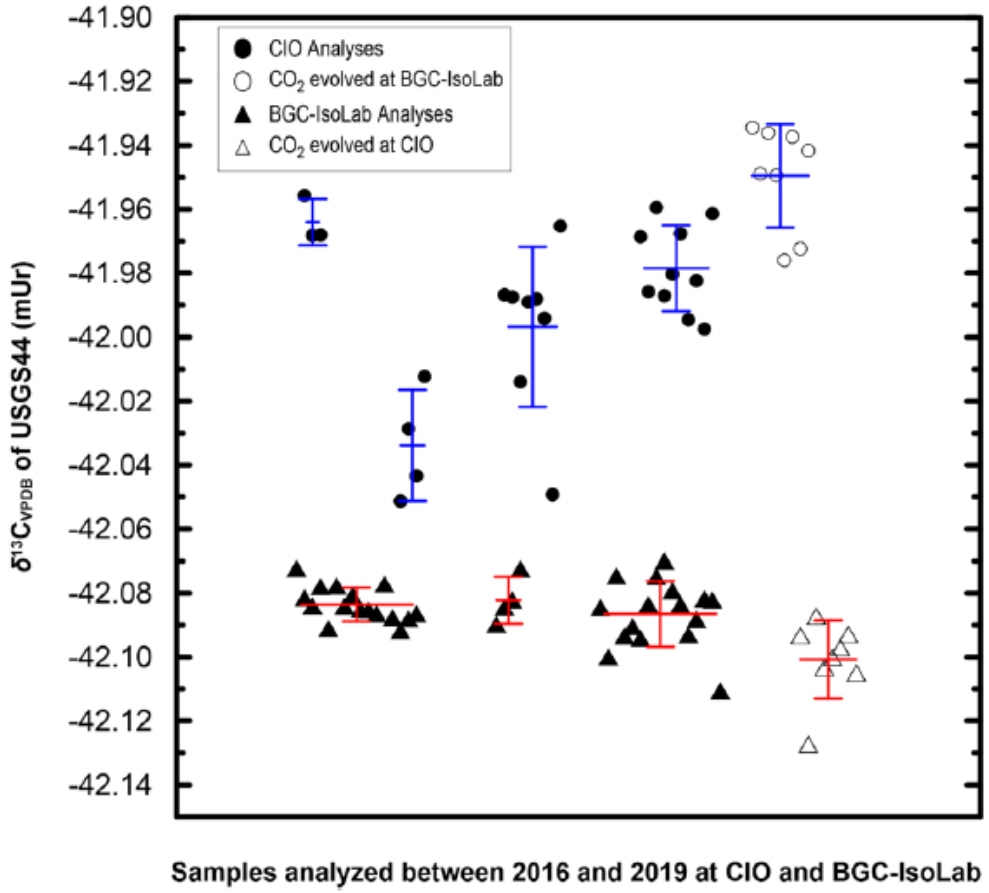


FIGURE 5 Individual DI-IRMS $\delta^{13}C_{VPDB}$ measurements of USGS44 by BGC-IsoLab and CIO between 2016 and 2019. Values are corrected for cross contamination

$\delta^{13}C_{VPDB\text{-}CO2}$ value assignment comparability is constrained by:

- scale contraction / instrumental factors

Qi et al., 2020

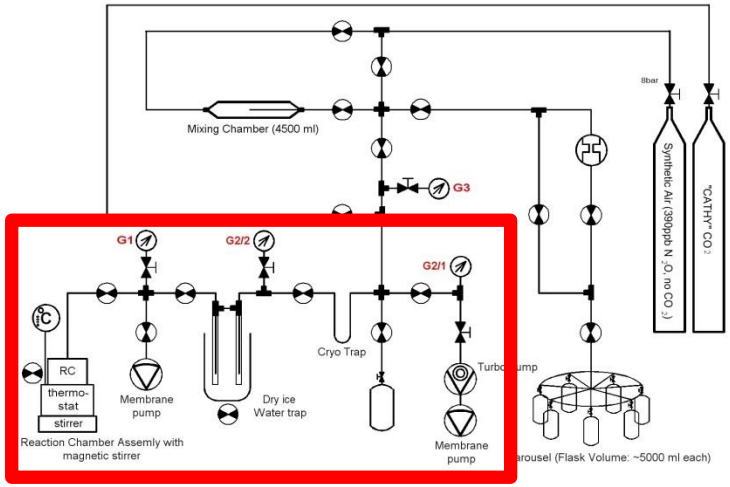
$\delta^{13}C$-CO_2 measurments from $CaCO_3$ standards.

Measurement constraints:

$CaCO_3$ + 2 H_3PO_4 →

Ca^{2+} + 2$(H_2PO_4)^-$ + H_2O + **CO_2**

scale contraction
instrumental factors

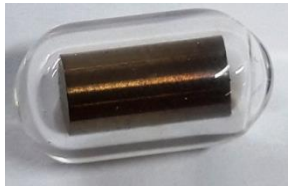


ARAMIS – Acid Reaction and Air Mixing System

1 Syntheses = one 300 ml Flask containing ~ 30 mbar CO_2
25°C, 24 hours

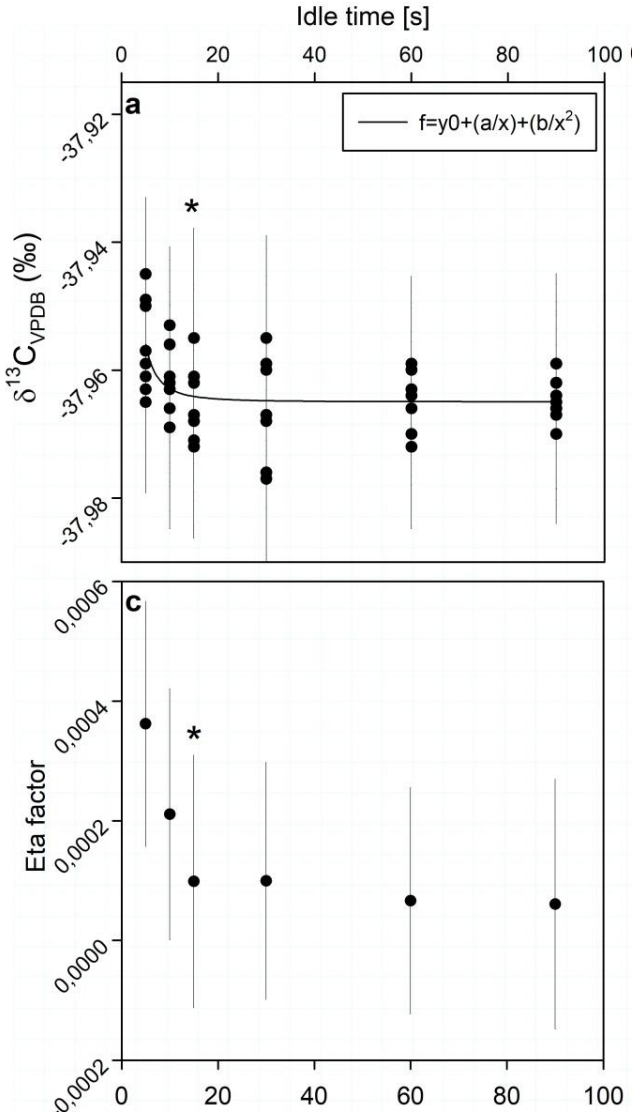
MAT 253 (Candira): Dual Inlet measurements

20 µm Gold coating



New magnetic stirrer

Scale contraction – BGC-IsoLab MAT253



standard idle time experiment to determine sample/reference gas cross-contamination.

cross-contamination leads to scale contraction

Sample/reference gas cross-contamination is subject to change with changing ion source conditions.

<u>Idle time experiments 2021:</u>

$\delta^{13}C_{\eta}$: 0.000097 ± 0.00021

<u>Idle time experiments 2018:</u>

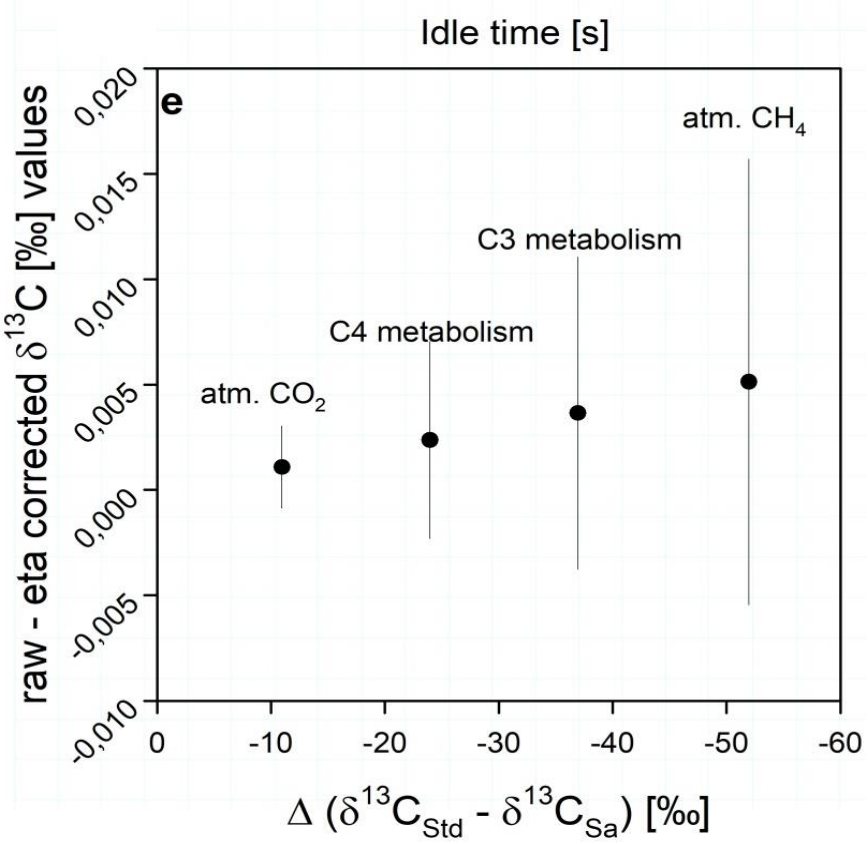
$\delta^{13}C_{\eta}$: 0.00046 ± 0.0005

Qi et al., (2020)

Cross-contamination changes with changing ion source conditions

Scale contraction – BGC-IsoLab MAT253

The impact of the scale contraction correction increases with isotopic „distance“ between sample and standard.

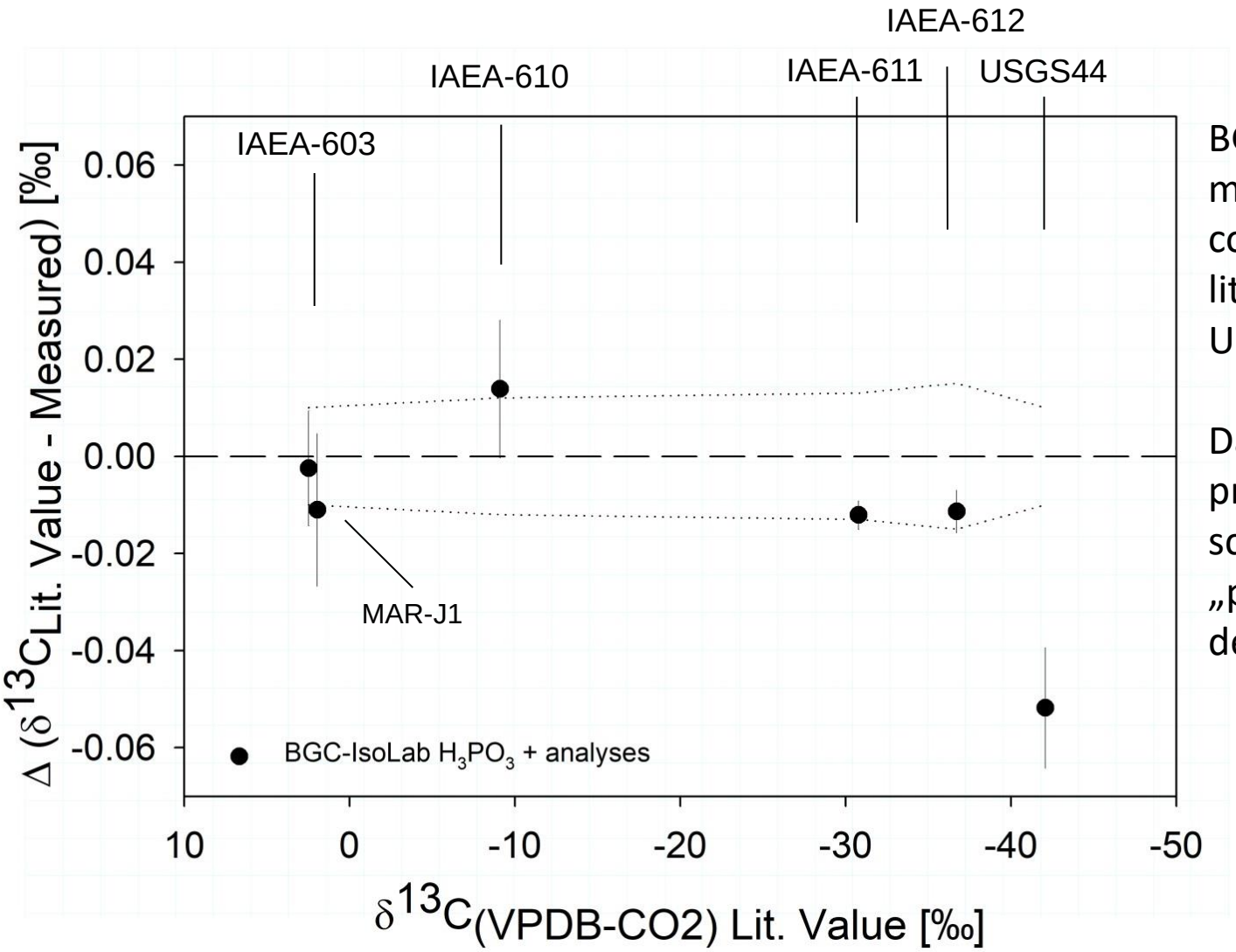


Impact of the scale contraction correction on different samples analysed against NBS19-CO_2.

eta-correction is negligible for isotopic measurements of atmospheric CO_2

eta-correction can add significant uncertainty for isotopic measurements of atmospheric CH_4.

Realising the VPDB scale at BGC-IsoLab

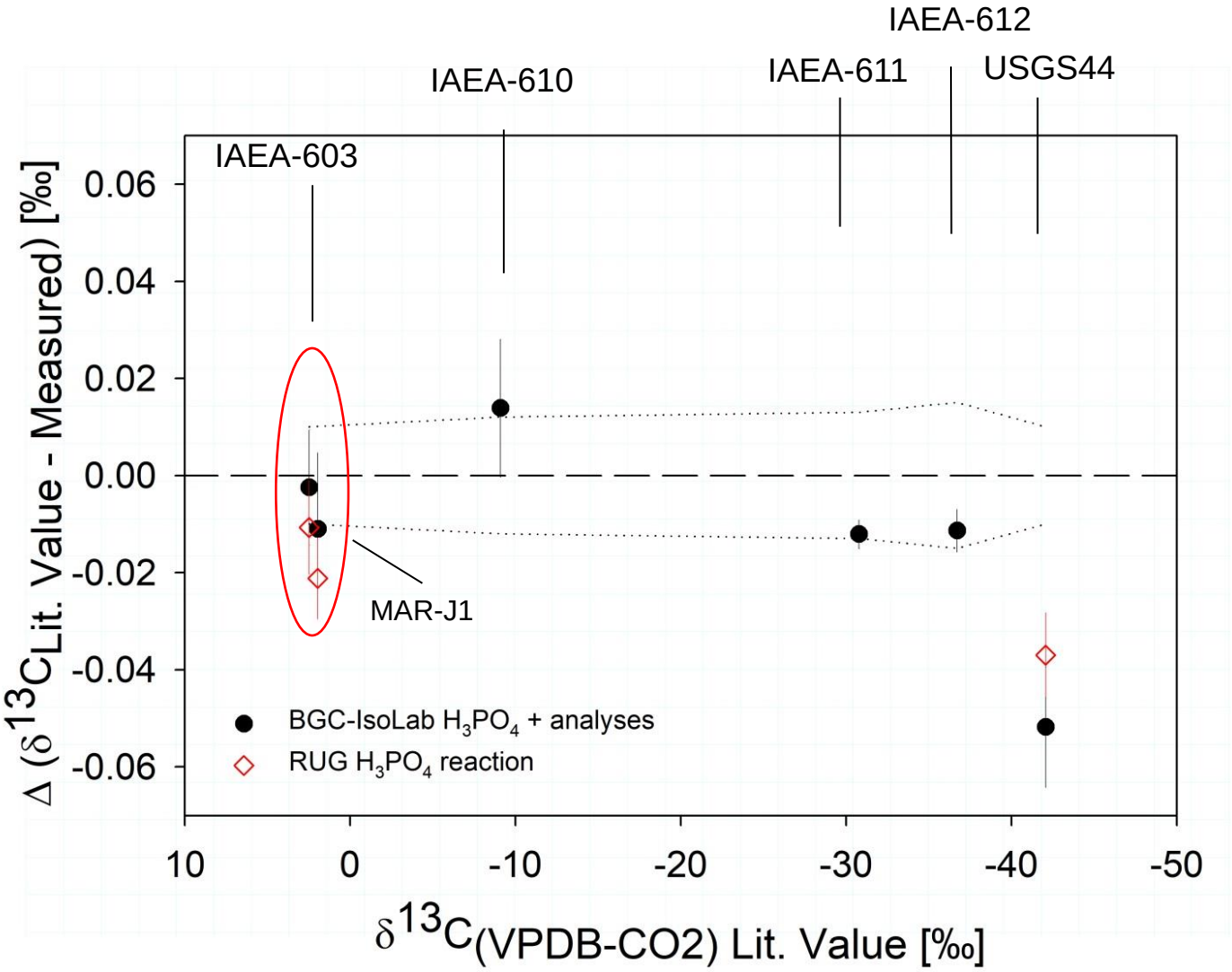


BGC-IsoLab measurements correspond very well to lit. values, except of USGS44.

Data indicates that the proposed VPDB2020 scale is identical to the „pre-LSVEC“ VPDB scale defined by NBS19.

All values are scaled to NBS19-CO_2 via a working standard.

Comparing H_3PO_4 reaction between BGC and RUG



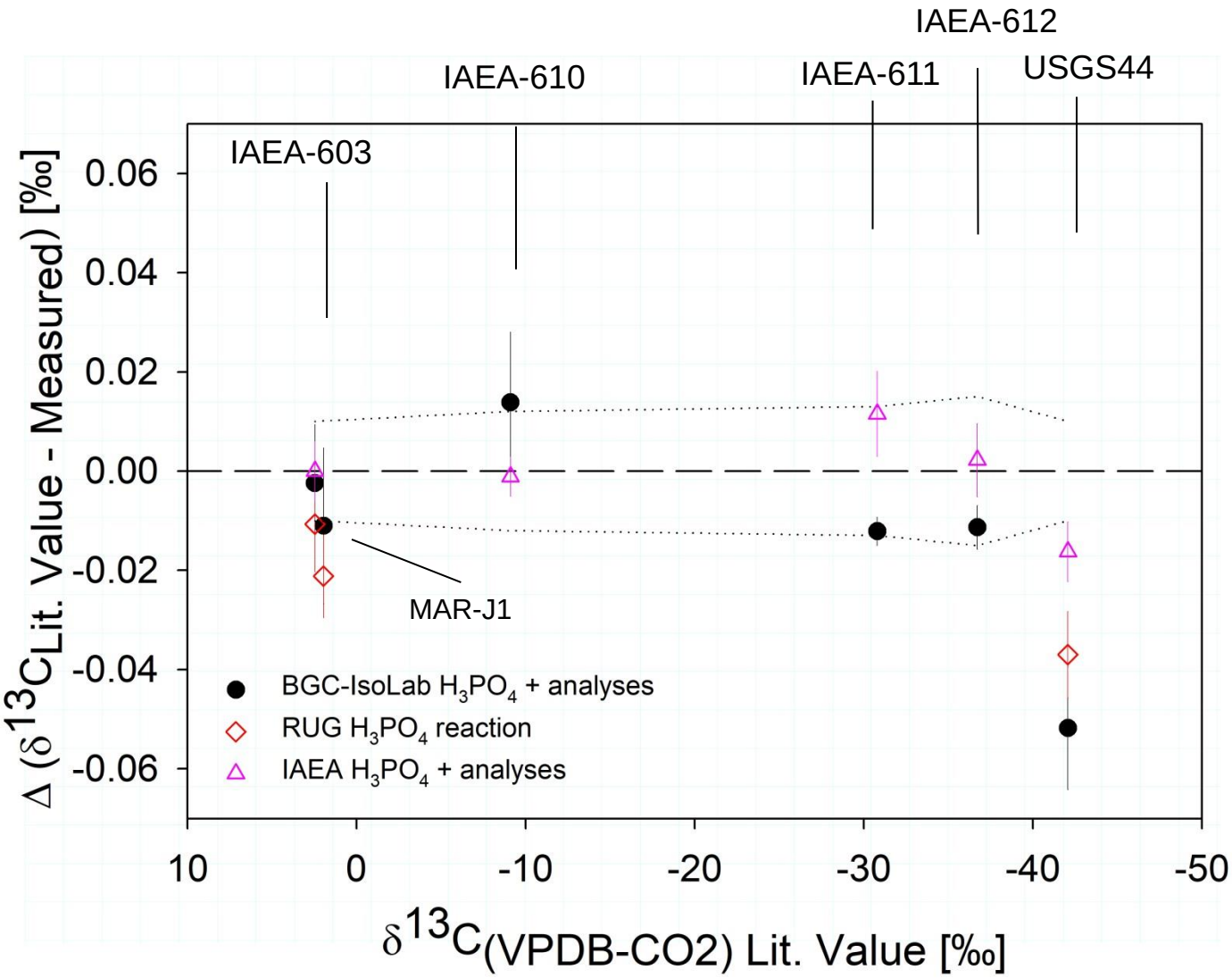
The RUG and BGC-IsoLab phosphoric acid preparations are indistinguishable for IAEA-603 and MAR-J1-CO_2.

USGS44-CO_2 from RUG and BGC-IsoLab are isotopically distinct

Grain size issue?

All values are scaled to NBS19-CO_2 via a working standard.

Comparing IAEA and BGC-IsoLab VPDB scale realisations



IAEA and BGC-IsoLab scale realisation in good agreement over VPDB scale spanned by IAEA standards.

Larger offsets with increasing sample/standard isotopic difference.

USGS44 data suffers from larger variability

All values are scaled to NBS19-CO_2 via a working standard.

Conclusion and Outlook

Conclusion:

The CCL and IAEA $CaCO_3$-CO_2 Data show good agreement on the VPDB-CO_2 scale defined by NBS19.

Scale revision, i.e. setting up a new scale may not be necessary.

Inter-laboratory comparability of VPDB scale realisation is still constrained by:

- phosphoric acid reaction
- instrument specific scale contraction
- (type of standard material) – more USGS44 work necessary.

Recommendation:

- Continue collaboration between CCL and IAEA and further stakeholders where necessary.

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Thank you.

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