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Towards improved in situ microanalysis of boron & boron isotopes in carbonates using Nano-Pellets as reference materials

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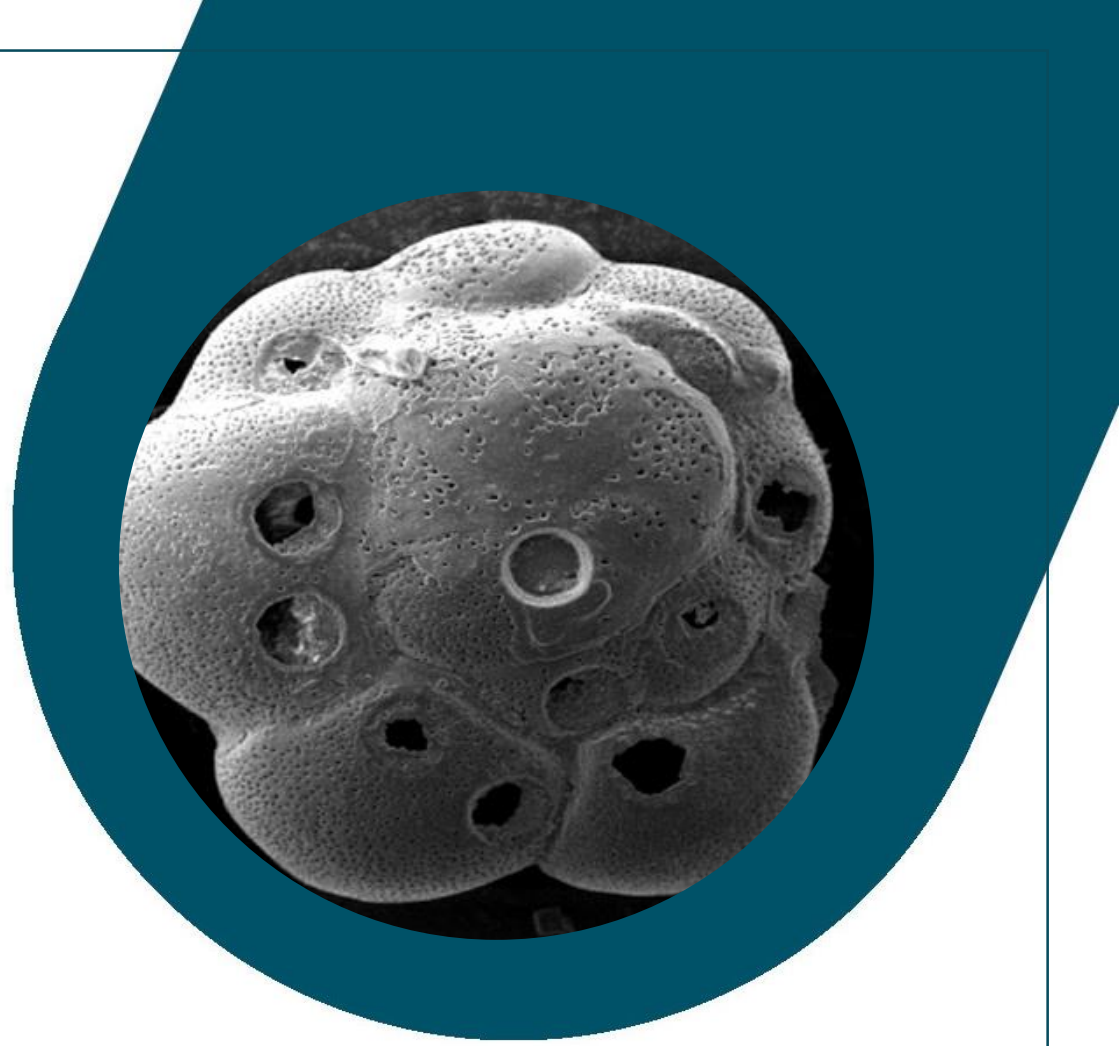
Introduction



- A lack of matrix-matched reference materials (RM) for *in situ* microanalysis is generally recognised (Miliszkiewicz et al. 2014)
- Commonly used soda glasses (NIST series), while ubiquitous cause matrix-related offsets in analytical data (Jochum et al. 2019)
- Nano-particulate pressed powder pellets have been shown to be a promising remedy for this issue (Jochum et al. 2019)

Introduction

- Nano-Pellets can be pressed without any binders
- The small particle size results in improved homogeneity and ablation behaviour compared to conventional pressed pellets
- Natural zonation and other heterogeneities are eliminated

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Candidate RM N°1

- **N**IOZ **F**oraminifera **H**ouse **S**tandard N° 2 **N**ano **P**ellet (NFHS-2-NP)
- Forams from calcareous ooze in gravity core from the Walvis Ridge at 2878 m water depth
- Characterised for major- and trace elements as well as isotopic ratios using solution techniques (ICP-MS, ICP-OES, TIMS, MC-ICP-MS, XRF)
- Homogeneity investigated using LA-ICP-MS at NIOZ

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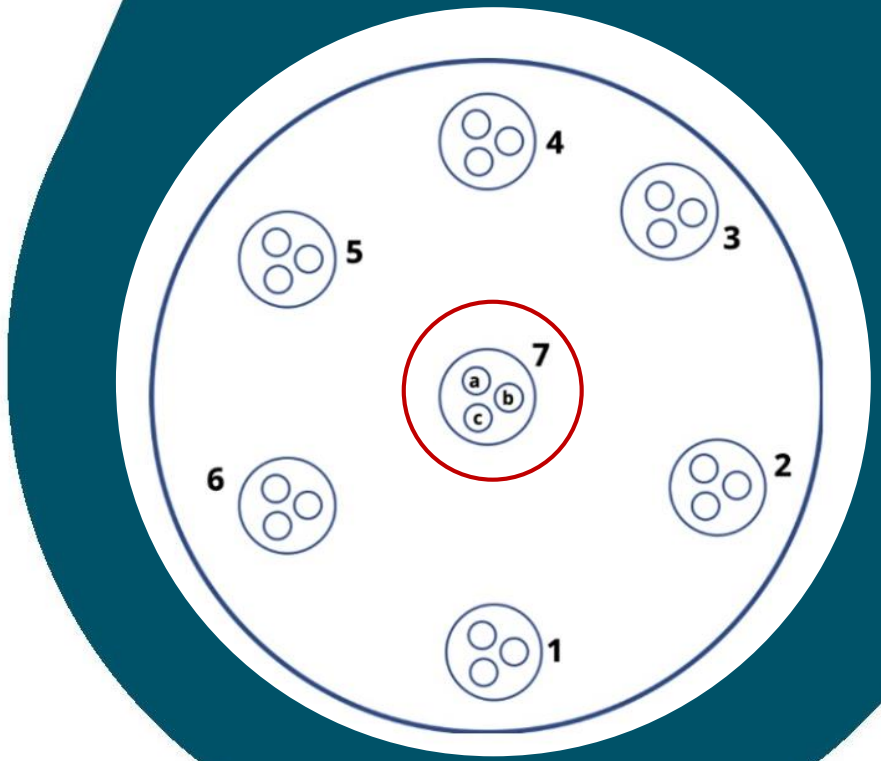
Homogeneity of Boron

- ASTM Guide E 826-14 methodology
- Further data evaluation following ISO-Guide 35
- Modus operandi for homogeneity testing of microanalytical RM



Homogeneity of Boron

B/Ca [µmol/mol]

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Avg.	RSD-%
Run 1 a)	75,2	77,9	76,9	78,8	79,7	77,4	82,7	78,4	***3,05***
Run 2 b)	75,7	74,7	79,8	79,0	75,8	78,2	80,7	77,7	***2,99***
Run 3 c)	78,2	78,3	77,3	79,5	75,7	78,8	75,6	77,6	***1,94***
Avg.	76,4	77,0	78,0	79,1	77,1	78,1	79,7		
RSD-%	***2,07***	***2,62***	***1,99***	***0,48***	***2,96***	***0,92***	***4,60***		

- *Overview of within-pellet homogeneity*

Homogeneity of Boron

ASTM E826-14 Evaluation

Number of measurements prer Zone	**3**
Number of Zones	**7**
degrees of freedom	**12**
SSt	2,59113E-05
SSb	2,38367E-06
SST	8,24555E-05
s	0,002124471
q	4,88
w	0,005985631
0,003339656	maximum(t')-minimum(t')

- As long as the calculated “w” value is larger than the absolute value of “t´” the sample can be considered homogenous
- If this test should fail it is still within the rights of the manufacturer to consider if the achieved results are fit for purpose
- **Objective measure of homogeneity**

Homogeneity of Boron

B/Ca [µmol/mol]

	Result 1	Result 2	Result 3	Result 4	Result 5	Result 6	Result 7
Pellet 1	77,2	78,9	77,4	78,7	80,9	77,9	77,6
Pellet 2	76,4	77,0	78,0	79,1	77,1	78,1	79,7
Pellet 3	75,6	75,4	75,4	77,4	76,3	75,4	78,5
Pellet 4	76,7	77,5	77,8	78,3	77,5	79,6	77,5

- Averaged results from each zone on each of the 4 Nano-Pellets
- Each certified reference material (ISO 17034) needs an uncertainty statement calculated from three components: *characterisation, homogeneity & stability*
- ISO Guide 35 shows how the uncertainty component for homogeneity can be calculated

Homogeneity of Boron

[mmol/mol]		
s^2 between	0,0000006	$s^2_{between} = \frac{MS_{Between\ Groups} - MS_{Within\ Groups}}{Count}$
Between-unit Std.dev.	0,001	$s_{between} = \sqrt{s^2_{between}}$
Repeatability Std.dev	0,001	$s_r = \sqrt{MS_{Within\ Groups}}$
Unc. Homogeneity	0,001	$Uncertainty_{Homogeneity} = \sqrt{s_r^2 + s^2_{between}}$

- Uncertainty component homogeneity for NFHS-2-NP
- Amount of pellets tested insufficient according to ISO Guide 35 – lack of lab-time due to COVID
- General principle can be shown

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Boron in NFHS-2-NP

Consensus value:	**74.0** [µmol/mol]
$Uncertainty_{Characterisation}$:	4.0 [µmol/mol]
$Uncertainty_{Homogeneity}$:	1.0 [µmol/mol]
$Uncertainty_{Stability}$:	unknown

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Boron in NFHS-2-NP - Stability

[µg/g]

Measurement on May 19th 2021:	9.36 ± 0.70 [2SD] n = 21
Measurement on May 25th 2021:	9.51 ± 0.51 [2SD] n = 21

Quantified using NIST 610 & 612

Boron in NFHS-2-NP

$$Uncertainty_{NFHS-2-NP} = k \times \sqrt{Unc._{Char}^{2} + Unc._{Hom}^{2} + Unc._{Stab}^{2}}$$

$$k = expansion\ factor_{Student's\ t-distribution}$$

$$Uncertainty_{NFHS-2-NP} = 2 \times \sqrt{4.0_{Char}^{2} + 1.0_{Hom}^{2} + Unc._{Stab}^{2}}$$

Assigned Value & expanded Uncertainty:

74,0 ± 8,0 [µmol/mol] 95 % CL

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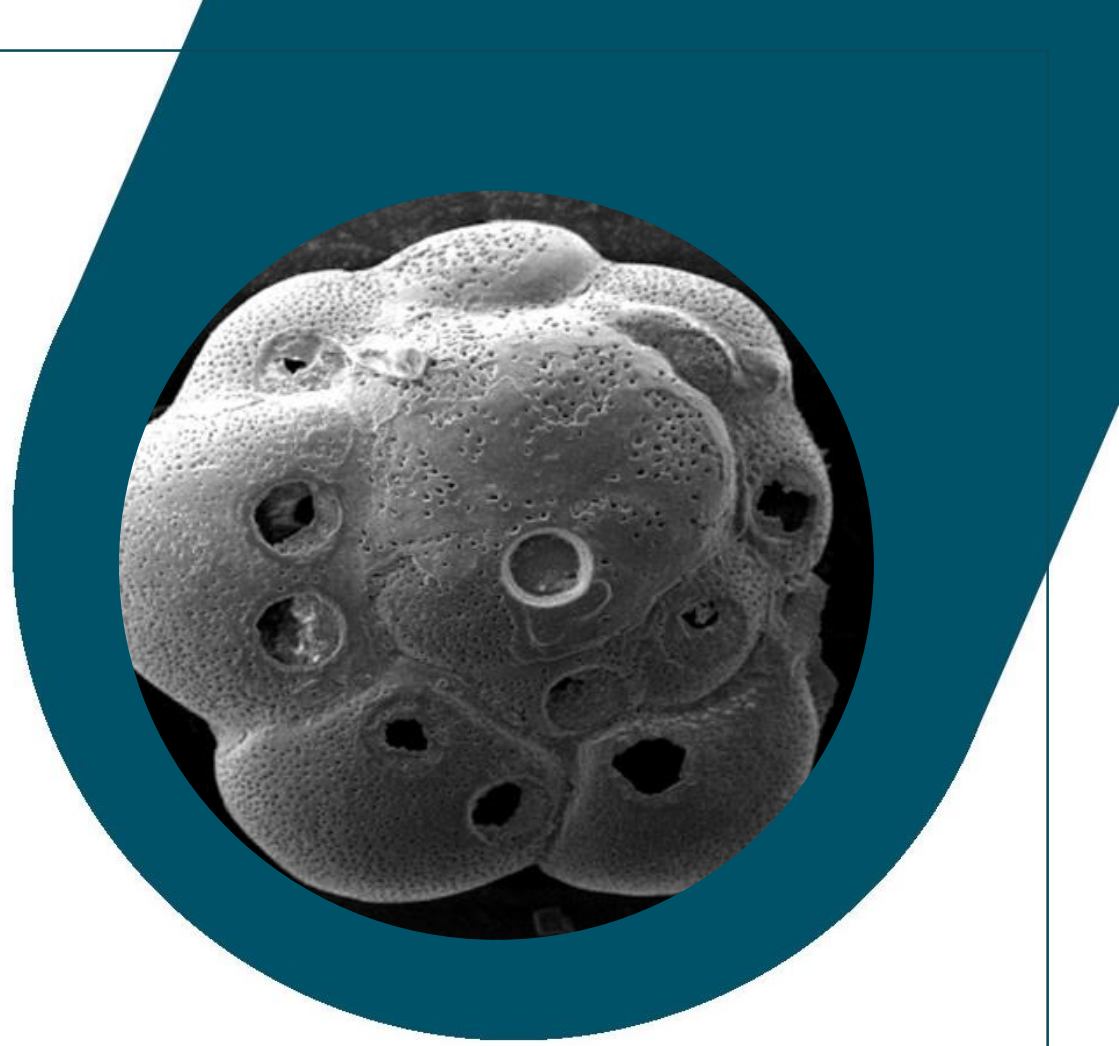
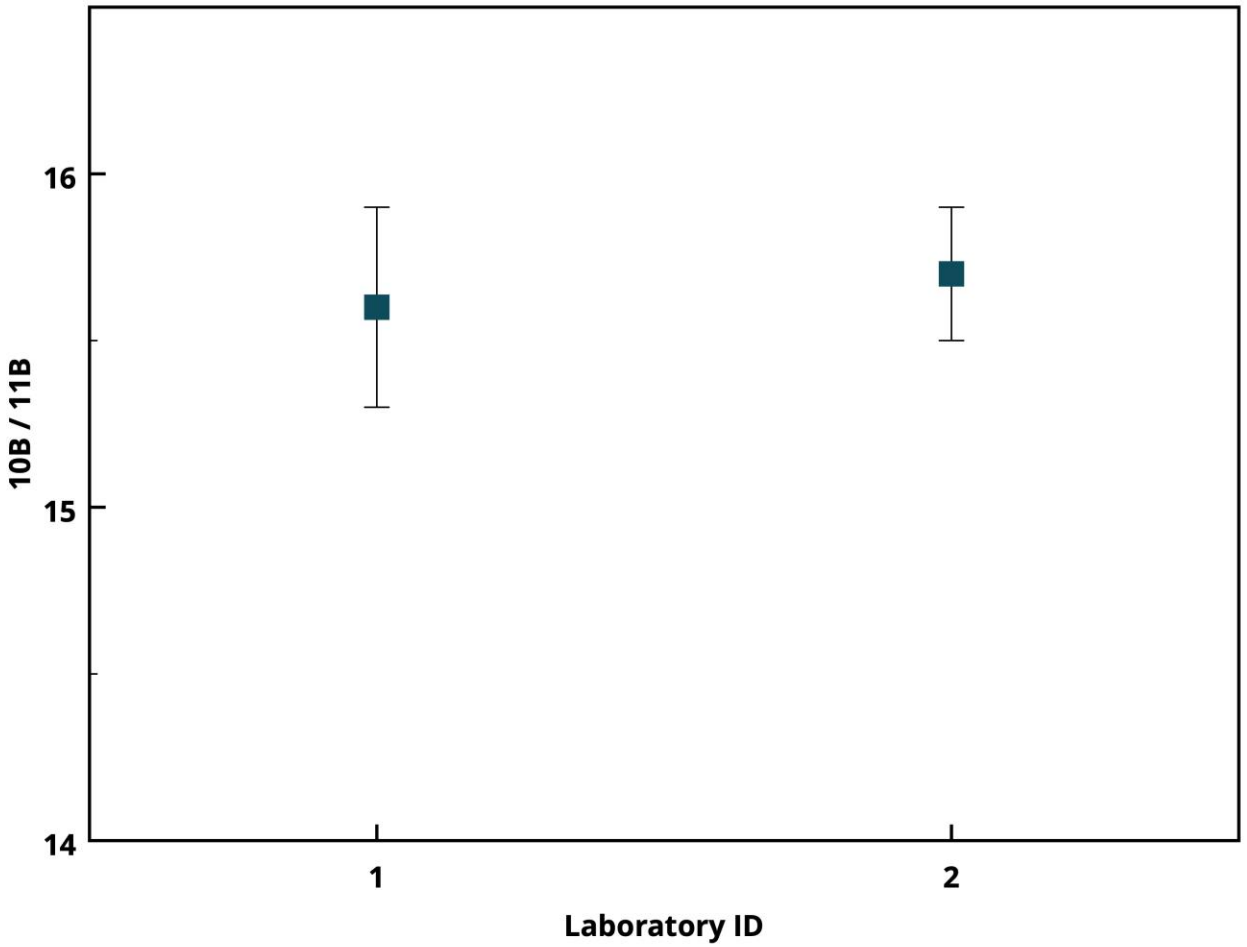
Boron Isotopes



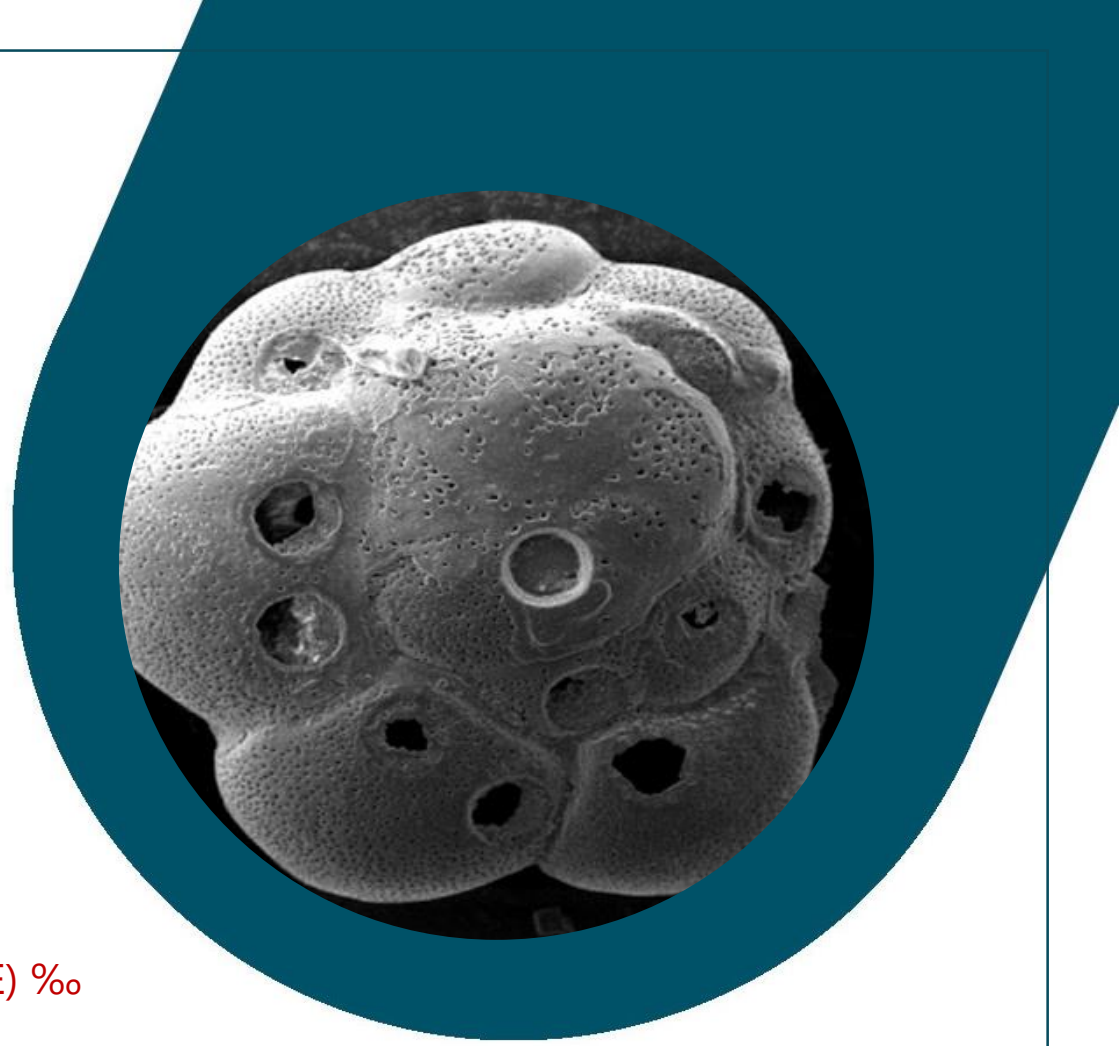
- Characterised with MC-ICP-MS and TIMS
- Relative to NIST 951a
- All data not yet acquired
- So far limited LA-MC-ICP-MS to show homogeneity of boron isotopic value. Homogeneous elemental boron is encouraging

Characterisation until now



- Preliminary value : **15.64 ± 0.14 [95 % CL]**
- More data acquired than shown here
- Data were inconsistent due to different dissolution techniques

NFHS-2-NP Summary



- LA-ICP-MS analyses at NIOZ were able to show excellent homogeneity for boron, between and within Nano-Pellets

- Preliminary data on boron isotopes are already encouraging and will be improved by further analyses (LA-MC-ICP-MS & TIMS)
- First boron LA-MC-ICP-MS data received June 30th: 14.96 ± 0.6 (2SE) ‰

- Work on publication showing entire characterisation is on-going

Candidate RM N°2

- **N**IOZ **B**oron **I**sotopic **S**tandard-**N**ano **P**ellet (NBIS-2-NP)

- Mixture of 99.999 % pure $CaCO_3$ with NIST 951a: NBIS-1-NP

- Dilution of NBIS-1-NP with $CaCO_3$ to match natural concentration of foraminifera:

- Boron isotopic value and concentration investigated using MC-ICP-MS and LA-ICP-MS respectively

NIOZ Sea Research

Homogeneity of elemental Boron

RSD [%]

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Average RSD [%]	Conc. [µg/g]
NBIS-1-NP	8,6	1,9	1,7	6,3	10,1	2,5	11,4	6,1	1842
NBIS-2-NP	7,4	6,3	19,7	14,6	2,8	16,9	9,9	11,1	8,9
NBIS-3-NP	2,0	11,2	3,3	14,4	12,9	7,4	3,6	7,8	192

- Less homogenous than NFHS-2-NP
- 9.95 g of $CaCO_3$ were mixed with 0.05 g of NBIS-1-NP large ratio and few boron "particles" in many $CaCO_3$ particles → NBIS-2-NP
- 9 g of $CaCO_3$ mixed with 1 g of NBIS-1-NP → NBIS-3-NP
- Elemental heterogeneity does not necessarily negate isotopic homogeneity

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Boron Isotopes - Initial Analysis

		$\delta^{11}B$ ‰	SD ‰
NBIS-1 NP	U11784480	-0.06	0.22
NBIS-1 NP, r.2	U11784480	-0.09	0.26
NBIS-2 NP	U11784481	0.31	0.58
NBIS-2 NP, t.2	U11784481	0.16	0.51

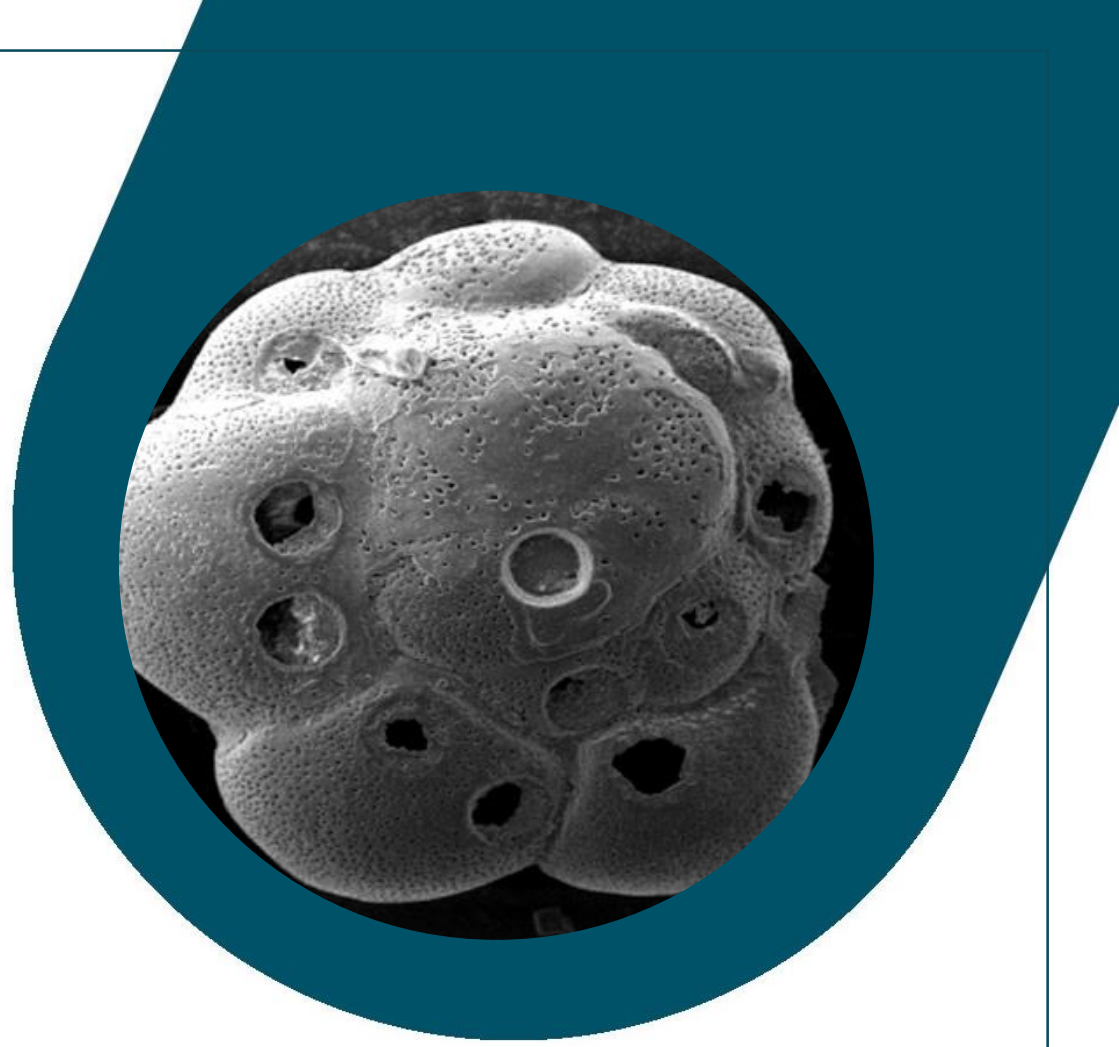
- Commercial Laboratory
- Values statistically indistinguishable from “zero”
- High uncertainties
- More precise data needed

NBIS-2-NP Summary

- Initial analyses showed encouraging signs of having achieved a delta $^{10}B/^{11}B$ value close to zero in $CaCO_3$

- Elemental heterogeneity potential issue for isotopic ratio

- Further investigation using LA-MC-ICP-MS, and TIMS are on-going



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Thank You
for Your attention

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Q & A