Assessing the precision and accuracy of foraminifera elemental analysis at low ratios

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Abstract

The minor and trace element compositions of biogenic carbonates such as foraminifera are important tools in paleoceanography research. However, most studies have focused primarily on samples with element to calcium (El/Ca) ratios higher than the El/Ca range often found in benthic foraminifera. Here, we systematically assess the precision and accuracy of foraminifera elemental analysis across a wide range of El/Ca especially at relatively low ratios, using a method on a Thermo Scientific iCAP Qc quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS). We focus on two benthic foraminifera species, *Hoeglundina elegans* and *Cibicidoides pachyderma*, and prepared a suite of solution standards based on their typical El/Ca ranges to correct for signal drift and matrix effects during ICP-MS analysis and to determine analytical precision. We observe comparable precisions with published studies at high El/Ca, and higher relative standard deviations for each element at lower El/Ca, as expected from counting statistics. The overall long-term analytical precision (2σ) of the *H. elegans*-like consistency standard solutions was 6.5%, 4.6%, 5.0%, for Li/Ca, Mg/Ca, Mg/Li, and 6.4%, 10.0%, 4.2% for B/Ca, Cd/Ca, Sr/Ca. The precision for *H. elegans*-like Mg/Li is equivalent to a temperature uncertainty of 0.5 – 1.1 °C. Measurement precisions were also assessed based on three international standards (one solution and two powder standards) and replicate measurements of *H. elegans* and *C. pachyderma* samples. We provide file templates and program scripts that can be used to design calibration and consistency standards, prepare run sequences, and convert the raw ICP-MS data into molar ratios.

Keywords: ICP-MS, iCAP Qc, foraminifera, trace element, calcium

Key points:

- Higher relative standard deviations are reported at lower element/calcium values, as expected from counting statistics.
- Consistency standards having similar ratios to the unknown samples provide an accurate estimate of errors.
- For the *Hoeglundina elegans* Mg/Li - temperature proxy, analytical precision (2σ) is equivalent to a temperature uncertainty of 0.5 – 1.1 °C.

1. Introduction

Elemental ratios of foraminiferal shells are widely used to reconstruct past ocean conditions, such as Mg/Ca or Mg/Li for seawater temperature (Bryan & Marchitto, 2008; Elderfield et al., 2006; Rosenthal et al., 2006), Cd/Ca for nutrients (E. A. Boyle, 1992; Bryan & Marchitto, 2010), B/Ca and Sr/Ca for carbonate ion concentrations (Rae et al., 2011; Rosenthal et al., 2006; Yu & Elderfield, 2007), and the utility of many other elemental ratios to reconstruct past ocean conditions are being explored. To robustly apply these proxies, accurate, high-precision elemental measurements are needed.

However, most studies so far focus primarily on samples with relatively high element to calcium ratios (El/Ca) such as Mg/Ca in planktonic foraminifera, and few studies have explicitly examined the analytical precision at low El/Ca such as those often found in benthic foraminifera. For example, for Li/Ca and Mg/Ca, published methods have yielded good precision at high El/Ca, e.g., 1 relative standard deviation [RSD, calculated as (SD/average ratio*100%)] generally < 2% for Li/Ca of 5 – 30 μmol/mol and Mg/Ca of 0.4 – 5 mmol/mol. It is not always clear how these methods perform at lower El/Ca. The possibility of poor precision at low El/Ca may be problematic, especially for foraminifera species with significantly lower El/Ca. For example, Li/Ca, B/Ca, Mg/Ca, Cd/Ca, and Sr/Ca in core-top samples for three commonly studied benthic foraminifera species (*Hoeglundina elegans*, *Cibicidoides* spp., and *Uvigerina* spp.) vary by up to a factor of 10, e.g., Li/Ca of *Uvigerina* > *Cibicidoides* > *H. elegans*, and B/Ca of *Cibicidoides* > *H. elegans* > *Uvigerina*, reaching values as low as ~1 μmol/mol for Li/Ca and ~10 μmol/mol for B/Ca (Fig. 1). The Mg/Ca and Cd/Ca are generally comparable among the three species, with Atlantic core-top *H. elegans* showing the lowest Mg/Ca (median value of 1 mmol/mol) and Cd/Ca (median value of

0.02 μmol/mol). The Sr/Ca values are similar in *Cibicidoides* and *Uvigerina*, but the data spread is larger in *H. elegans* (Fig. 1).

For paleo-reconstructions, especially quantitative reconstruction of seawater parameters such as temperature, it is important to robustly constrain both the precision and accuracy of the measurements. It is expected that samples with low molar ratios are more likely to be impacted by measurement errors than those with higher ratios. For example, a relatively small inter-laboratory offset in Li/Ca (+2.4%) and Mg/Ca (-2.6%) between Woods Hole Oceanographic Institution (WHOI) and INSTAAR, University of Colorado can lead to temperature difference up to 3 °C when applying the *H. elegans* Mg/Li - temperature proxy (Oppo et al., 2023), highlighting that accurate measurements, not only good precision, are also needed.

Here we systematically assess the precision and accuracy of foraminiferal minor and trace element analysis across a wide range of El/Ca ratios on a Thermo Scientific iCAP Qc quadrupole Inductively Coupled Plasma Mass Spectrometer (ICP-MS), with a focus on relatively low ratios. To achieve this goal, we design species-specific El/Ca calibration standards, matrix standards, and consistency standards that closely match specific foraminiferal ratios. We also routinely measure international standards treated as unknowns. In addition, we provide machine-specific instrumentation parameters that can be used as references for the labs using or planning to use the iCAP Qc quadrupole ICP-MS. We also provide a generalized method with a user guide and file templates that begins with making a set of new standards and ends with obtaining El/Ca results (in molar ratios, which are generally used for ocean property reconstructions).

2. Methods

2.1. Instrumentation

Element analyses were conducted on a Thermo iCAP Qc quadrupole ICP-MS interfaced to an ESI SC4 DX autosampler at WHOI. During each analysis, sample solutions were pulled through a peristaltic pump and nebulized at about 1 ml/min, and a quartz cyclonic spray chamber was used to minimize memory effects due to sample washout. Nickel sampler and skimmer cones were used with a quartz injector and torch. The instrument sensitivity was optimized at the beginning of each day of analysis using the Thermo TuneB solution.

The iCAP uses two detection modes: standard (STD) mode, and kinetic energy discrimination (KED) mode using helium gas in the collision cell. In the KED mode, unwanted polyatomic interferences are filtered out based on the difference in collision cross-section sizes of the analyte and polyatomic interferences, and lower masses have less kinetic energy and are less likely to make it beyond the kinetic energy barrier. When both KED and STD modes are used for one element, the raw counts per second (CPS) data are typically lower in KED mode than those in STD mode. The El/Ca values are usually very similar in both modes. Table S1 lists the isotopes and their modes used in this study.

The instrument detection limits (IDL) were determined from 16 replicates of the blank solution (2% HNO_3) during the first analytical session, following the calculation method described in U.S. EPA (2014). The IDL of the major and minor elements are Ca: 3.1 ppb; B: 0.05 ppb; Na: 17.77 ppb; Mg: 0.05 ppb; Al: 0.03 ppb; Ti: 0.06 ppb; Mn: 0.01 ppb; Fe: 0.16 ppb; Zn: 0.06 ppb; and Sr: 0.01 ppb. The IDL of four minor elements are in the level of ppt, Li: 0.15 ppt; Cd: 0.47 ppt; Ba: 0.44 ppt; and U: 0.01 ppt.

2.2. Standards: Species-specific design

Three distinct types of El/Ca standard solutions were prepared and employed in this study: 1) calibration standards, which were used to calibrate the raw CPS data into molar ratios; 2) matrix standards, which were used to correct for the matrix effects during the ICP-MS analysis, and 3) consistency standards, which were used to monitor long-term data quality and to compare our results to those of other laboratories. All standard solutions were prepared gravimetrically using high purity Ca stock solution (10,000 ppm), and 14 minor or trace elements, which were each added separately: lithium (Li), boron (B), magnesium (Mg), aluminum (Al), manganese (Mn), iron (Fe), strontium (Sr), cadmium (Cd), barium (Ba), uranium (U), zinc (Zn), titanium (Ti), sodium (Na), neodymium (Nd). Each stock standard solution has a volume of 250 mL containing ~1,000 ppm Ca and different amounts of minor and trace elements in a solvent of 2% HNO_3, and is freshly diluted to a target Ca concentration for each analytical session. Note that the Ca stock solution (10,000 ppm) should only contain minimum amounts of impurities that are much lower than in foraminifera samples.

2.2.1. Calibration standards

We designed and prepared two separate sets of standards for each benthic species, based on the El/Ca distribution in core-top samples (Fig. 1). Each standard set includes five calibration standards (labeled as GLU in Fig. 2, file templates available in Table S1-S2), which were designed to scatter throughout the El/Ca ranges among all core-top data of each species. The target Ca concentrations in the analytical sessions range from 25 to 160 ppm in most labs (Cook et al., 2022; Dai et al., 2023; Farmer et al., 2019; Stewart et al., 2021; Yu et al., 2005; Marchitto, 2006; Rosenthal et al., 1999). We chose 100 ppm Ca as target concentration because we also evaluated Cd (a nutrient tracer), whose concentrations are typically very low (on the order of < 0.10 μmol/mol for Cd/Ca, Fig. 1). A higher target Ca concentration would result in higher CPS for Cd (thus also smaller RSD).

2.2.2. Matrix standards

Because foraminiferal shells generally experience varying degrees of sample loss during the cleaning processes (see section 2.3), the final sample solutions may have a wide range of Ca concentrations, potentially causing matrix-related changes in instrumental mass bias (i.e., increased ion transmission with mass may cause deviations of measured ratios from true ratios). Two approaches are typically used to overcome such matrix effects. One is through a pre-screening of Ca concentrations by analyzing a small aliquot of sample solutions on an ICP-MS or ICP atomic emission spectrometer (ICP-AES) or optical emission spectroscopy (ICP-OES), then diluting the remainder to a near-constant Ca concentration for ICP-MS analyses (Yu et al., 2005). The other one is by analyzing matrix-matched internal standards with a wide range of Ca concentrations, fitting matrix curves to these data, and finally applying the corrections to the measured ratios of the unknown samples (Marchitto, 2006; Rosenthal et al., 1999). The first approach is not feasible on the iCAP at WHOI for most benthic foraminiferal samples because the sample uptake rate (1 ml/min) combined with the large number of elements we measure requires a minimum of 1 ml solution. For relatively small samples, using an aliquot for pre-screening of Ca concentration may lead to insufficient solution for iCAP analyses at 100 ppm Ca (our target matrix). We thus use the second approach as it is relatively more efficient, assuming the matrix corrections work.

We designed and prepared three internal standards (designated as AFS for artificial foraminifera solutions) for each benthic species, with a particular focus on Mg/Ca, Li/Ca, and Mg/Li, given the

implication of small differences in Mg/Li values for paleotemperature reconstructions. Similar to the calibration standards, Mg/Li values of these AFS standards were selected to mimic those of the benthic foraminifera analyzed with low, moderate, and high Mg/Li values (thus from different temperature conditions) (Fig. 2). For each analytical session, we measure only one species of benthic foraminifera and select two internal standards as matrix standards. These matrix standards have El/Ca values close to those expected in the foraminiferal samples (e.g., AFS2 and AFS3 for *H. elegans*, AFS4 and AFS5 for *C. pachyderma*). These AFS standards are then diluted to solutions with Ca concentrations of 40, 60, 80, 100, 120, 150, 180, and 200 ppm, in order to produce matrix correction curves for each session.

2.2.3. Consistency standards

To monitor the performance of our method, we use a third internal standard (AFS, see above) as the consistency standard for each benthic species, e.g., AFS1 for *H. elegans*, and AFS6 for *C. pachyderma* samples (Fig. 2). Note that AFS1 has lower elemental ratios than most core-top *H. elegans* whereas AFS6 ratios are generally higher than core-top *C. pachyderma* (e.g., Fig. 2). The selected internal consistency standard is diluted to different Ca concentrations (e.g., 60, 100, 150 ppm) and analyzed as an unknown for data quality control and to test the effectiveness of matrix corrections. For elements of interests in this study (i.e., Li, Mg, B, Cd, and Sr), the ion concentrations in the AFS1 solution at 100 ppm Ca, are much higher than the IDL, (e.g., >150 times for Li, >300 times for Mg, >15 times for B, >15 times for B, >25 times for Cd, and > 10,000 times for Sr).

In addition to the internal solution consistency standards, we use three international standards (one solution and two powder standards) as consistency standards: RM8301-foram (solution, National Institute of Standards and Technology, USA, Stewart et al., 2021), ECRM-752-1 (limestone powder, Bureau of Analyzed Samples Ltd, UK, Greaves et al., 2008), and BAM-RS3 (calcite powder, Bundesanstalt für Materialforschung und -prüfung, Germany, Greaves et al., 2008)). Limestone ECRM-752-1 and calcite BAM-RS3 are used in every session for long-term quality monitoring. RM8301-foram is only used in the sessions when we analyze *Cibicidoides* samples, because its El/Ca values (e.g., Li/Ca, Mg/Ca, B/Ca, and Sr/Ca) are close to those in *Cibicidoides* samples (Table 1).

2.3. Foraminifera sample preparation

Each of our measurements on the iCAP takes ~4 mins and requires ~1 ml solution to determine 14 El/Ca values. At our target Ca concentration of 100 ppm, ~240 µg of calcite is required for each measurement, corresponding to approximately 300 to 400 µg of foraminiferal shells per sample before cleaning. Foraminifera samples are weighed, then gently crushed to open chambers, and, where sample size allows, split into two or more samples for replicate analysis. Samples are cleaned following the full trace metal protocol (Boyle & Keigwin, 1985; Boyle & Rosenthal, 1996) including clay removal (using methanol), reductive cleaning (using anhydrous hydrazine), oxidative cleaning (using H_2O_2), and weak acid leaches (using 0.001 M HNO_3). After they are cleaned, samples are dissolved with 100 µl of 2% HNO_3, sonicated for 15 mins, then centrifuged for 10 mins at 10,000 rpm. Lastly, the samples are transferred to a set of new clean vials (already containing 900 µl of 2% HNO_3) and mixed well using a vortex shaker before being analyzed on the iCAP. The Ca concentration in the final 1 ml solution typically ranges between 40 and 150 ppm.

2.4. Analytical sequence

Our analytical session begins after daily tuning to optimize the instrument sensitivity, and consists of three types of blocks: cone conditioning, matrix, and sample blocks (Fig. 3). The cone conditioning consists of injecting one selected internal solution standard (in our example, AFS3 in 100 ppm Ca) for a few hours, in order to allow Ca deposition on cones to reach a maximum or saturation state (thus resulting in stable signals), similar to the protocol reported in Yu et al. (2005). A blank solution (2% HNO_3) is run every five AFS3 solutions for low background monitoring. The cone conditioning typically takes 3 - 4 hours on the WHOI iCAP (Fig. S1).

After the cone is well-conditioned, the analytical session begins with two matrix blocks. Two matrix blocks are placed in the beginning, middle, and the end of the sequence; and five sample blocks are placed between the set of two matrix blocks. The structures of matrix and sample blocks are similar, both starting with a blank solution (2% HNO_3), followed by sequences of two calibration standards (GLU) bracketing every two unknown matrix standards or samples, ending with a calibration standard (GLU4 in our example, file template in Table S4). For the matrix blocks, two internal standards (AFS2 and AFS3 in our example) are analyzed across a range of Ca

concentrations that covers most foraminiferal samples, in order to produce matrix correction curves for each session.

One or two consistency standards are randomly placed within each sample block for quality control, including the internal solution standard (e.g., AFS1 for *H. elegans*, and AFS6 for *C. pachyderma*, diluted to 60, 100, and 150 ppm Ca), powder limestone ECRM-752-1 and calcite BAM-RS3 (both freshly weighed, dissolved, and diluted to 100 ppm Ca), and RM8301-foram (freshly diluted to 100 ppm Ca, and only measured in the sessions analyzing *Cibicidoides* samples). Each consistency standard is run two to three times during each session. All foraminifera samples, matrix and consistency standards are run as unknowns in a randomized order during each session to avoid machine memory effects.

2.5. Data processing

The data collected from the iCAP are processed in four steps using an in-house Matlab script, to convert the raw CPS data offline into molar ratios:

(1) Blank correction: Our blank correction consists of two parts. First, we apply the conventional blank correction, which aims to correct for potential impurities introduced by the 2% HNO_3 used in standards, samples, and the rinse solution on iCAP. For this, we estimate the expected blank values for each sample or standard through linear interpolation of the measured values of adjacent blank solutions, and then subtract these estimated blank values from the measured sample/standard values. Second, one additional blank correction, applied only to calibration standards (GLU), corrects for impurities in the Ca stock solutions used to prepare these standards. Specifically, we subtract the measured values of standard GLU0 (prepared from only the Ca stock solution) from the measured values of all other calibration standards (GLU).

(2) Standard calibration: For all samples, we convert the measured CPS for each element (except Ca) to its respective molar abundance based on standard calibration lines which depict the relationship between the measured CPS for each element and its respective gravimetrically-determined molar abundance within the standard solutions. Since samples are embedded in repeated sequences of standards, multiple standard calibration lines are typically generated for each sample, with each calibration line consisting of one complete

set of standards (e.g., from GLU0 to GLU4) that encloses the sample in the analytical sequence (Fig. 3C-D). The molar abundances derived from all calibration lines are then averaged to derive the final corrected values for each element in the sample. Similarly, we determine the Ca abundance in each sample by comparing the measured Ca CPS in the sample, the average Ca CPS measured in each calibration standard, and the gravimetrically-determined Ca molar abundances of the standard solutions.

(3) Matrix correction: Matrix effects are quantified by fitting the correlation between the measured El/Ca in the two matrix standards and their respective Ca abundances (2^{nd}-order polynomial). These equations are then applied to the measured sample El/Ca to derive the final El/Ca for each sample or consistency standard (treated as unknowns).

3. Results and Discussion

3.1. Signal drift and correction

Similar to other types of ICP-MS (Marchitto, 2006; Yu et al., 2005), the sensitivity of most elements measured on the iCAP typically decreases throughout the session, due to salt deposition on the sampling cones. Signal drift varies among elements and from run to run. Among the five elements of interest (Li/Ca, Mg/Ca, B/Ca, Cd/Ca, and Sr/Ca), the signal corrections typically vary between 0 and 10 % during a 24-hr session (Fig. S2-3). The signal drift is usually gradual and effectively corrected by our calibration standards (Fig. S2-3). As an example, we selected consistency standards AFS2 and AFS3 (all at 100 ppm Ca) measured at the beginning, middle, and end of one analytical session, and normalized their El/Ca values to their respective first measurements before (CPS/CPS) and after (molar ratios) the standard corrections (Fig. 4). Their El/Ca values after the standard corrections are typically within ± 5% and do not show consistent trends with time, confirming the signal drifts have been effectively corrected.

3.2. Matrix effects and correction

Matrix effects also vary among elements and analytical sessions, typically ranging from ~ 5 to 10% for Li/Ca, Mg/Ca, and Cd/Ca, and as high as 20 % for B/Ca and Sr/Ca over the range of 40-200 ppm measured Ca concentrations (relative to El/Ca values measured at 100 ppm Ca) (Fig. S4). During most sessions, negative matrix effects were observed in B/Ca and Cd/Ca, and a positive matrix effect was observed in Sr/Ca, whereas the signs of the trends varied for Li/Ca and Mg/Ca.

Since the fitted matrix effect equations vary among analytical sessions, each session requires its own set of matrix corrections. The overall magnitudes of matrix effects we observed (mostly ± 5-10% in all analytical sessions) are comparable to those observed on other types of ICP-MS (Marchitto, 2006; Rosenthal et al., 1999; Yu et al., 2005), although the trends for each El/Ca differ among these machines.

Fig. 5 shows an example of fitted matrix curves of five El/Ca in one analytical session. In this session, both matrix solutions (AFS2 and AFS3) with high Ca (expected concentrations of 150, 180, 200 ppm based on pipette dilution) yielded lower measured Ca concentrations (140, 160, and 180 ppm, respectively), indicating signal suppression, possibly due to salt precipitation on the cones during the analysis. However, signal suppression seems to have occurred to a similar extent for Li/Ca, Mg/Ca, B/Ca, and Cd/Ca, thus leading to overall relatively small El/Ca matrix effects (within ±5% in this session) across the 150 - 200 ppm range of true Ca concentrations. Relatively larger variations of Li/Ca, B/Ca and Cd/Ca are found in the solutions of 40 ppm Ca, possibly due to their lower counting statistics as fewer atoms would be introduced into the plasma and ionized (also see section 3.3).

To evaluate the effectiveness of our matrix corrections, we use two datasets: (1) internal consistency standard solutions (AFS1 and AFS6); and (2) a large set of foraminifera sample replicates (a total of 18 *H. elegans* and 24 *C. pachyderma* samples from several cores in the Atlantic Ocean, with 3-7 measurements for each sample). Both the internal consistency standard solutions and foraminifera samples were measured across a wide range of Ca concentrations and treated as unknowns in the analyses. We first normalize each measured El/Ca value to the respective average value of its replicates [unit in %, calculated as (measured/average*100-100)], then group the data by their measured Ca concentrations in 20 ppm bins (Fig. 6). We observe no consistent trends in the normalized El/Ca across the whole range of Ca concentrations, suggesting our matrix correction is overall effective. The range of normalized El/Ca values is generally larger in foraminifera samples (~± 10%) compared to those in the AFS1 and AFS6 solutions (~± 5%), as expected from larger heterogeneity within the natural foraminifera samples than lab-prepared standard solutions. The normalized El/Ca variations are relatively larger in *H. elegans* than in *C. pachyderma* samples, and similarly, the *H. elegans*-like AFS1 solutions show larger normalized

El/Ca variations than those in *Cibicidoides*-like AFS6. We infer these differences are amplified in *H. elegans* and AFS1 because of their relatively lower average El/Ca (also see section 3.3).

For AFS1 solutions, the mean El/Ca values at different Ca concentrations are within error of each other, although the variations are generally larger at 60 ppm Ca than at higher Ca, particularly for Li/Ca, potentially due to larger uncertainty at lower counting statistics (Li/Ca of ~1.3 μmol/mol). To further examine this issue, we checked the AFS1 data in all analytical sessions, comparing the normalized data of raw CPS/CPS to the ratios after calibration correction and after matrix corrections (Fig. S5). We find that for Li/Ca, Mg/Ca, and Cd/Ca, neither the calibration correction nor matrix corrections seem to increase or reduce the scatter, suggesting the El/Ca variations mainly derive from the raw data noise. For B/Ca and Sr/Ca, matrix corrections effectively correct for El/Ca variations induced by different Ca concentrations in the solution (Fig. S5). Furthermore, because we used AFS2 and AFS3 (Li/Ca of ~3.3 and 4.3 μmol/mol, respectively) as matrix standards to correct AFS1 which has much lower Li/Ca (1.31 μmol/mol, or 40% of AFS2), it is possible that using a matrix standard having Li/Ca closer to the expected mean value of the unknowns would improve the outcome. For example, using AFS4 and AFS5 (Li/Ca of ~12.2 and 16.4 μmol/mol, respectively) as matrix standards to correct AFS6 (Li/Ca of ~10.2 μmol/mol, or ~ 80% of ASF4) run at different Ca concentrations yields better results, with fewer systematic differences in mean value and standard deviations (Fig. 6), perhaps because of the higher elemental ratios and the greater proximity (as a percent) of AFS6 to the matrix standards used.

3.3. Precision and accuracy

The long-term precision and accuracy of this method were determined using nine consistency standards, including six internal solutions (AFS1-AFS6), one external solution (RM8301-foram), and two external powder materials (limestone ECRM-752-1, and calcite BAM-RS3), over a period of 15 months from May 2022 to August 2023 (Table 1). We note that AFS2-AFS5 solutions at 100 ppm Ca were treated as unknowns during data processing, thus they are also used for long-term data quality control. The El/Ca 2SD in the two solid standards are generally similar to those reported in both AFS and RM8301-foram solutions. Across the full range of the El/Ca measured in both internal and external standards, the average long-term precisions (2σ) are Li/Ca = 0.21 μmol/mol (4.8%), Mg/Ca = 0.06 mmol/mol (3.8%), B/Ca = 3.8 μmol/mol (4.4%, for B/Ca > 5

326 μmol/mol), Cd/Ca = 0.006 μmol/mol (10.0%, for Cd/Ca < 0.15 μmol/mol), and Sr/Ca = 0.03
327 mmol/mol (4.2%) (Table 1). The average 2RSD are within 5% for Na/Ca, Mn/Ca, Ba/Ca, and U/Ca;
328 10-20% for Ti/Ca and Fe/Ca; higher for Al/Ca (33%) and Zn/Ca (37%) (supplementary tables).

329 The accuracy of most El/Ca are within 5%, except for Al/Ca and Fe/Ca. Because we typically
330 use Al/Ca and Fe/Ca ratios to assess potential sample contamination (e.g., > 100 μmol/mol
331 suggests suspected contamination), the semi-quantitative measured values are sufficient for most
332 paleoceanography research purposes. For the five elements of interest, the measured mean values
333 closely follow the 1:1 line with reference values (Fig. 7). Notably, the internal standards generally
334 show smaller deviations from the 1:1 line (mostly ±2%) than external standards (mostly ±2-5%).
335 The reference El/Ca values of internal standards are most likely true values as they were
336 gravimetrically determined. In contrast, the reference El/Ca values of external standards (calcite
337 BAM-RS3, limestone ECRM-752-1, and solution RM8301-foram) are the mean values reported
338 by other labs, and the larger deviation from the 1:1 line may reflect a contribution from inter-lab
339 differences.

340 The relative standard deviations of El/Ca are expected to positively correlate with the 1/[square
341 root (El/Ca)] if the measurement noise follows counting statistics and the El/Ca << 1 (similar to
342 what has been theoretically derived for stable isotope ratio measurements, (Hayes, 1983)). Our
343 precisions across a wide range of El/Ca generally follow this expectation, yielding higher RSD
344 values at lower El/Ca (Fig. 8). For example, for Li/Ca and Mg/Ca, their 2RSD values increase
345 from 2.4% to 5.0% and from 3.0% to 8.2%, respectively, with a factor of ~2 decrease in the El/Ca.
346 Together, these yield precisions of 2.3% to 7.7% (2RSD) for Mg/Li, with AFS1 and AFS6 (our
347 two internal consistency standards at varying Ca concentrations) showing 7.7% and 2.3% 2RSD
348 respectively (Fig. 8). At the high El/Ca end, our precisions are comparable to other labs, which use
349 either an iCAP (Dai et al., 2023; Ford et al., 2016) or a different type of ICP-MS (Ford et al., 2016;
350 Marchitto, 2006; Yu et al., 2005).

351 **3.4. Implications for the *H. elegans* Mg/Li thermometry**

352 The precisions we report at low El/Ca have implications for *H. elegans* paleothermomemetry.
353 Note that Mg/Li of *C. pachyderma* should not be used to estimate temperature, because dividing

Mg/Ca by Li/Ca in *C. pachyderma* does not fully correct for the influence of carbonate saturation state on Mg/Ca (Oppo et al., 2023). Using the *H. elegans* Mg/Li-temperature calibration equation of Oppo et al. (2023), the 7.7% 2RSD of Mg/Li in AFS1 (±0.016 mol/mmol) is equivalent to a temperature error of ±1.1 °C (at 1.5 °C). For AFS2, the 4.0% 2RSD (±0.007 mol/mmol) is equivalent to ±0.5 °C (at 0.3 °C), and for AFS3, the 3.3% 2RSD (±0.010 mol/mmol) is equivalent to a temperature error of ±0.7 °C (at 8.7 °C).

Importantly, the temperature precision is not only a function of temperature or Mg/Li itself, but related to the specific Mg/Ca and Li/Ca of the sample, which can vary considerably for a single temperature (Marchitto et al., 2018) (Fig. 8). For example, although the Mg/Li of AFS1 and AFS2 were both designed to mimic foraminifera calcifying in cold water, their elemental compositions, and associated measurement precisions, are different. The very low Li/Ca (1.3 μmol/mol) and Mg/Ca (0.26 mmol/mol) in AFS1 occur in core-top *H. elegans* from the deep subpolar North Atlantic where temperatures are ~ 1.1°C. The higher Li/Ca (4.4 μmol/mol) and Mg/Ca (0.8 mmol/mol) in AFS2 correspond to *H. elegans* found in the glacial Atlantic sediments, where estimated temperatures are ~ 0.5°C (Valley et al., 2019; Umling et al., 2019; Oppo et al., 2023). Thus, the temperature error is larger for AFS1 than for AFS2, despite the similarity in their Mg/Li values. This finding underscores the need to match the El/Ca of consistency standards to those of the unknown for accurate estimation of measurement precisions.

4. Summary

We assess the precision and accuracy of foraminiferal minor and trace element measurements on an iCAP across a range of El/Ca values, using a species-specific method. In particular, the internal consistency solution standards are designed to match the expected elemental ratios of real samples being measured, and are run with a range of Ca concentrations similar to foraminifera samples. Based on the results from these consistency solution standards, we estimate the precision for *H. elegans* Mg/Li measurements range from 3.3 to 7.7 % (0.007 to 0.016 mol/mmol), which is equivalent to an uncertainty in Mg/Li-derived temperatures of 0.5 – 1.1 °C. Overall, the precision of foraminiferal element analysis depends on the actual El/Ca values in the samples, which can vary depending on oceanic regions, temperature, or time frame. The 2RSDs are higher at low El/Ca values as expected from counting statistics. Due to the heterogeneity of foraminifera samples, the

average errors on replicate samples of foraminifera are ~ 8.0 %, larger than on internal consistency solution standards, and are thus associated with larger Mg/Li-derived temperature uncertainties.

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Open Research

The file templates for standard preparation, session sequence, and standard dilution, and the Matlab scripts to process the raw ICP-MS data are available in the supplementary materials and Zenodo (citation link will be available upon acceptance).

Author contributions

Conceptualization: W. Guo, D.W. Oppo, W. Lu
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Investigation: W. Lu, W. Guo, D.W. Oppo
Methodology: W. Lu, W. Guo, D.W. Oppo
Project administration: D.W. Oppo
Resources: D.W. Oppo
Software: W. Guo, W. Lu
Supervision: W. Guo, D.W. Oppo
Validation: W. Lu, W. Guo, D.W. Oppo
Writing – original draft: W. Lu
Writing – review & editing: W. Lu, W. Guo, D.W. Oppo

413 Table 1. Long-term precision and accuracy for five selected El/Ca determined from internal and external consistency standards, and
414 average precision of foraminifera samples based on 3-7 replicates (n = 18 for *H. elegans*, n = 24 for *C. pachyderma*).

Standard/samples	n	LiCa_mean µmol/mol	LiCa_2sd µmol/mol	LiCa_2rsd %	Expected µmol/mol	Reference value µmol/mol	Accuracy %	MgCa_mean mmol/mol	MgCa_2sd mmol/mol	MgCa_2rsd %	Expected mmol/mol	Reference value mmol/mol	Accuracy %	MgLi_mean mol/mmol	MgLi_2sd mol/mmol	MgLi_2rsd %	Expected mol/mmol	Reference value mol/mmol	Accuracy %
AFS1	66	1.31	0.06	5.0	1.31		-0.4	0.26	0.02	8.2	0.26		2.7	0.20	0.016	7.7	0.20		3.2
AFS2	58	4.36	0.12	2.8	4.33		0.7	0.80	0.03	3.8	0.81		-0.4	0.18	0.007	4.0	0.19		-1.1
AFS3	24	3.32	0.11	3.4	3.30		0.3	1.02	0.03	3.0	1.02		0.6	0.31	0.010	3.3	0.31		0.2
AFS4	15	16.40	0.39	2.4	16.39		0.1	1.52	0.05	3.3	1.51		0.9	0.09	0.003	3.6	0.09		0.8
AFS5	15	12.35	0.43	3.5	12.24		0.9	2.84	0.08	2.9	2.81		1.1	0.23	0.006	2.5	0.23		0.2
AFS6	33	10.32	0.28	2.7	10.24		0.7	3.24	0.10	3.1	3.20		1.0	0.31	0.007	2.3	0.31		0.3
BAM-RS3	17	1.23	0.15	11.9		1.22		0.75	0.03	3.4		0.79		0.61	0.072	11.8		0.65	
ECRM-752-1	29	1.57	0.15	9.6		1.39		3.57	0.13	3.8		3.75		2.28	0.217	9.5		2.70	
RM8301_foram	16	8.81	0.22	2.5		9.01		2.52	0.07	2.9		2.62		0.29	0.004	1.6		0.29	
H.elegans			0.41	12.2					0.14	16.9					0.020	8.0			
C. pachyderma			0.39	3.2					0.09	8.6					0.008	8.9			

Standard/samples	n	BCa_mean µmol/mol	BCa_2sd µmol/mol	BCa_2rsd %	Expected µmol/mol	Reference value µmol/mol	Accuracy %	SrCa_mean mmol/mol	SrCa_2sd mmol/mol	SrCa_2rsd %	Expected mmol/mol	Reference value mmol/mol	Accuracy %	CdCa_mean µmol/mol	CdCa_2sd µmol/mol	CdCa_2rsd %	Expected µmol/mol	Reference value µmol/mol	Accuracy %
AFS1	66	32.3	2.6	8.2	30.0		7.4	0.51	0.02	4.3	0.50		1.5	0.047	0.004	9.3	0.046		2.2
AFS2	58	41.7	3.0	7.2	40.4		3.1	1.01	0.03	3.3	1.00		0.9	0.067	0.004	5.3	0.066		1.1
AFS3	24	52.1	2.0	3.9	49.8		4.5	2.02	0.05	2.6	2.02		0.1	0.080	0.006	7.5	0.077		3.6
AFS4	15	203.0	6.0	3.0	200.8		1.1	1.31	0.03	2.2	1.32		-0.2	0.077	0.004	5.5	0.076		2.1
AFS5	15	183.7	5.3	2.9	181.4		1.3	1.51	0.04	2.9	1.50		0.7	0.048	0.005	11.3	0.046		6.0
AFS6	33	142.1	4.3	3.0	139.9		1.6	1.02	0.04	3.4	1.01		1.1	0.127	0.008	6.5	0.126		0.5
BAM-RS3	17	4.7	4.7	101.0				0.19	0.02	7.7		0.18		0.038	0.009	24.8		0.033	
ECRM-752-1	29	3.9	2.4	60.5				0.18	0.01	8.0		0.18		0.584	0.097	16.6		0.544	
RM8301_foram	16	138.7	3.4	2.4		138.9		1.30	0.04	3.4		1.34		0.570	0.024	4.3		0.580	
H.elegans			8.4	17.2					0.16	10.2					0.006	15.7			

C. pachyderma	5.5	3.7		0.04	3.2		0.007	10.7

Notes:

1. Because the AFS and GLU standards were prepared from the same bottle of high purity Ca stock solution, we calculated the expected values of AFS solutions by first determining the impurities of Ca stock solutions (using the GLU calibration standard curves), and then accounting for the impurities in the gravimetric values of AFS solutions.
2. The reference values of BAM-RS3 and ECRM-752-1 refer to those reported from INSTAAR, University of Colorado (Greaves et al., 2008), and those of RM8301-foram refer to the average values reported from several laboratories (Stewart et al., 2021).
3. Accuracy = (measured mean - expected)/expected*100%.
4. The B/Ca 2RSD of BAM-RS3 and ECRM-752-1 are relatively high due to their low average B/Ca, and the Cd/Ca in ECRM-752-1 and RM8301-foram are outside of the calibration standard range, thus these values are excluded from the calculation of average long-term precisions.

Figures

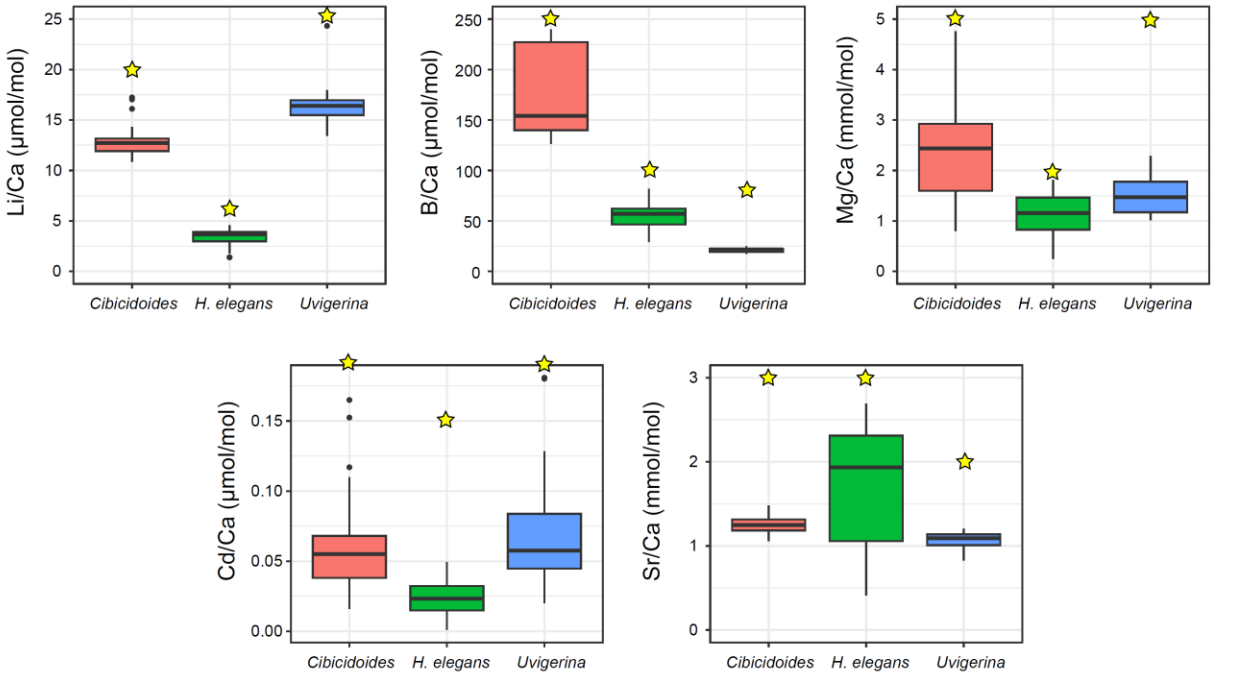
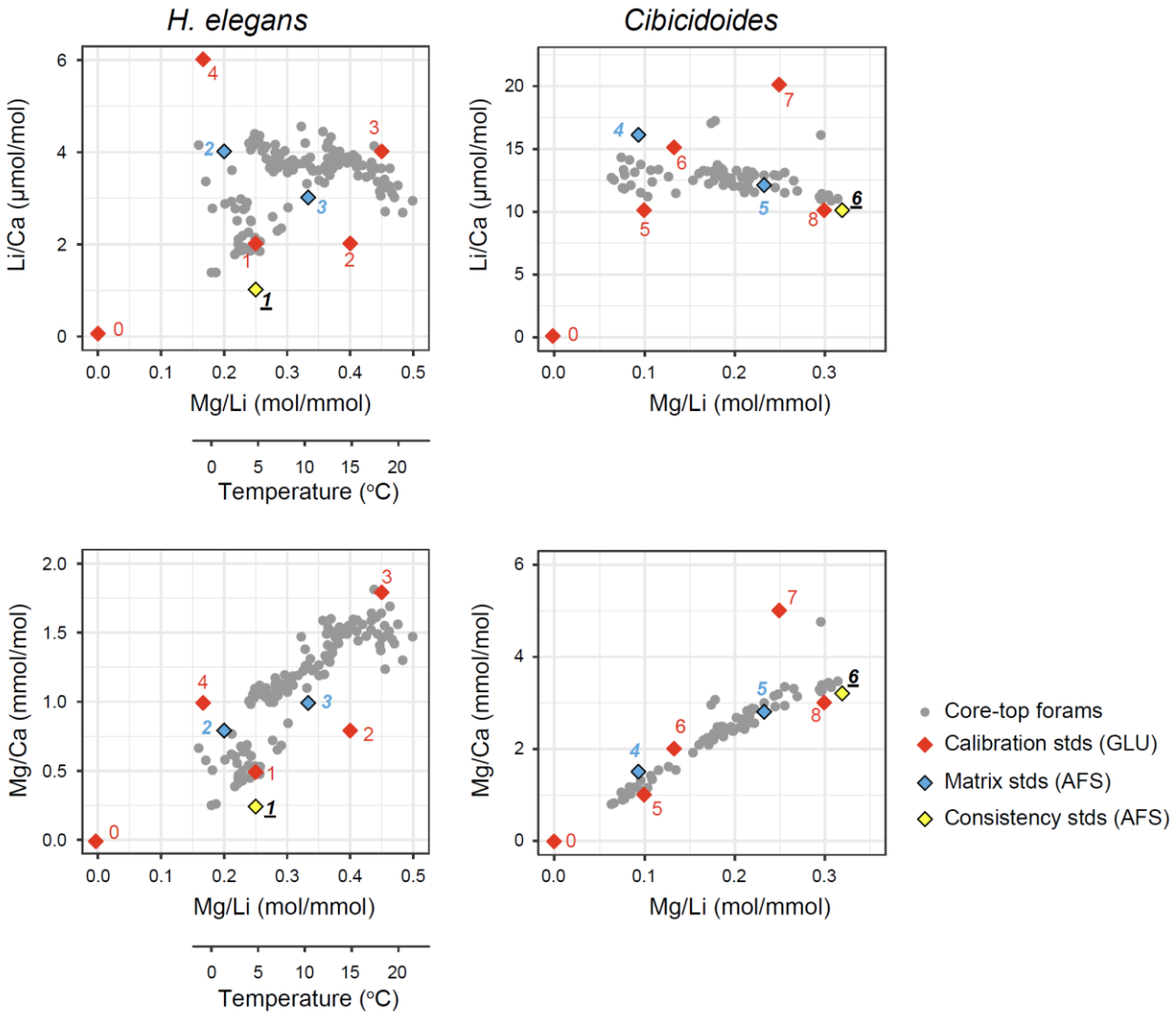


Fig. 1. Boxplot of five selected El/Ca in three benthic foraminifera species from core-top samples. The Li/Ca, B/Ca, Mg/Ca, and Cd/Ca data are only from three Atlantic regions (Bryan & Marchitto, 2008, 2010; Oppo et al., 2023; Umling et al., 2019), but they are comparable to those from global core-tops (Elderfield et al., 2006; Rae et al., 2011; Stirpe et al., 2021; Tisserand et al., 2013; Yu & Elderfield, 2007); Sr/Ca data are from global core-tops (Oppo et al., 2023; Yu et al., 2014). The El/Ca data distributions are used to guide the design of calibration and internal consistency standards. Yellow stars mark the maximum El/Ca in each calibration standard set.



437

438 **Fig. 2.** Cross-plot of Mg/Li vs. Li/Ca and Mg/Ca in two benthic foraminifera species from core-
439 top samples and their corresponding standard sets prepared at WHOI. The calibration standards
440 (GLU, label numbers with red fonts) are designed to scatter at four corners of all core-top data,
441 whereas the matrix and consistency standards (AFS) are designed to match low, moderate, high
442 Mg/Li (thus temperature) endmembers. The *H. elegans* Mg/Li - temperature conversions use the
443 equation from Oppo et al. (2023).

444

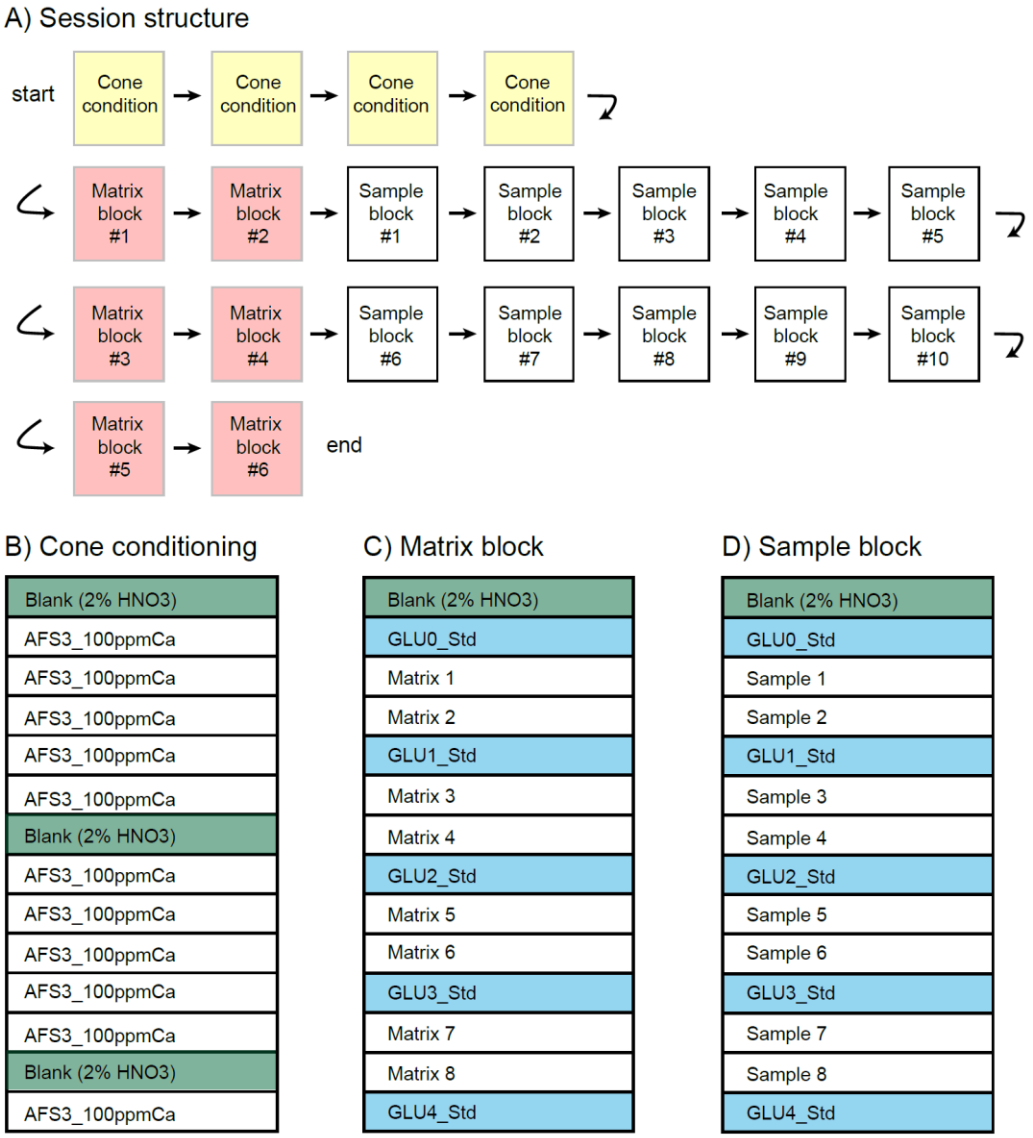


Fig. 3. Schematic illustration of a full session sequence used to run *H. elegans* samples. After cone conditioning, the matrix blocks are placed in the beginning, middle, and end of the session. One or two consistency standards (e.g., AFS, and international standards) are placed within each sample block for quality control. Note that all matrix standards, consistency standards, and unknown samples are run in randomized order to avoid memory effects.

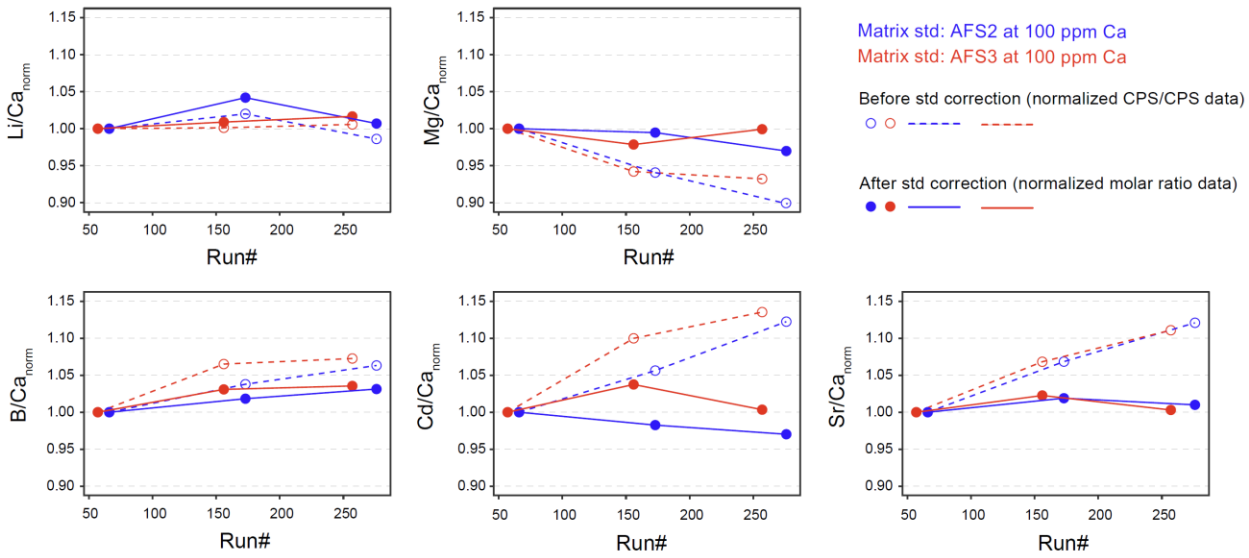


Fig. 4. Effect of signal drift correction in a representative session, based on Li/Ca, Mg/Ca, B/Ca, Cd/Ca, and Sr/Ca of two internal standard solutions - AFS2 and AFS3 (matrix standards, all at 100 ppm Ca concentration).

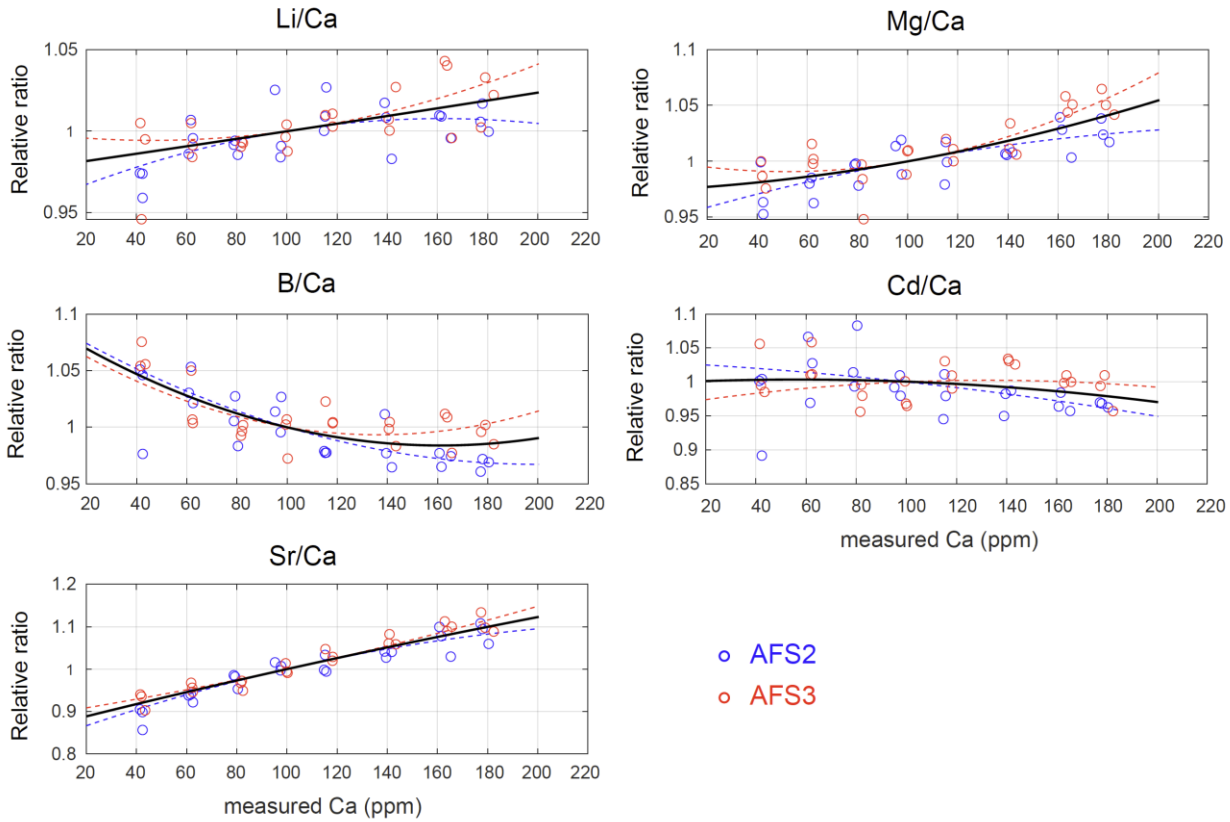
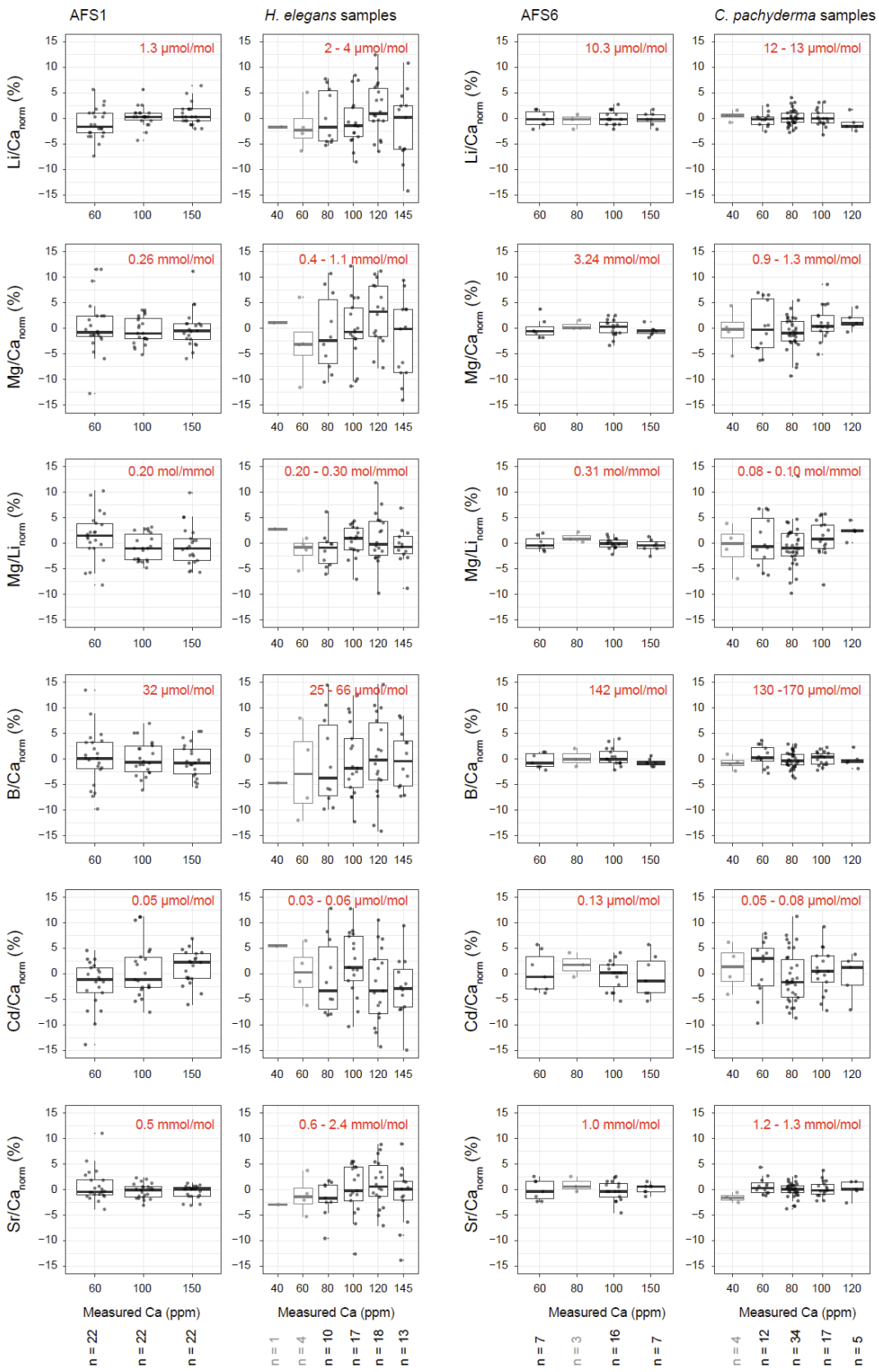


Fig. 5. Matrix effects and curves determined in a representative session, for Li/Ca, Mg/Ca, B/Ca, Cd/Ca, and Sr/Ca ratios over measured Ca concentrations of 40 to 180 ppm. The blue and red dashed lines denote the fitting for the AFS2 and AFS3 matrix standards, respectively, and show generally minor differences. The black line which fits all AFS data is used in the final matrix correction. Note that at high Ca concentrations, there are differences between measured (140, 160, 180 ppm) and expected values (150, 180, 200 ppm based on pipette dilution), indicating signal suppression. However, the signal suppression occurs for all other elements (except for Sr) to a similar extent, leading to minor drifts in El/Ca values. Note varying range of vertical axes.


AFS1
H. elegans samples
AFS6
C. pachyderma samples
Li/Ca norm (%)
Mg/Ca norm (%)
Mg/Li norm (%)
B/Ca norm (%)
Cd/Ca norm (%)
Sr/Ca norm (%)
1.3 µmol/mol
2 - 4 µmol/mol
10.3 µmol/mol
12 - 13 µmol/mol
0.26 mmol/mol
0.4 - 1.1 mmol/mol
3.24 mmol/mol
0.9 - 1.3 mmol/mol
0.20 mol/mmol
0.20 - 0.30 mol/mmol
0.31 mol/mmol
0.08 - 0.10 mol/mmol
32 µmol/mol
25 - 66 µmol/mol
142 µmol/mol
130 -170 µmol/mol
0.05 µmol/mol
0.03 - 0.06 µmol/mol
0.13 µmol/mol
0.05 - 0.08 µmol/mol
0.5 mmol/mol
0.6 - 2.4 mmol/mol
1.0 mmol/mol
1.2 - 1.3 mmol/mol
Measured Ca (ppm)
n = 22 n = 22 n = 22
n = 1 n = 4 n = 10 n = 17 n = 18 n = 13
n = 7 n = 3 n = 16 n = 7
n = 4 n = 12 n = 34 n = 17 n = 5

471

Fig. 6. Matrix and drift corrected El/Ca ratios of internal solution consistency standards (AFS1 and AFS6) and benthic foraminifera sample replicates (3-7 measurements for each sample), normalized relative to the respective averages and binned by the measured Ca concentrations (20 ppm bin size). Normalized El/Ca at different measured Ca concentrations overlap, confirming the effectiveness of the matrix corrections. Red fonts show the average El/Ca of AFS1 or AFS6, or the El/Ca range of the sample replicates. Data with small sampling size ($n < 5$) are shown in grey. Note that the last bin in *H. elegans* is centered at 145 ppm Ca. Random jitters are added to the x-axis positions to avoid overlapping points.

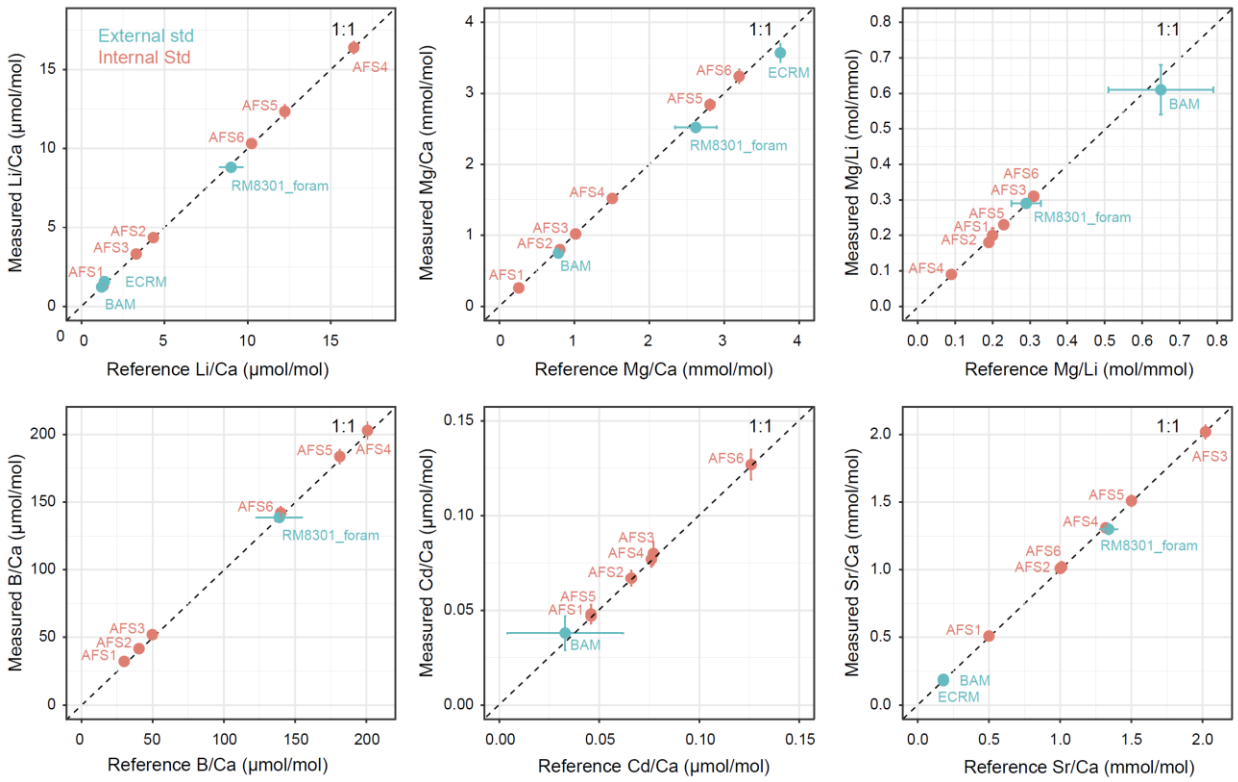


Fig. 7. Comparisons of the measured mean El/Ca values of internal and external standards vs. their corresponding reference values (Table 1). The reference El/Ca for internal standards are determined from known gravimetric values corrected for impurities from the Ca stock solutions, whereas the reference El/Ca for external standards BAM-RS3 and ECRM-752-1 refer to those reported from INSTAAR, University of Colorado (Greaves et al., 2008), and those of RM8301-foram refer to the average values reported from several laboratories (Stewart et al., 2021). Note that the Cd/Ca in ECRM-752-1 and RM8301-foram are outside of the calibration standard range, thus these values are not plotted here (but listed in Table 1).

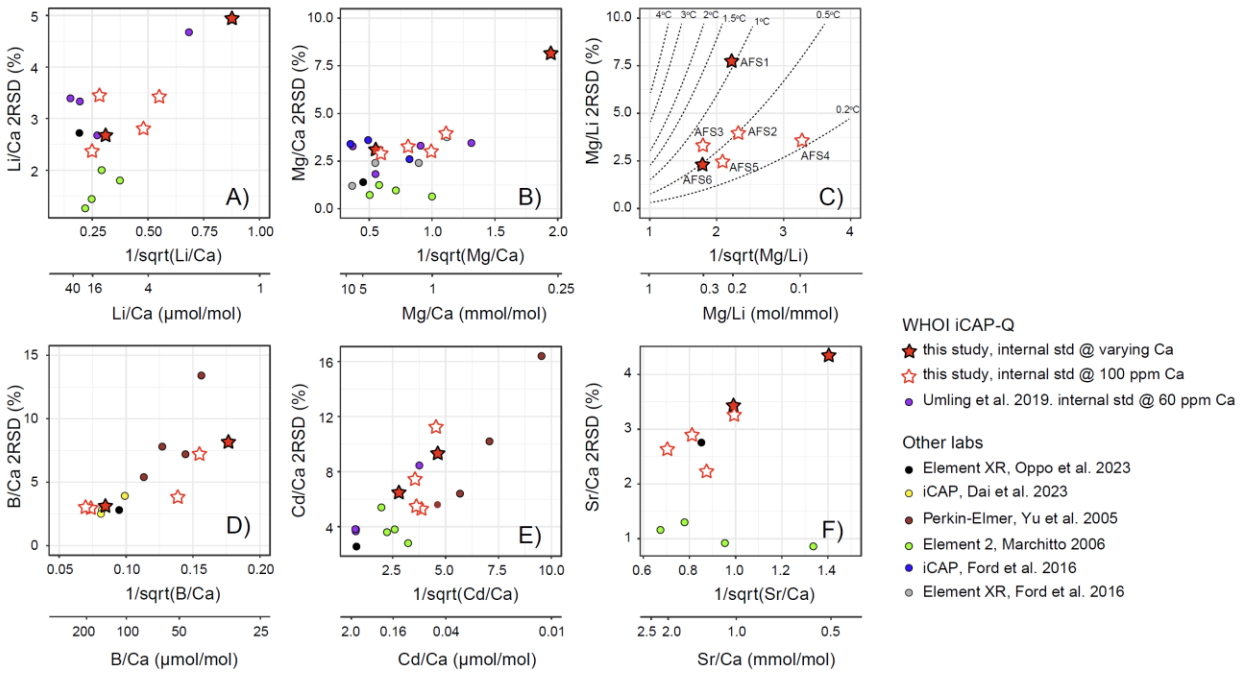


Fig. 8. Precisions of El/Ca measurements across a range of El/Ca ratios (this study, Table 1) and their comparison with published studies (Dai et al., 2023; Ford et al., 2016; Marchitto, 2006; Oppo et al., 2023; Umling et al., 2019; Yu et al., 2005). This compilation only includes lab-prepared solution consistency standards. Note varying range of vertical axes. The contour lines in panel C) denote the uncertainties in Mg/Li-derived temperatures (labels) at the corresponding Mg/Li values and 2RSD precisions, showing that the same Mg/Li 2RSD implies different temperature precision at different Mg/Li values (and hence temperatures). Note that the Mg/Li – temperature conversion is only applicable on *H. elegans* (Oppo et al., 2023).

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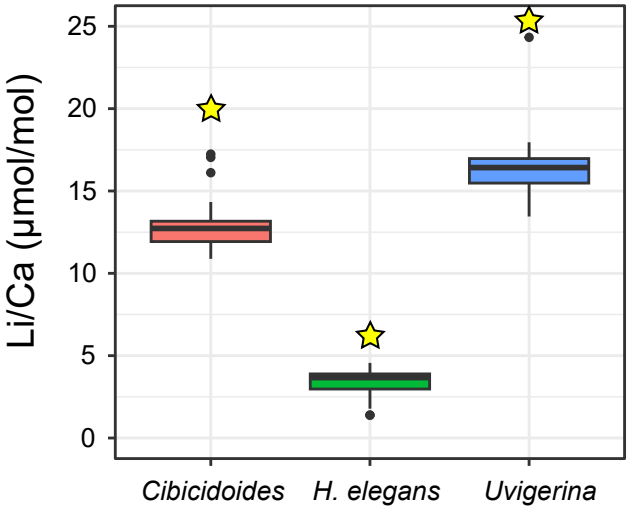
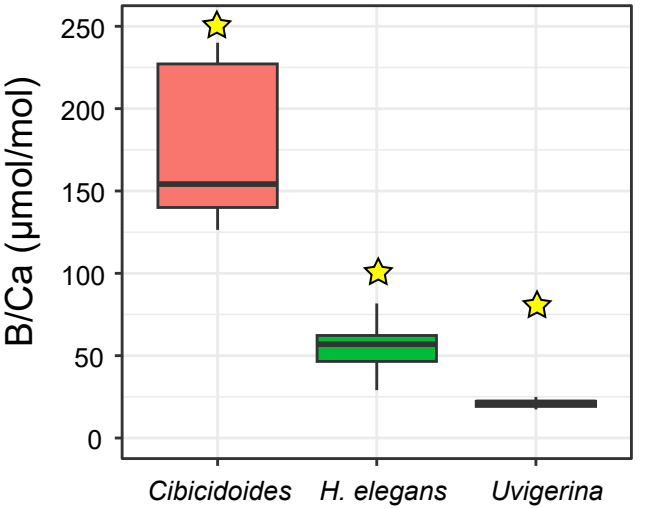
Figure 1.


Li/Ca (µmol/mol)
25
20
15
10
5
0
Cibicidoides
H. elegans
Uvigerina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100
50
0
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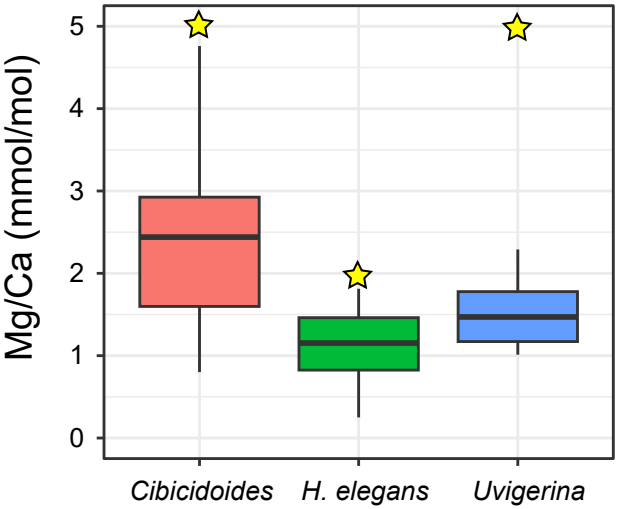
H. elegans
Uvigerina


Mg/Ca (mmol/mol)
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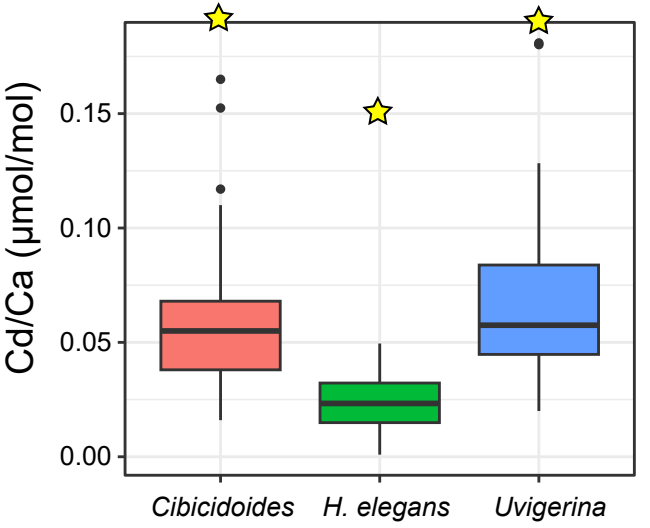
4
3
2
1
0
Cibicidoides
H. elegans
Uvigerina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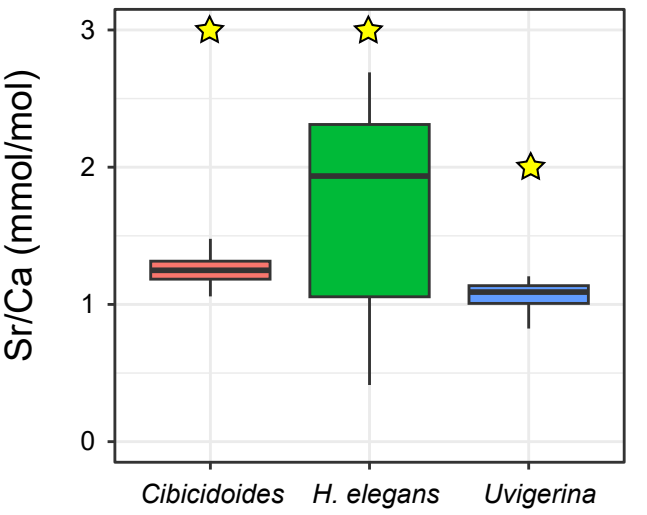
0.10
0.05
0.00
Cibicidoides
H. elegans
Uvigerina


Sr/Ca (mmol/mol)
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2
1
0
Cibicidoides
H. elegans
Uvigerina

Figure 2.

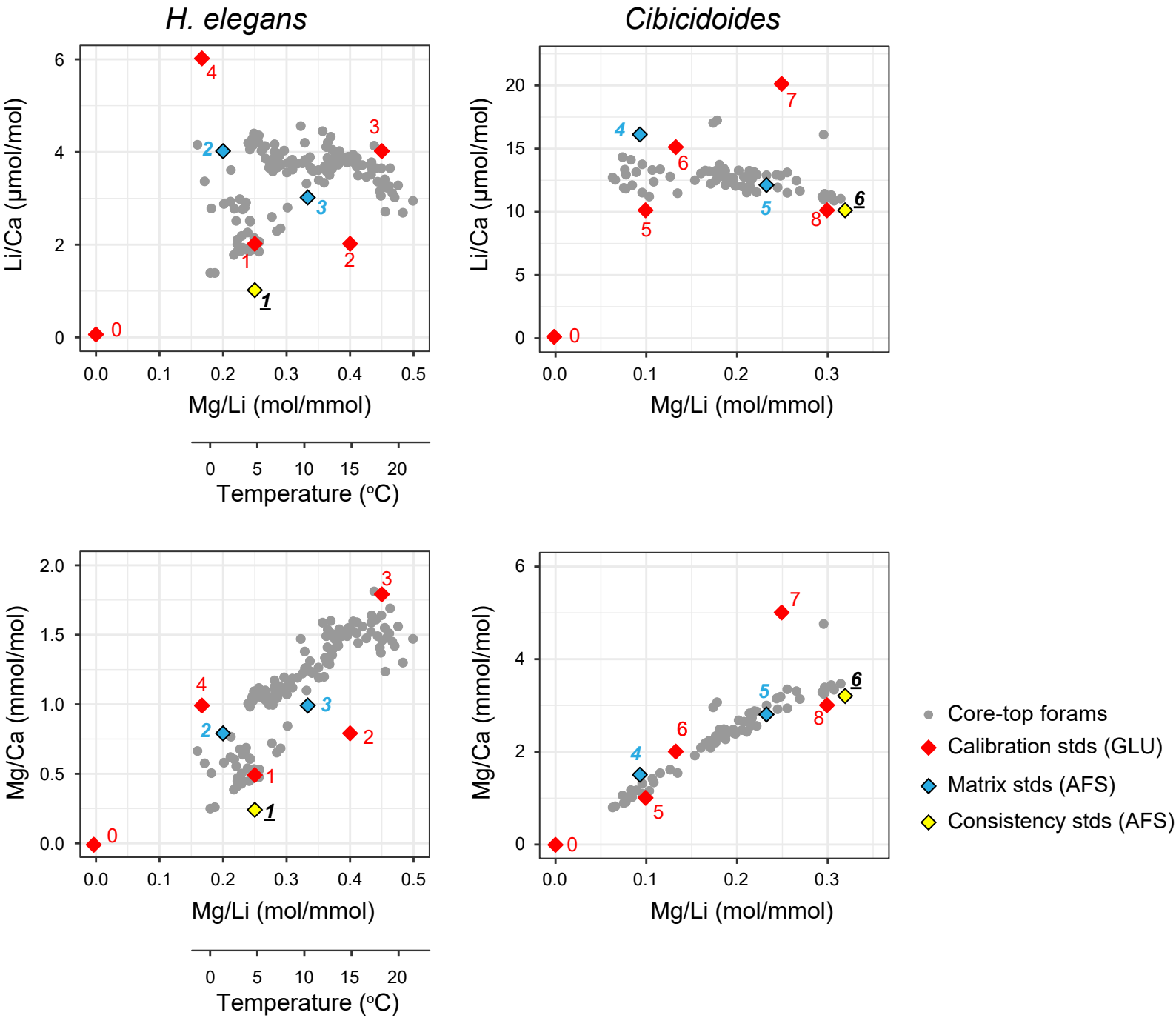
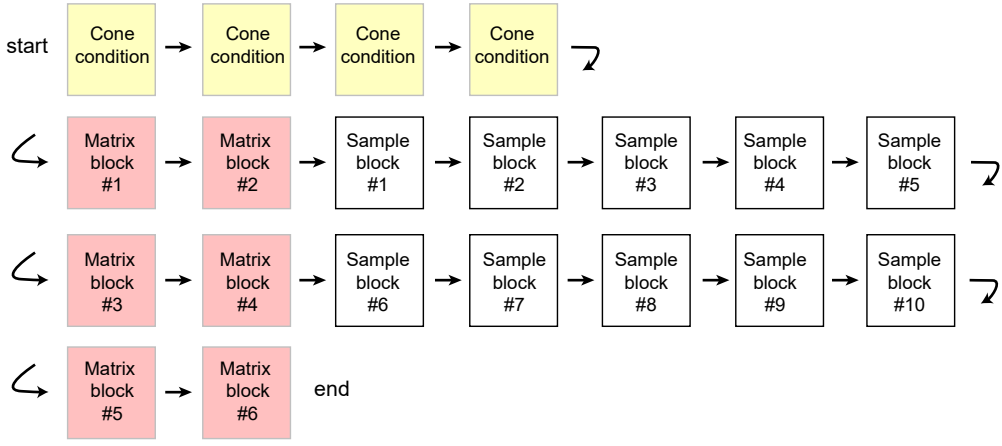

H. elegans
Cibicidoides
Li/Ca (µmol/mol)
Mg/Li (mol/mmol)
Mg/Ca (mmol/mol)
Temperature (°C)
Core-top forams
Calibration stds (GLU)
Matrix stds (AFS)
Consistency stds (AFS)

Figure 3.

A) Session structure



B) Cone conditioning

Blank (2% HNO3)
AFS3_100ppmCa
AFS3_100ppmCa
AFS3_100ppmCa
AFS3_100ppmCa
AFS3_100ppmCa
Blank (2% HNO3)
AFS3_100ppmCa
AFS3_100ppmCa
AFS3_100ppmCa
AFS3_100ppmCa
AFS3_100ppmCa
Blank (2% HNO3)
AFS3_100ppmCa

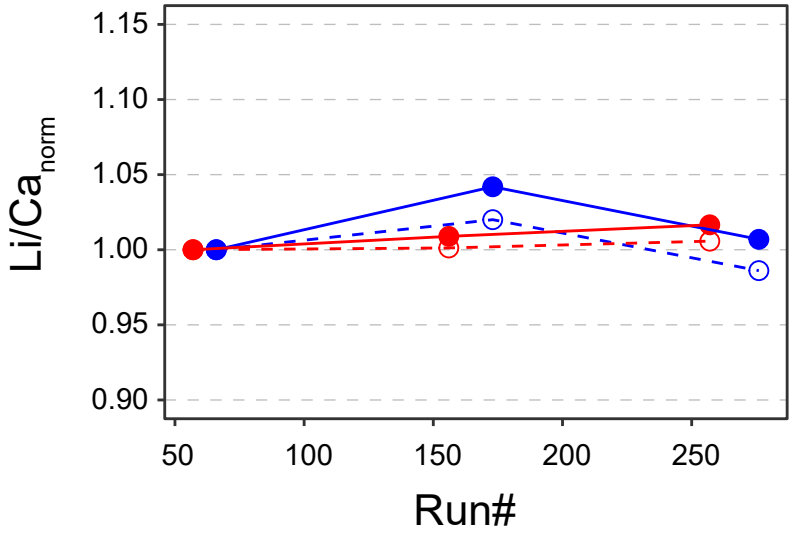
C) Matrix block

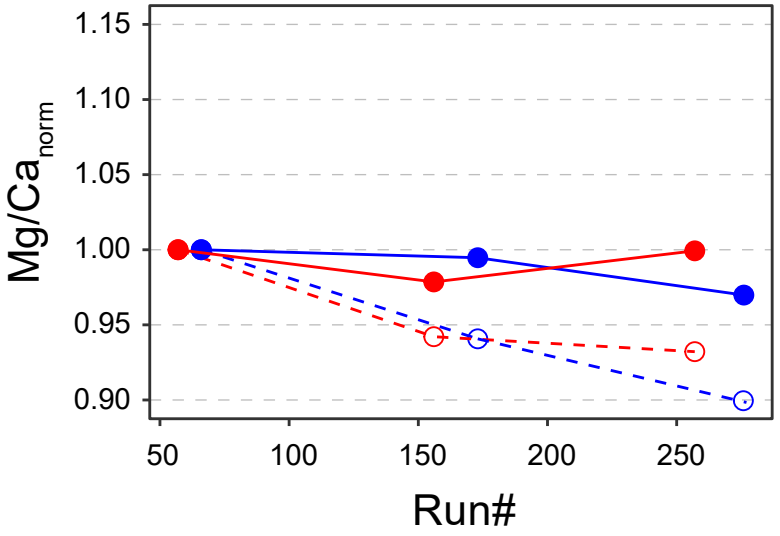
Blank (2% HNO3)
GLU0_Std
Matrix 1
Matrix 2
GLU1_Std
Matrix 3
Matrix 4
GLU2_Std
Matrix 5
Matrix 6
GLU3_Std
Matrix 7
Matrix 8
GLU4_Std

D) Sample block

Blank (2% HNO3)
GLU0_Std
Sample 1
Sample 2
GLU1_Std
Sample 3
Sample 4
GLU2_Std
Sample 5
Sample 6
GLU3_Std
Sample 7
Sample 8
GLU4_Std

Figure 4.



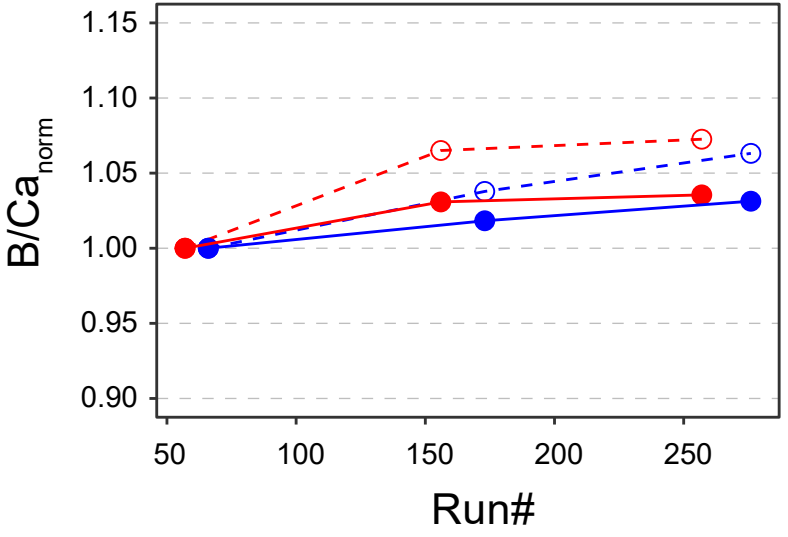


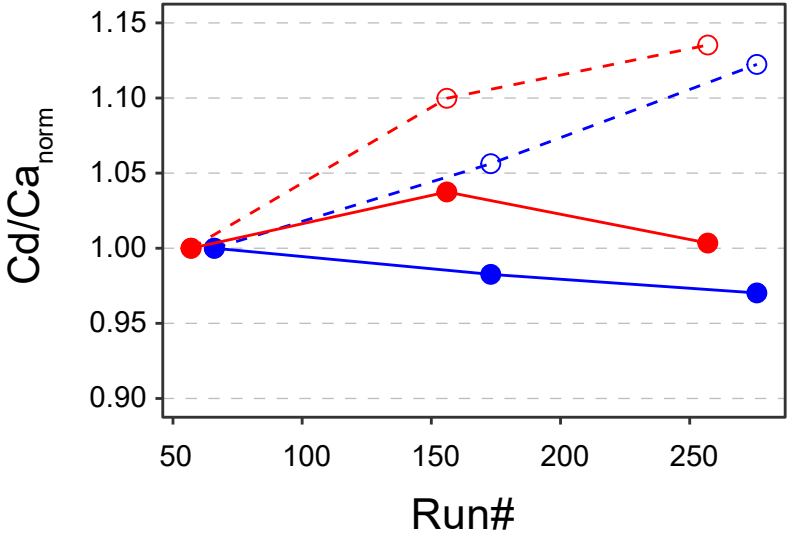
Matrix std: AFS2 at 100 ppm Ca

Matrix std: AFS3 at 100 ppm Ca

Before std correction (normalized CPS/CPS data)

After std correction (normalized molar ratio data)





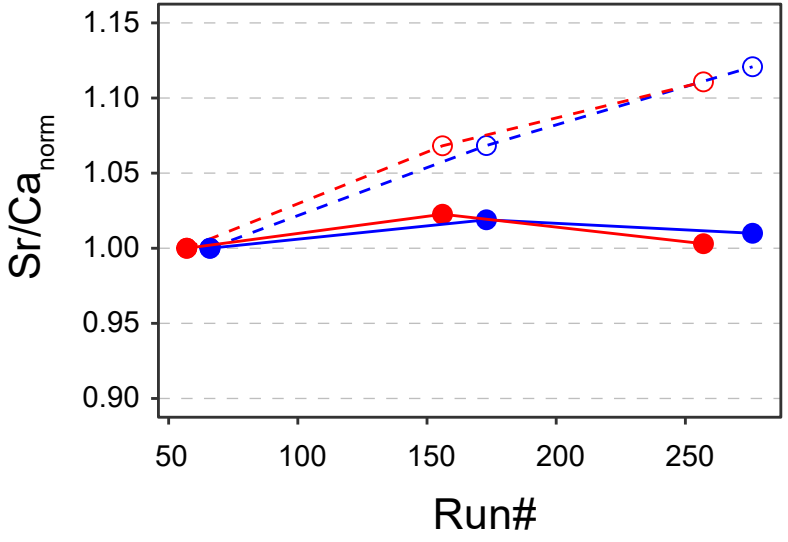


Figure 5.

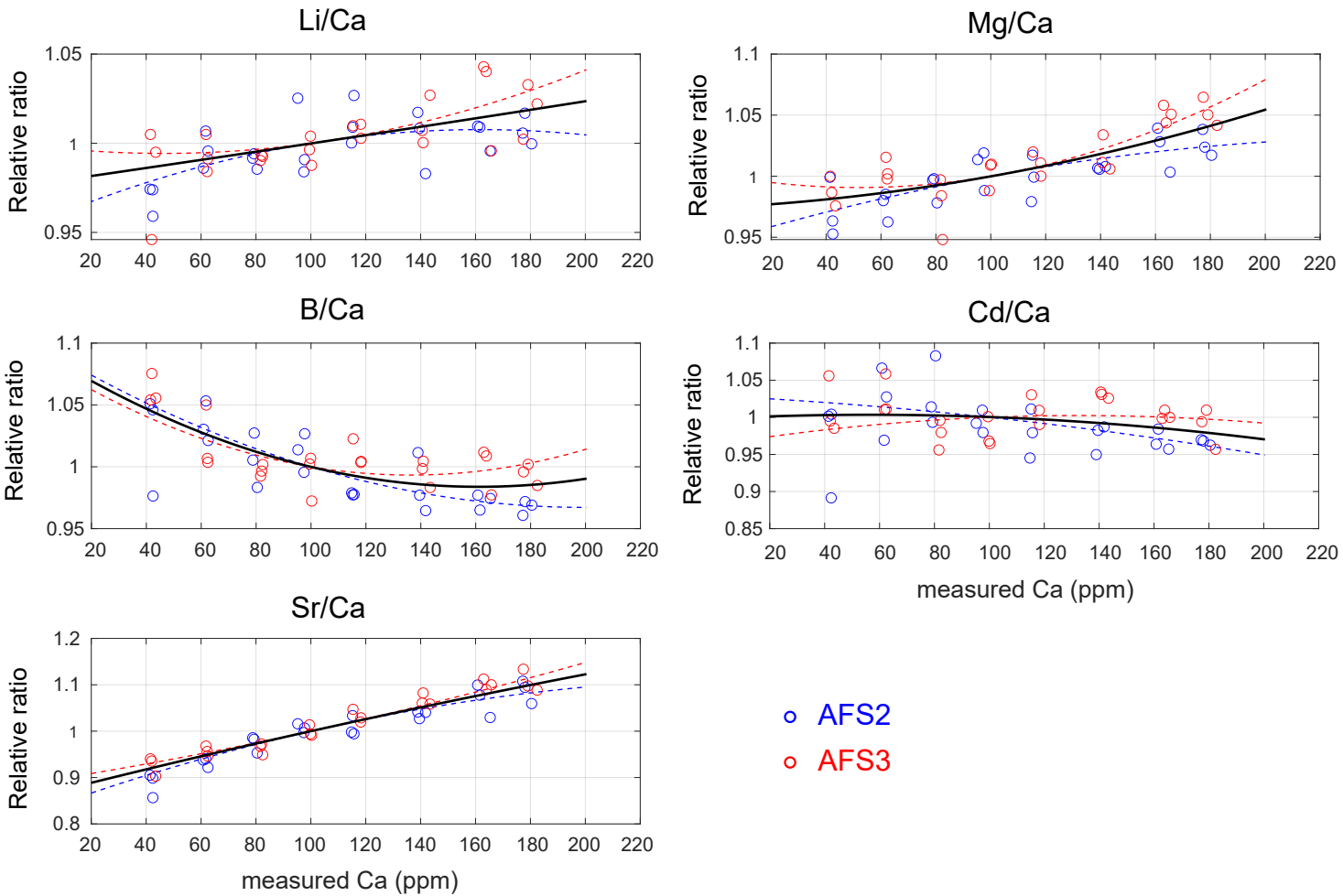

Li/Ca
Mg/Ca
B/Ca
Cd/Ca
Sr/Ca
Relative ratio
measured Ca (ppm)
AFS2
AFS3

Figure 6.

AFS1

H. elegans samples

AFS6

C. pachyderma samples

Li/Ca$_{norm}$ (%)

1.3 µmol/mol

2 - 4 µmol/mol

10.3 µmol/mol

12 - 13 µmol/mol

Mg/Ca$_{norm}$ (%)

0.26 mmol/mol

0.4 - 1.1 mmol/mol

3.24 mmol/mol

0.9 - 1.3 mmol/mol

Mg/Li$_{norm}$ (%)

0.20 mol/mmol

0.20 - 0.30 mol/mmol

0.31 mol/mmol

0.08 - 0.10 mol/mmol

B/Ca$_{norm}$ (%)

32 µmol/mol

25 - 66 µmol/mol

142 µmol/mol

130 -170 µmol/mol

Cd/Ca$_{norm}$ (%)

0.05 µmol/mol

0.03 - 0.06 µmol/mol

0.13 µmol/mol

0.05 - 0.08 µmol/mol

Sr/Ca$_{norm}$ (%)

0.5 mmol/mol

0.6 - 2.4 mmol/mol

1.0 mmol/mol

1.2 - 1.3 mmol/mol

Measured Ca (ppm)

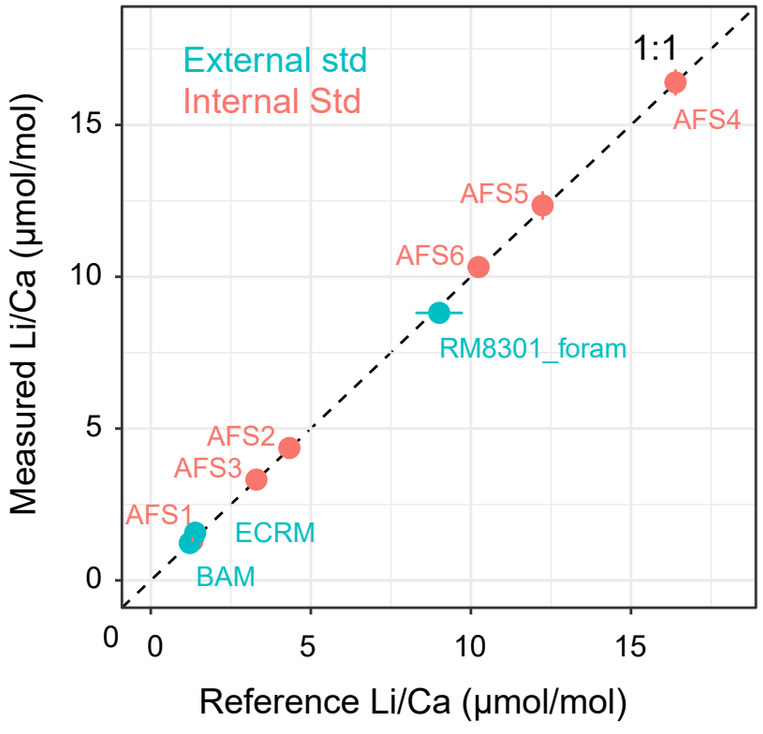
n = 22 n = 22 n = 22

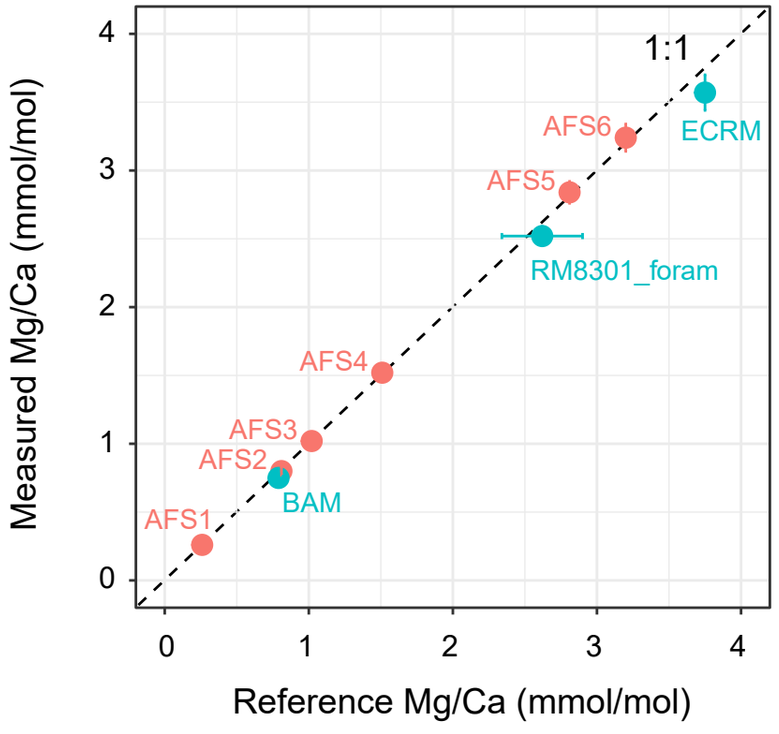
n = 1 n = 4 n = 10 n = 17 n = 18 n = 13

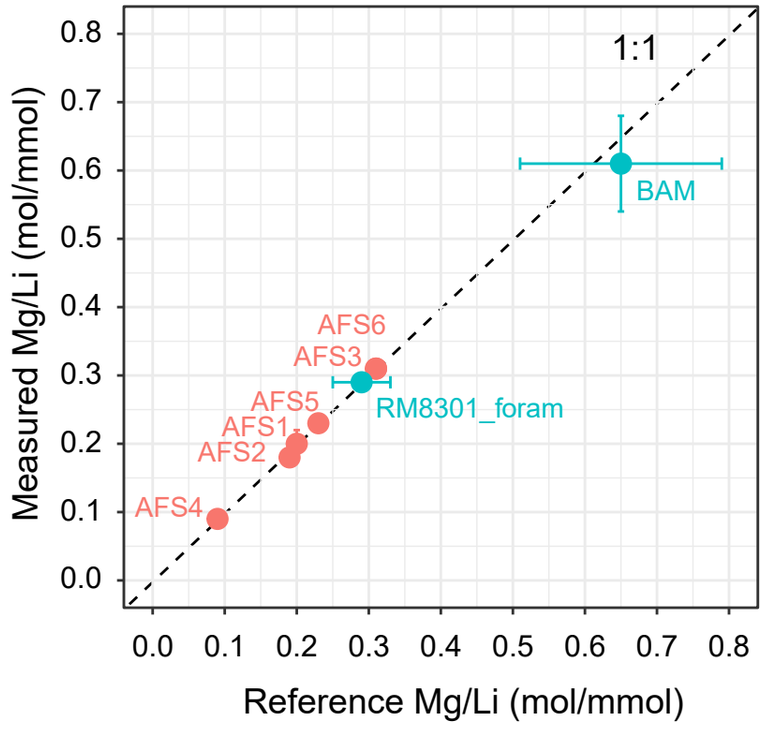
n = 7 n = 3 n = 16 n = 7

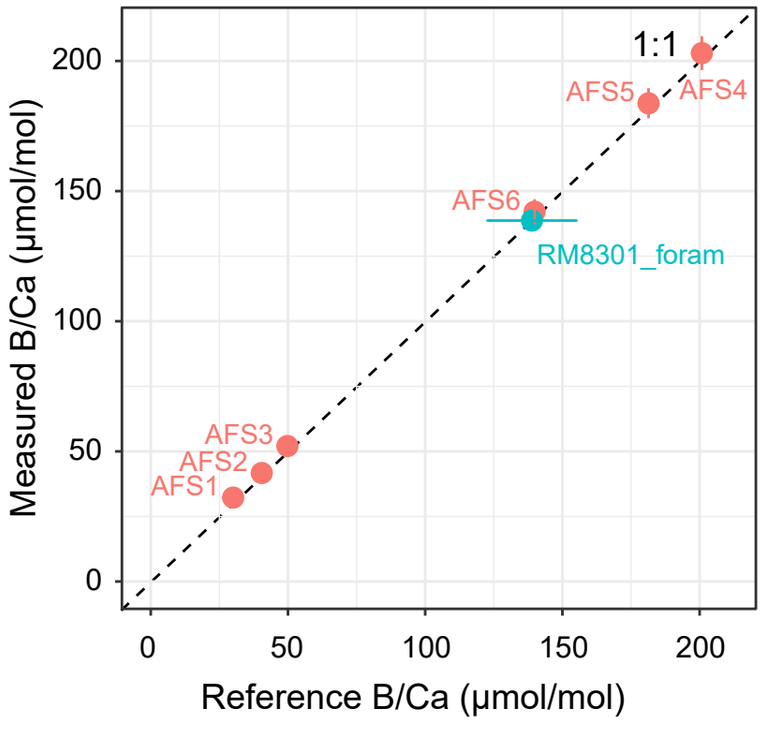
n = 4 n = 12 n = 34 n = 17 n = 5

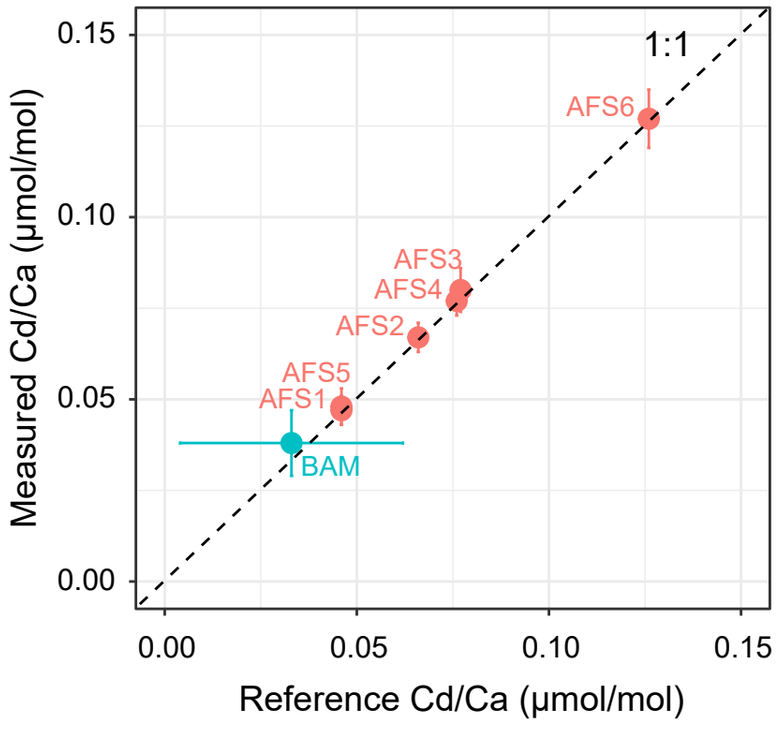
Figure 7.


External std
Internal Std
1:1
AFS4
AFS5
AFS6
RM8301_foram
AFS2
AFS3
AFS1
ECRM
BAM
Measured Li/Ca (µmol/mol)
Reference Li/Ca (µmol/mol)
0
5
10
15


1:1
AFS6
ECRM
AFS5
RM8301_foram
AFS4
AFS3
AFS2
BAM
AFS1
Measured Mg/Ca (mmol/mol)
Reference Mg/Ca (mmol/mol)
0
1
2
3
4


1:1
BAM
AFS6
AFS3
RM8301_foram
AFS5
AFS1
AFS2
AFS4
Measured Mg/Li (mol/mmol)
Reference Mg/Li (mol/mmol)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8


1:1
AFS5
AFS4
AFS6
RM8301_foram
AFS3
AFS2
AFS1
Measured B/Ca (µmol/mol)
Reference B/Ca (µmol/mol)
0
50
100
150
200


1:1
AFS6
AFS3
AFS4
AFS2
AFS5
AFS1
BAM
Measured Cd/Ca (µmol/mol)
Reference Cd/Ca (µmol/mol)
0.00
0.05
0.10
0.15

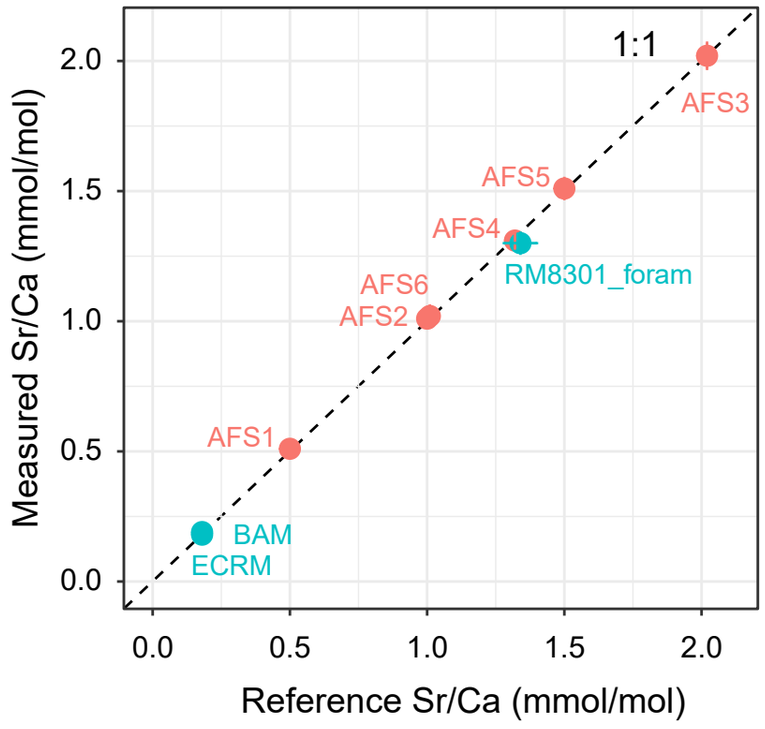
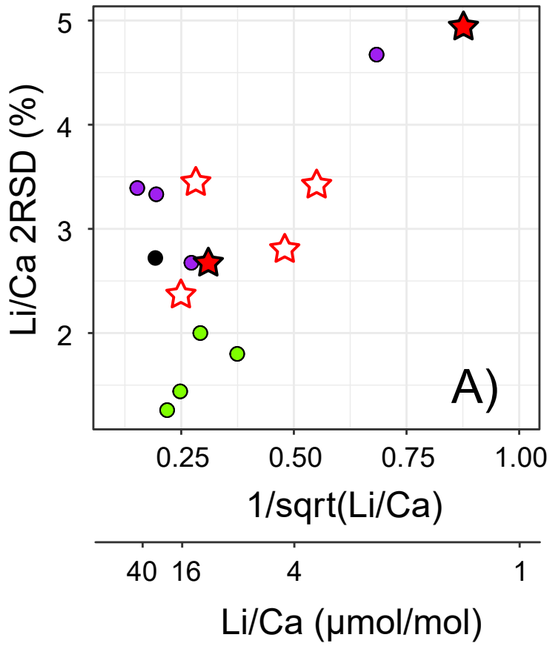
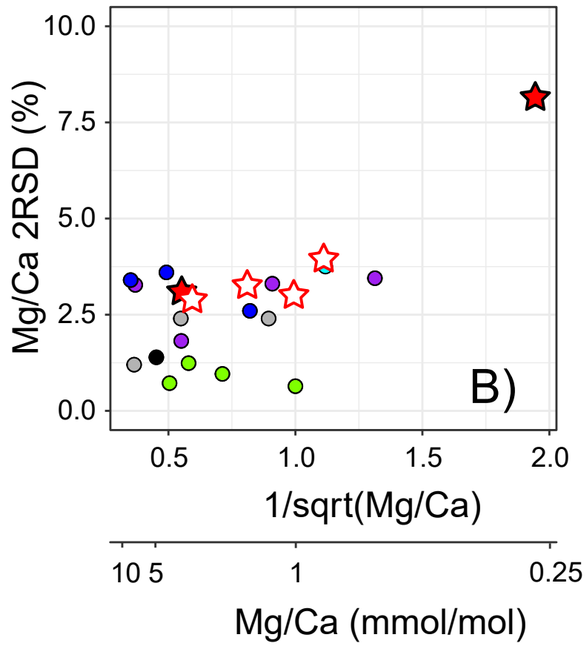
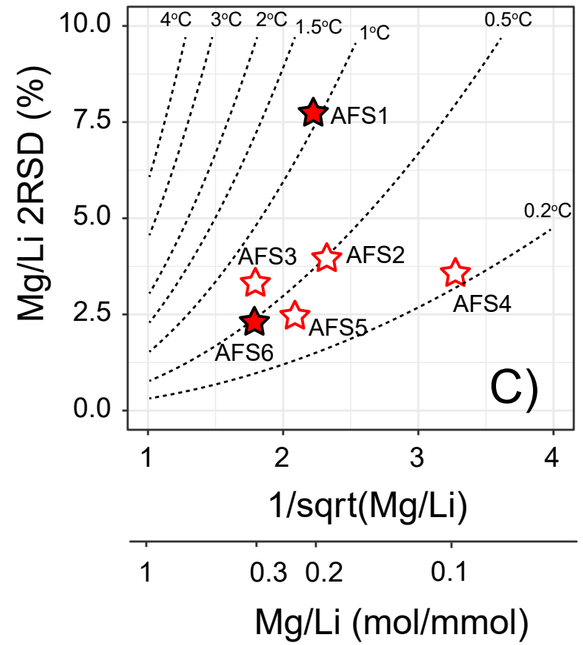
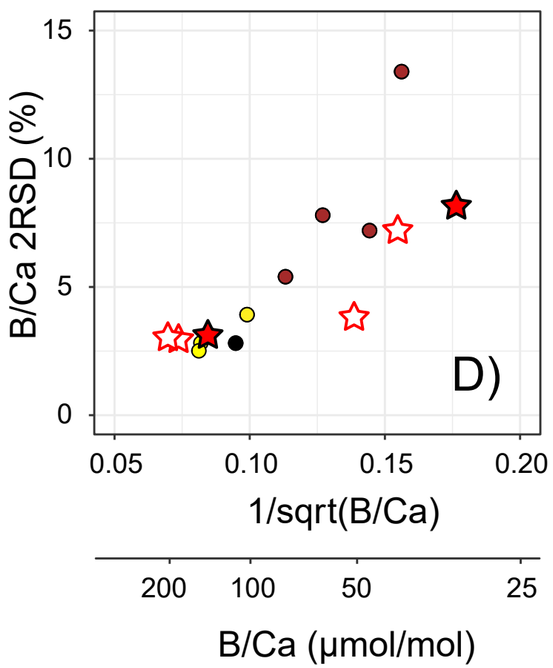

1:1
AFS3
AFS5
AFS4
RM8301_foram
AFS6
AFS2
AFS1
BAM
ECRM
Measured Sr/Ca (mmol/mol)
Reference Sr/Ca (mmol/mol)
0.0
0.5
1.0
1.5
2.0

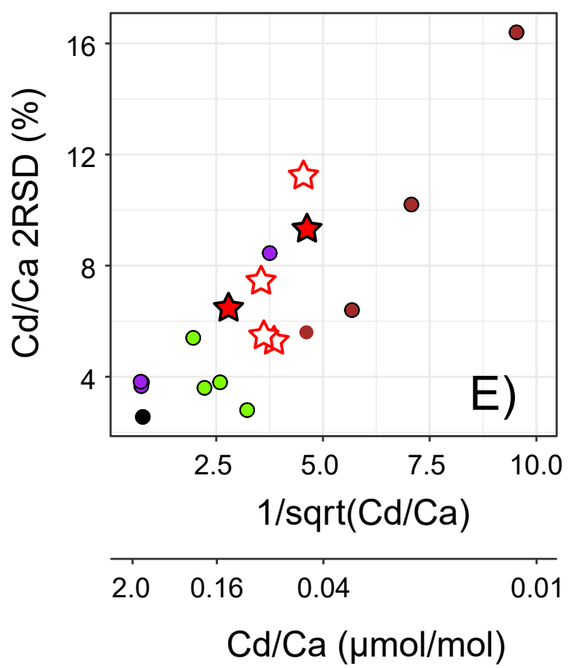
Figure 8.

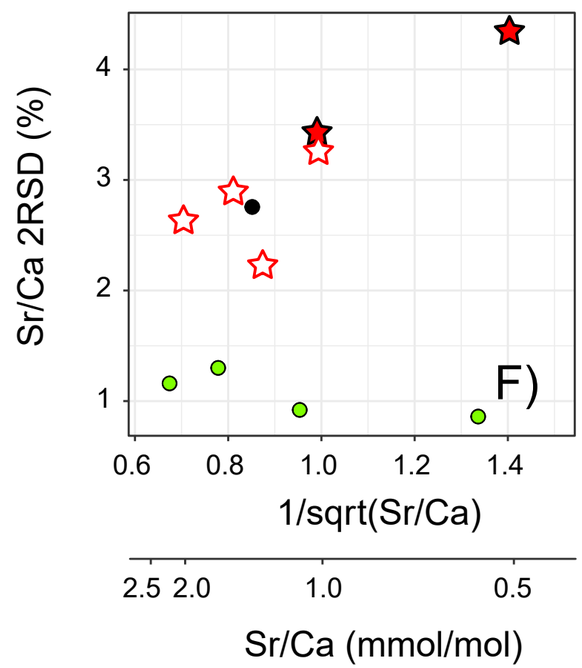












WHOI iCAP-Q

- this study, internal std @ varying Ca
- this study, internal std @ 100 ppm Ca
- Umling et al. 2019. internal std @ 60 ppm Ca

Other labs

- Element XR, Oppo et al. 2023
- iCAP, Dai et al. 2023
- Perkin-Elmer, Yu et al. 2005
- Element 2, Marchitto 2006
- iCAP, Ford et al. 2016
- Element XR, Ford et al. 2016