Constraining net calcification/dissolution in the open ocean using high precision ID measurement of dissolved Ca/Mg ratios in seawater

Ellen Cliff, Stephen Eggins, Les Kinsley, Linda McMorrow

Research School of Earth Sciences

The Australian National University, Canberra, ACT 2601, Australia

(Ellen Cliff) u5194105@anu.edu.au

Motivations and aims

The measurement of Ca anomaly (ΔCa) provides an unambiguous method for constraining $CaCO_3$ production, export and dissolution in the ocean cf. excess alkalinity (Alk*) which is subject to organic matter formation and remineralisation[1]. ΔCa could prove to be a valuable tool as seawater carbonate chemistry changes.

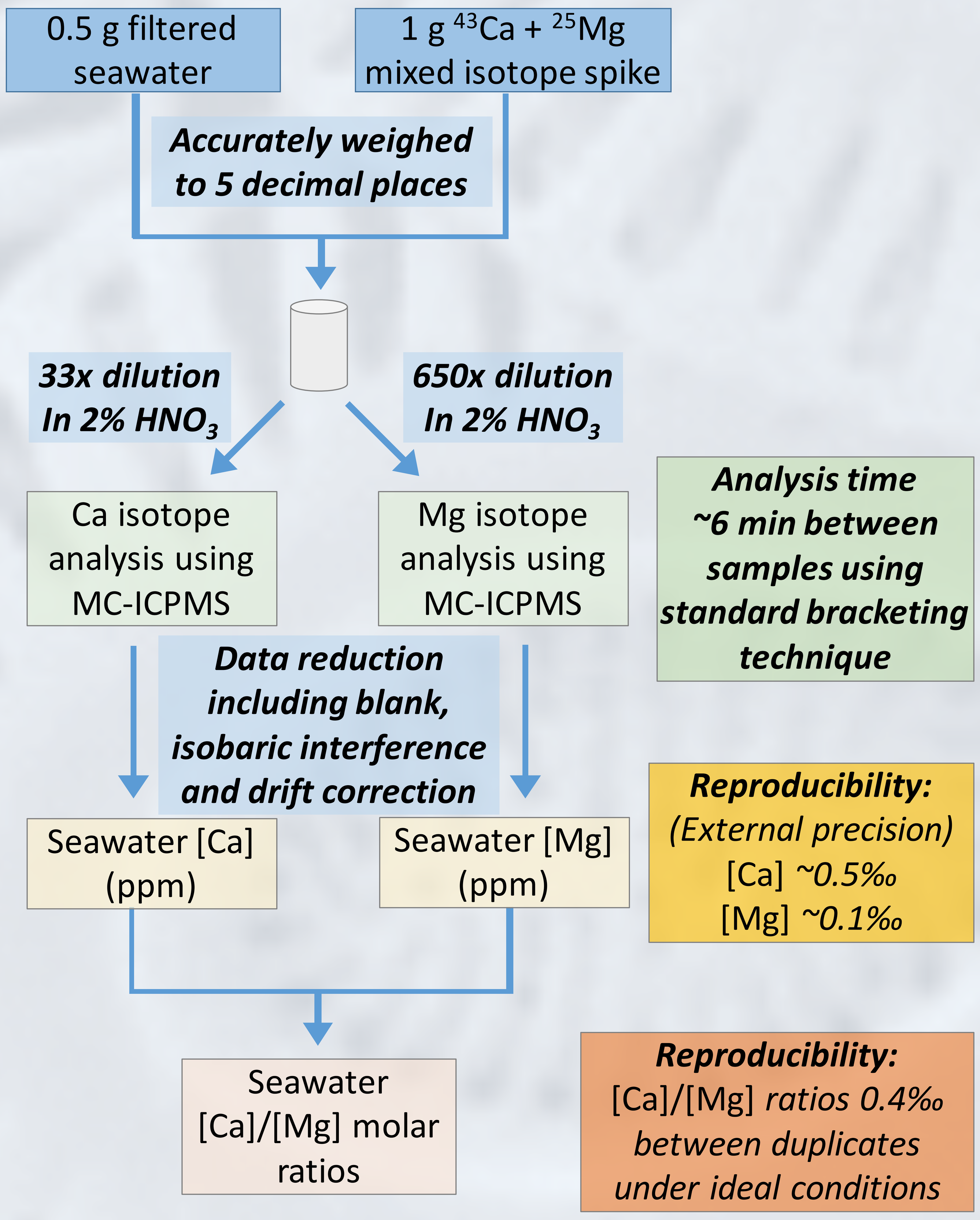
$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + H_2O + CO_2 \qquad \ldots \Delta Alk = 2, \Delta Ca = 1$$

The *challenge* is to develop a high precision and high throughput method for measuring ΔCa in seawater that could match the resolution of Alk* results and exceed the precision of existing Ca titration techniques[2].

The *aim* of this study is to develop methods for analysis of Ca and Mg abundances in seawater with sufficiently high precision that ΔCa can be determined and corrected for fresh water fluxes by ratio of Ca abundance to Mg abundance.

Analytical Methodology

Overview of isotope dilution Multi-Collector Inductively Coupled Plasma Mass Spectrometry approach:



Key challenges

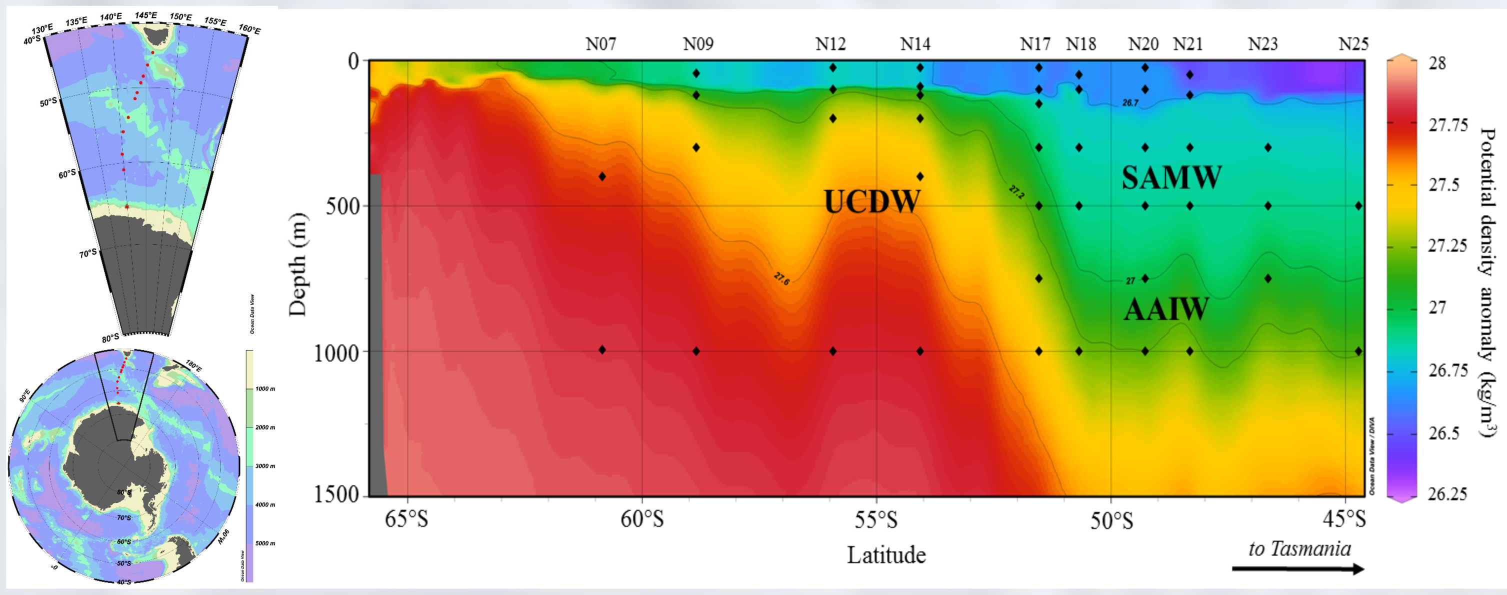
- Isotope dilution: accurate weighing of isotope enriched spike and seawater samples
- MC-ICPMS: matrix-matching of sample and bracketing standard
- MC-ICPMS: minimize both memory effects and blank variation on instrument drift
- MC-ICPMS: Improve [Ca] reproducibility to 0.1-0.2 ‰

Application to the Southern Ocean

Aims: Track $CaCO_3$ formation and dissolution in the Southern Ocean south of Tasmania, particularly along isopycnal surfaces - is any shallow depth dissolution occurring?

Test Great Calcite Belt hypothesis – is significant calcification occurring?

Study location: SR3 WOCE line – samples analysed to date are from the AU0806 cruise in the austral autumn (March-April) 2008

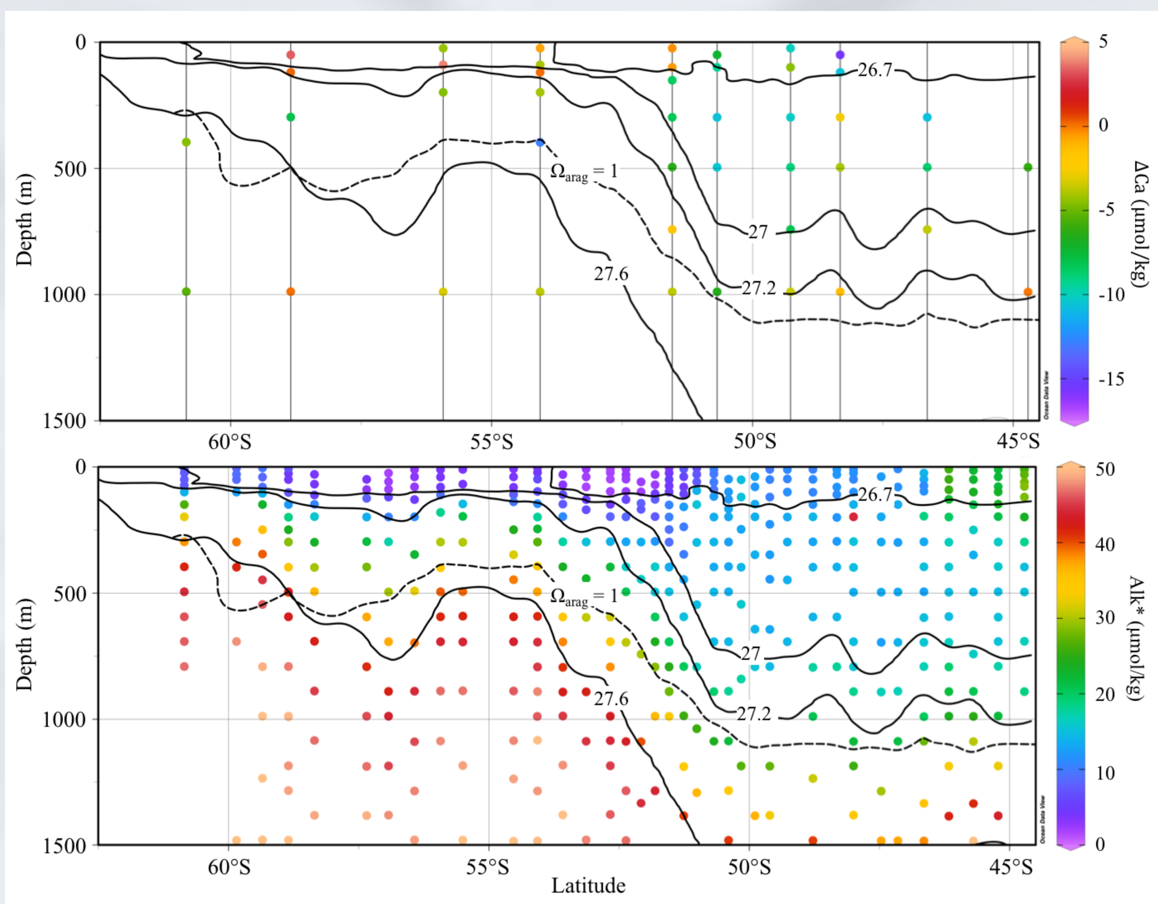


Sample locations along the 140°E-150°E SR3 line are shown along with the potential density anomaly, and Upper Circumpolar Deep Water (UCDW), Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW)[3].

Preliminary results

ΔCa (μmol/kg) is calculated relative UCDW source water, shown below.

$$\Delta Ca = \left(\frac{Ca}{Mg} - \frac{Ca}{Mg_{UCDW}}\right) \times [Ca]_{UCDW} \times \frac{S}{S_{UCDW}}$$



Isopycnals (pale grey) and aragonite saturation state (Ω = 1) (dark grey) contours are shown. Negative ΔCa values developed in SAMW reflect calcification relative to source UCDW. Elevated values near $\Omega_{arag} = 1$ may reflect aragonite dissolution at this depth.
Alk* from data provided by Bronte Tilbrook (CSIRO).

Conclusions

The method developed to date shows significant promise and requires further refinement, particularly of [Ca] measurements, to achieve a precision for ΔCa of 0.2‰.

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References

[1]Anderson and Sarmiento, 1994, Global Biogeochem. Cycles, 8, 65-80. [2] Olson and Chen, 1982, Limnol. Oceanogr., 27, 375-380. [3] Solokov and Rintoul, 2002, J. Marine Syst., 37, 151-184.