Building amorphous calcium carbonate into geochemical biomineralisation models

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1 Introduction

Amorphous calcium carbonate (ACC) has been identified or inferred to exist in many marine organisms that produce biominerals widely used as geochemical archives (e.g. foraminifera, molluscs, echinoderms). However, little is known about trace element incorporation into ACC, and thus it is not understood how an ACC precursor might impact the fidelity of climate proxies and biomineralisation models based on skeletal geochemistry.

We investigated the incorporation of (trace) elements into inorganic ACC precipitated from seawater, and build these data into a simple two-stage Rayleigh distillation model in order to assess whether the geochemistry of calcite-producing organisms can be reconciled with a ACC precursor phase.

2 ACC precipitation from seawater

ACC was precipitated from seawater via controlled, simultaneous titration of 0.45 M $CaCl_2$ and Na_2CO_3 solutions into seawater modified with respect to it's carbonate chemistry (pH 8.9-10.1, DIC ~5-25 mM).

Five principal experiments:
- pH (DIC covaried)
- seawater [Mg] (0-53 mM)
- seawater [Ca] (0-50 mM)
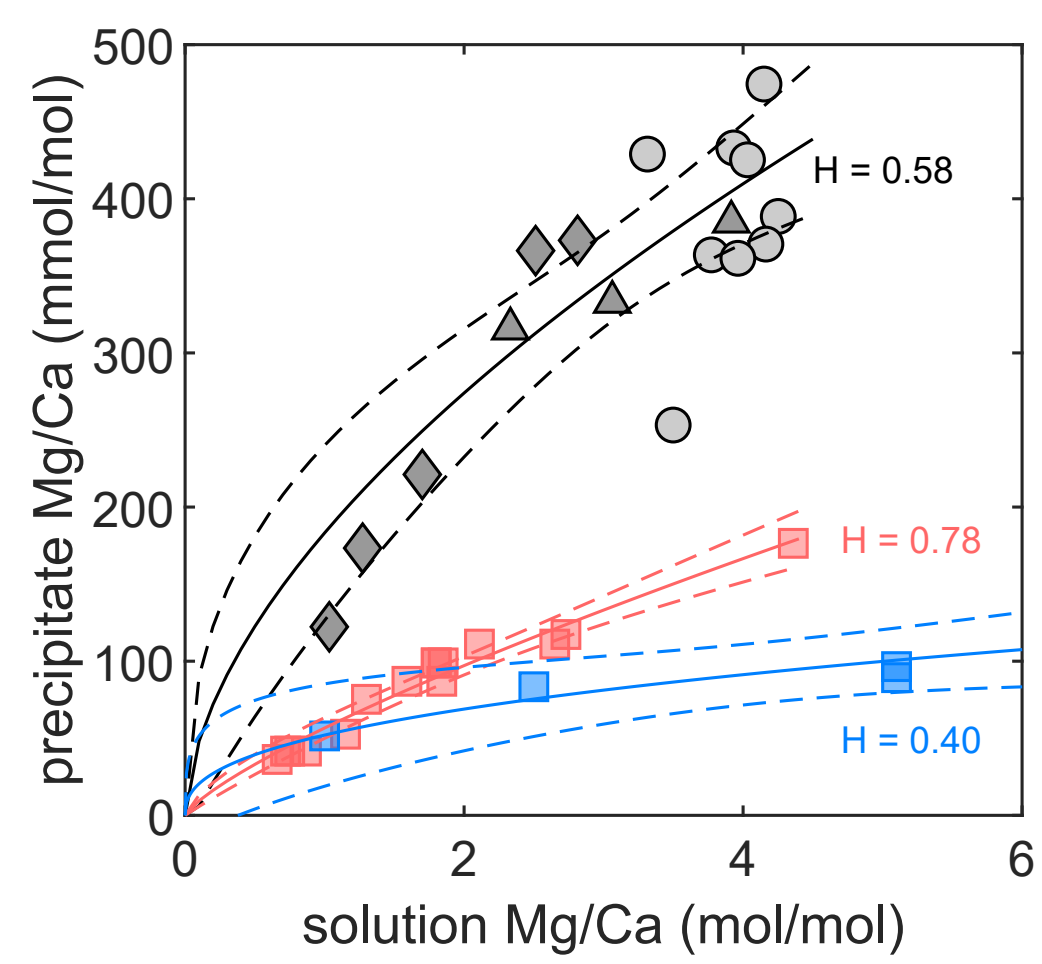- Aspartic acid (0-20 mM)
- Glutamic acid (0-20 mM)
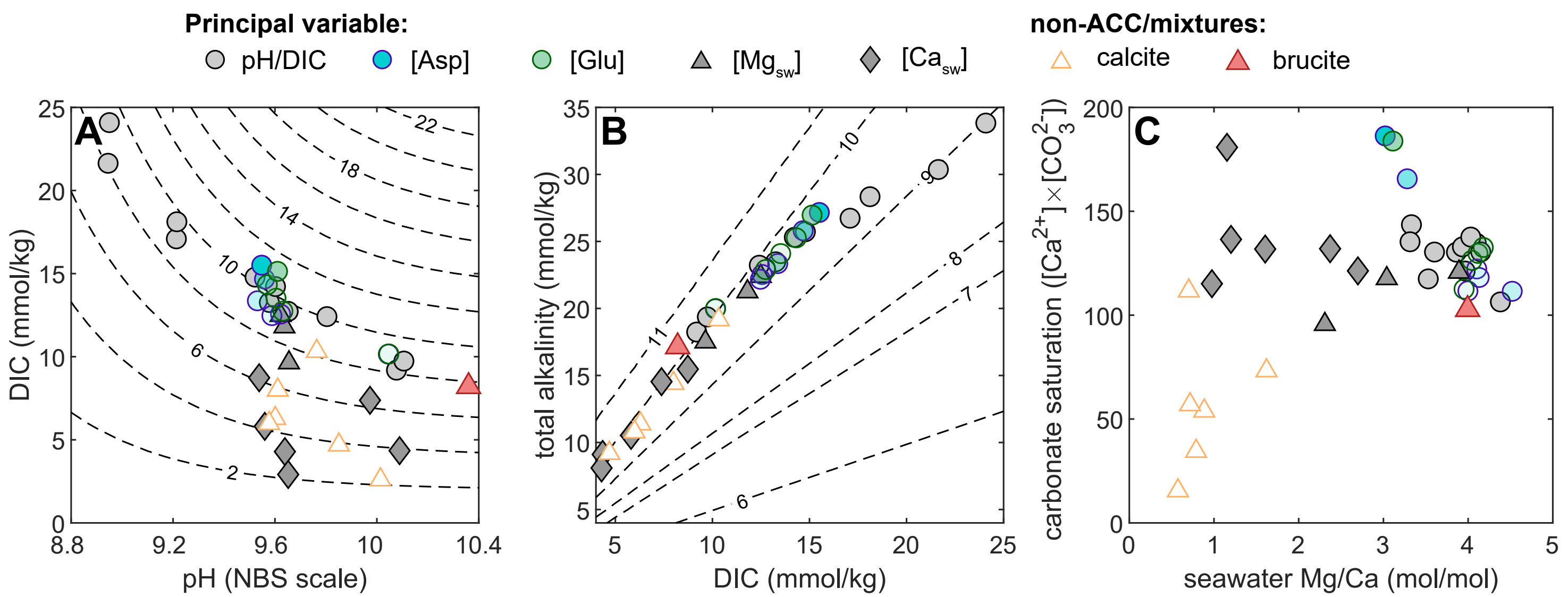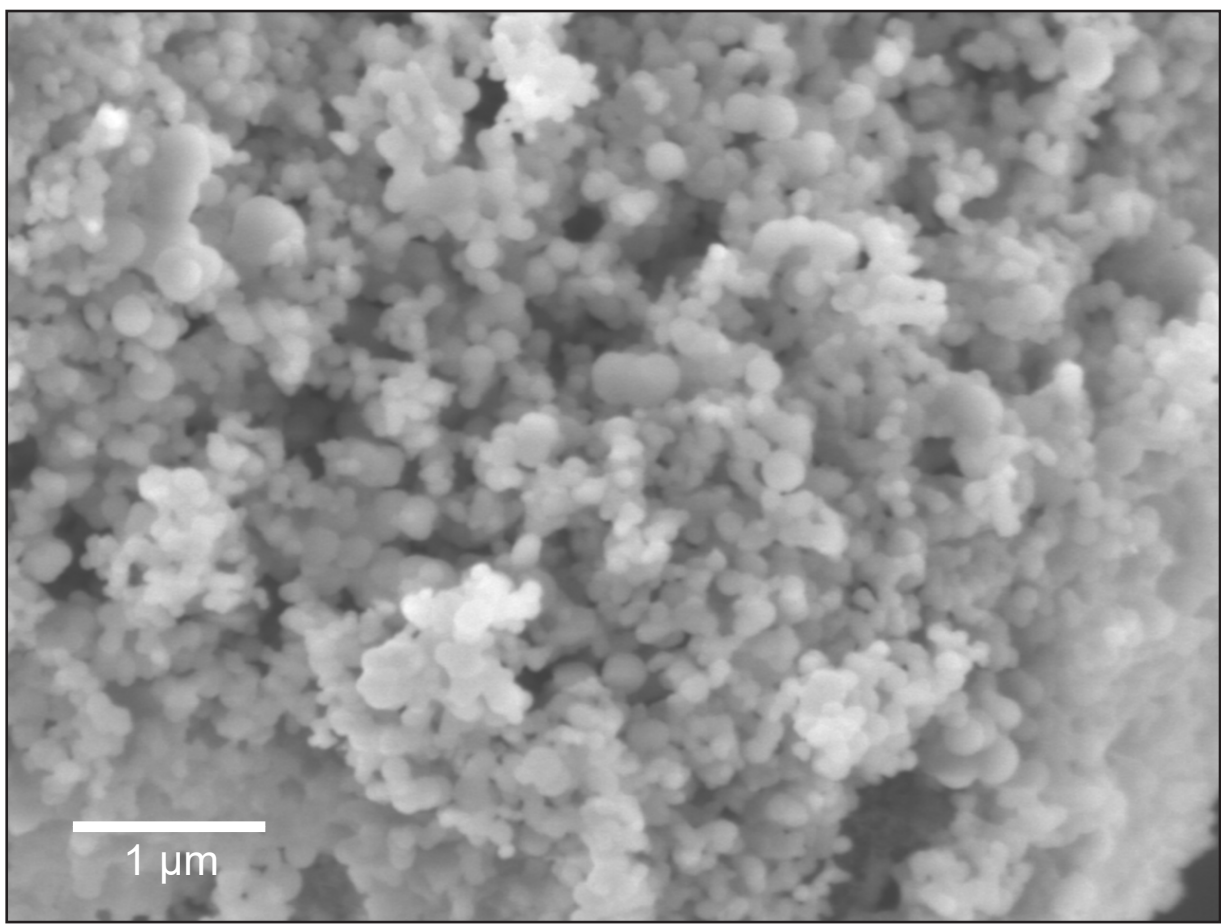
Experiments yielded only ACC in all but two cases (based on Raman, FTIR, XRD): Above pH ~10, mixtures of amorphous brucite & ACC were produced; Mg/Ca_{sw} ratios <~1 resulted in calcite-ACC mixtures.
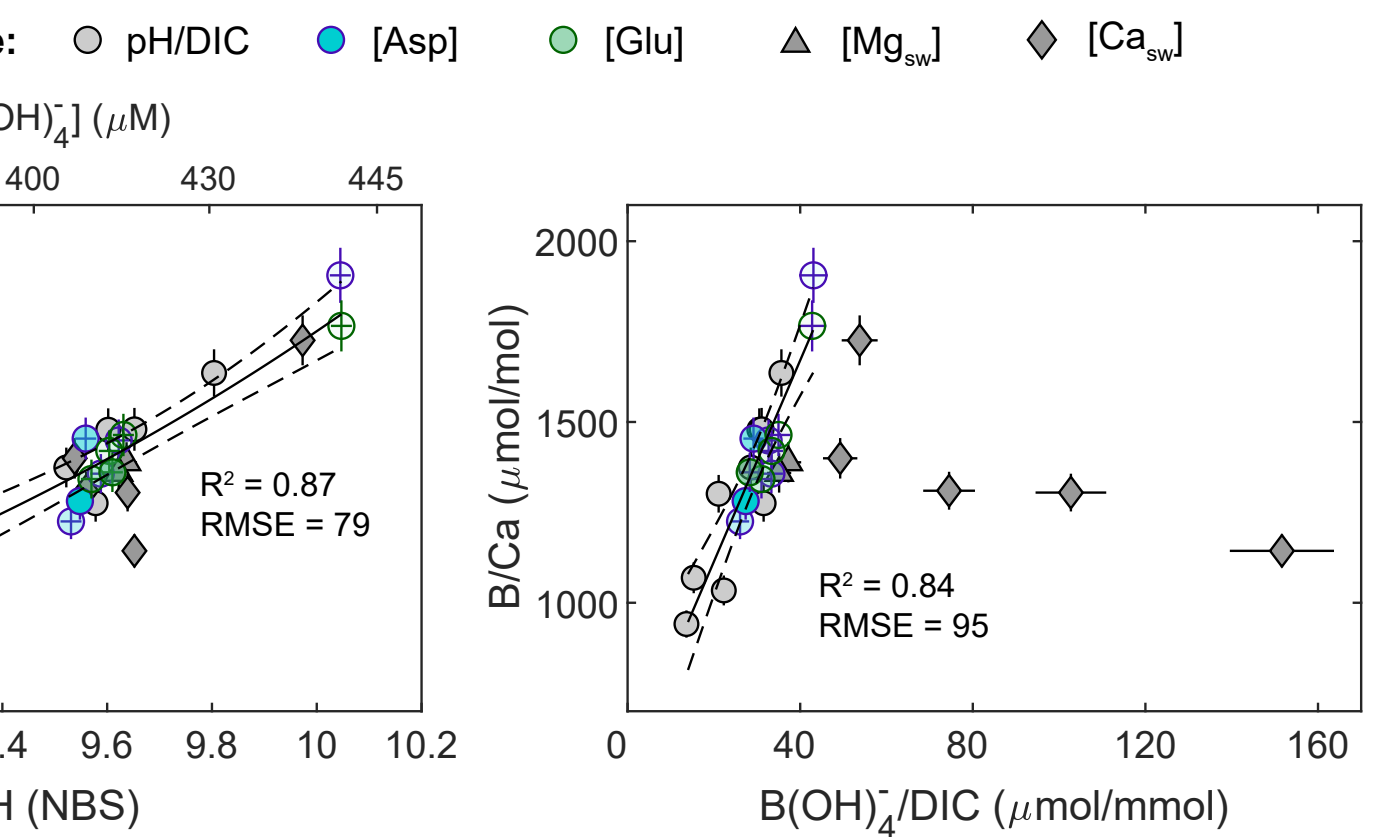
3 Major & trace element incorporation

The distribution coefficients of eight common major/trace elements were determined (Li, B, Na, Mg, Mn, Sr, Ba, U).

Detailed example 1: As for the crystalline carbonates, boron incorporation into ACC is strongly a function of the carbonate system, except(?) when seawater [Ca] is varied.

Detailed example 2: ACC Mg/Ca is principally (nonlinearly?) driven by the seawater Mg/Ca ratio.
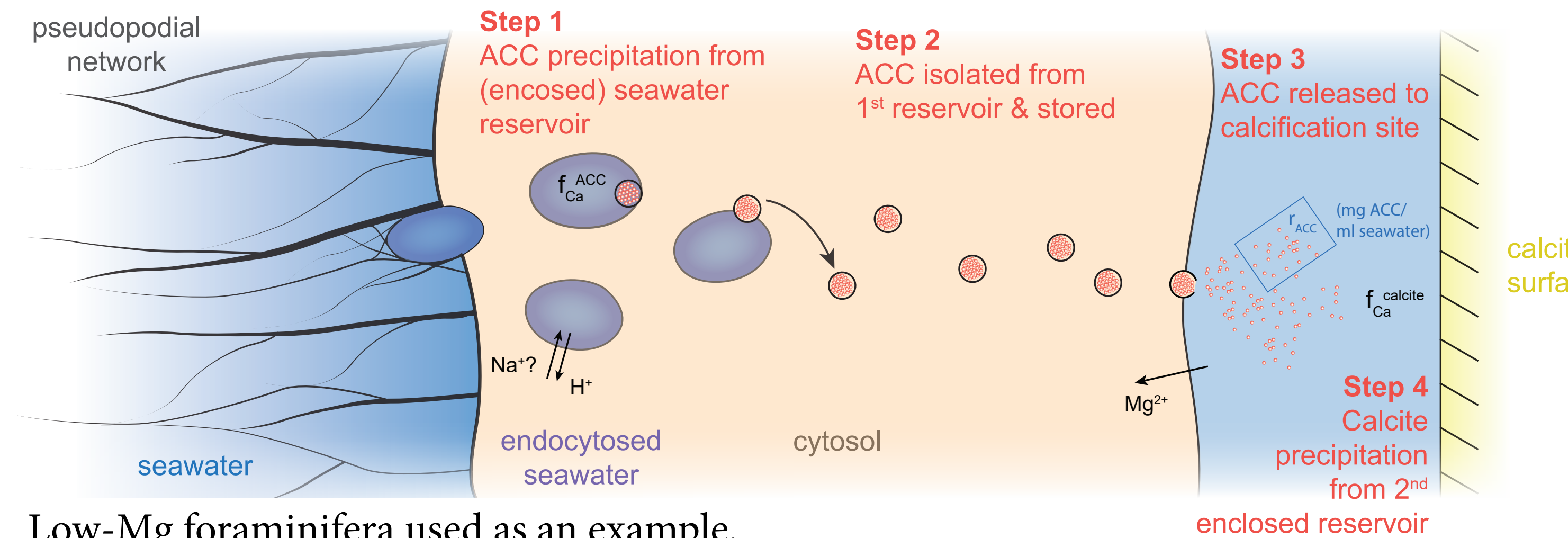

More broadly, all investigated trace elements have distribution coefficients in ACC 1-2 orders of magnitude higher than in calcite, with the exception of Mn.
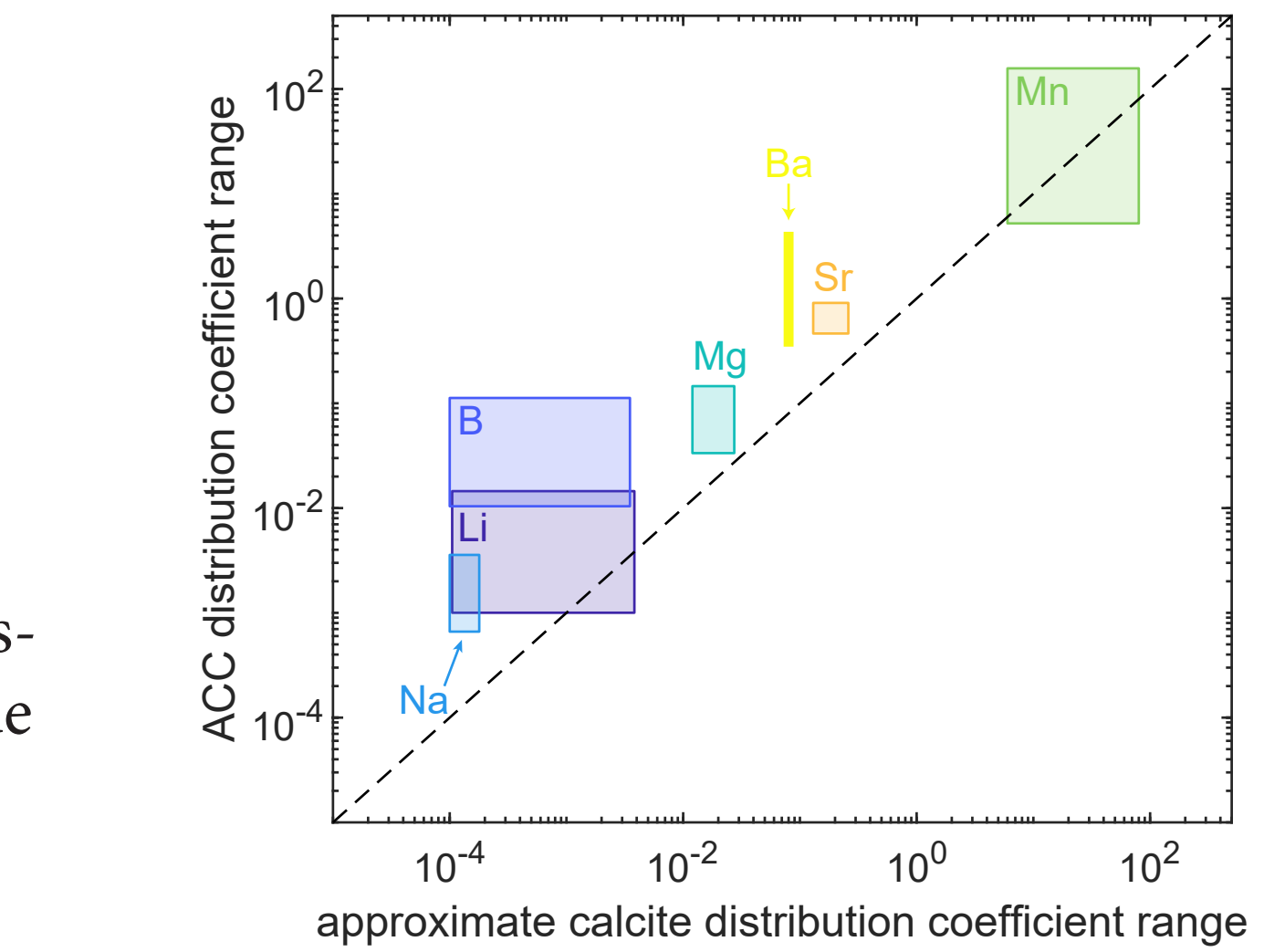
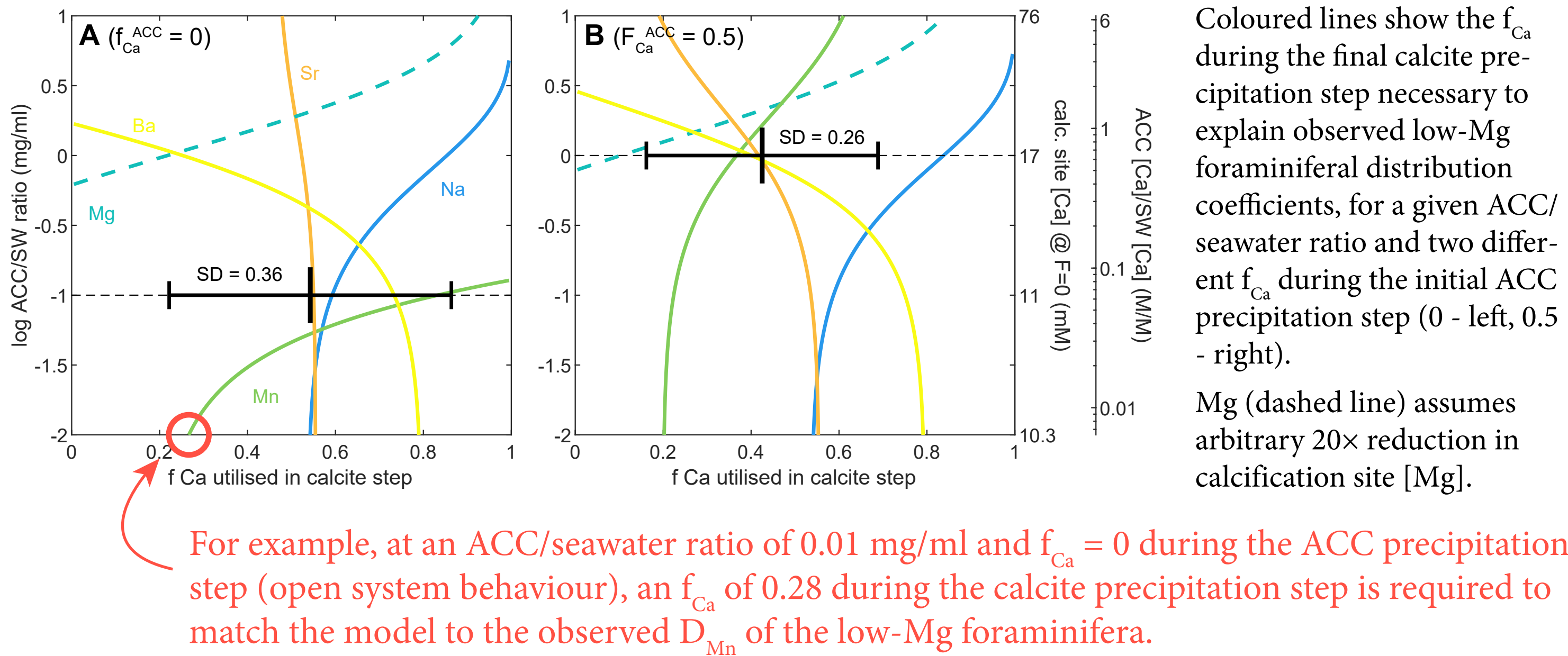## 4 Building a simple biomineralisation model

Low-Mg foraminifera used as an example.
The model is based on the observational evidence of Erez [2003], Bentov & Erez [2006], & Bentov et al. [2009].

$$D = (1 - f^{\alpha})/(1 - f) \cdot (([TE_{sw}] + r_{ACC\text{-}sw} \cdot D_{ACC} \cdot X/Ca_{sw})/[Ca_{cs}])/(X/Ca_{sw})$$

predicted apparent calcite distribution coefficients — Rayleigh distillation model — the model explores the impact of the ratio of ACC to seawater at the calcification site — delivery of trace elements & Ca to the calcification site from ACC — relative to ambient seawater

The model produces predicted calcite trace element distribution coefficients in 3D variable space: i) f_{Ca} utilised during ACC precipitation, ii) the calcification site ACC/seawater ratio, ii) f_{Ca} utilised during calcite precipitation

5 Model prediction I: Trace elements

Coloured lines show the f_{Ca} during the final calcite precipitation step necessary to explain observed low-Mg foraminiferal distribution coefficients, for a given ACC/seawater ratio and two different f_{Ca} during the initial ACC precipitation step (0 - left, 0.5 - right).

Mg (dashed line) assumes arbitrary 20× reduction in calcification site [Mg].

For example, at an ACC/seawater ratio of 0.01 mg/ml and f_{ca} = 0 during the ACC precipitation step (open system behaviour), an f_{ca} of 0.28 during the calcite precipitation step is required to match the model to the observed D_{Mn} of the low-Mg foraminifera.

Take home messages:
1. No part of the investigated parameter space can reproduce observed Mg and Li distribution coefficients. Within the constraint of the model, this necessitates outward Mg transport and inward Li delivery.
2. Especially informative trace elements are those with very low or very high distribution coefficients:
   i) **Mn:** Low degrees of Ca utilisation during ACC precipitation are difficult/impossible to reconcile with high degrees of ACC delivery and/or low degrees of Ca utilisation during calcite precipitation.
   ii) **Na:** Very high degrees of ACC delivery (>~3 mg/ml) are difficult to reconcile with observed Na distribution coefficients.
3. No model can perfectly reproduce the foraminifera data (e.g. due to growth rate effects on Ds), but precipitation through an ACC precursor can otherwise be reconciled with foraminifera geochemistry.

6 Model prediction II: Calcification site constraints

In which parameter space is the model best able to reconcile the data from all five trace elements shown above? I.e. where is the standard deviation in the f_{Ca} during the final calcite precipitation step minimised for all five trace element curves (examples shown above).
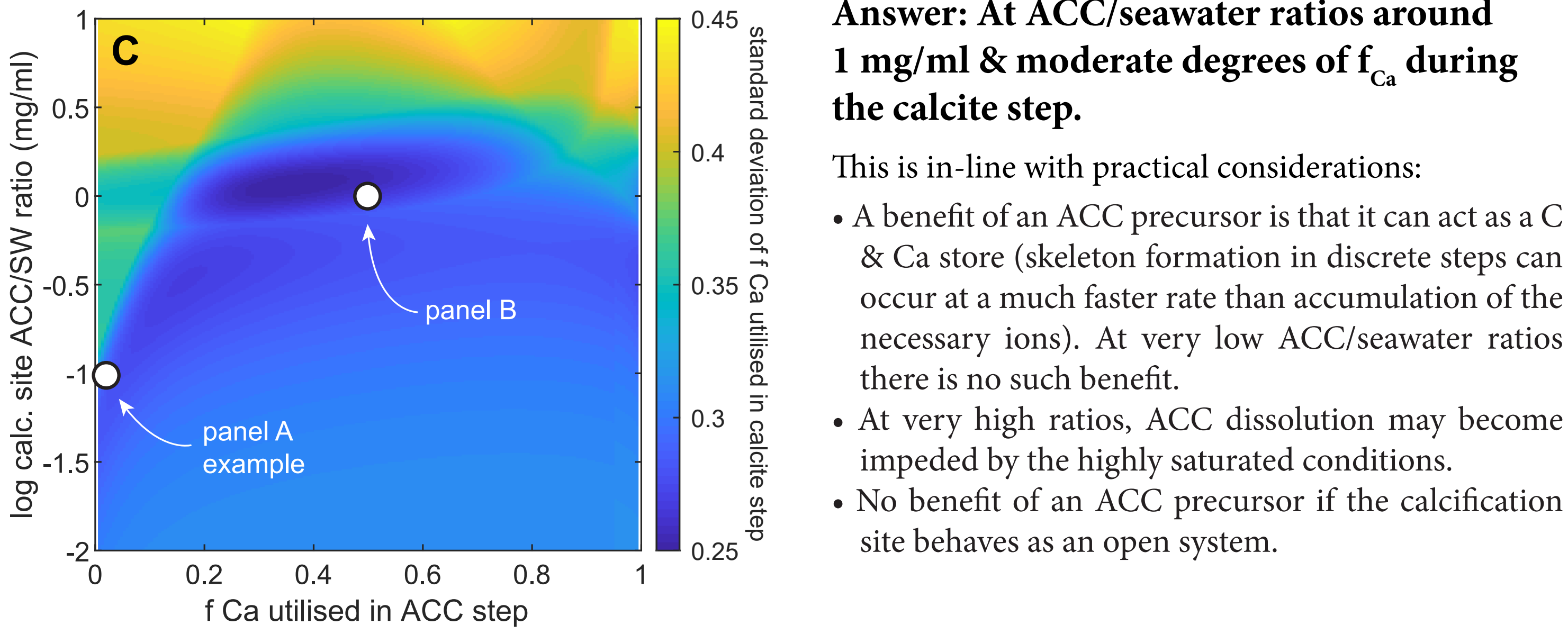
Answer: At ACC/seawater ratios around 1 mg/ml & moderate degrees of f_{Ca} during the calcite step.

This is in-line with practical considerations:
- A benefit of an ACC precursor is that it can act as a C & Ca store (skeleton formation in discrete steps can occur at a much faster rate than accumulation of the necessary ions). At very low ACC/seawater ratios there is no such benefit.
- At very high ratios, ACC dissolution may become impeded by the highly saturated conditions.
- No benefit of an ACC precursor if the calcification site behaves as an open system.