Characterization of carbonate crust from deep-sea methane seeps on the Northern US Atlantic Margin

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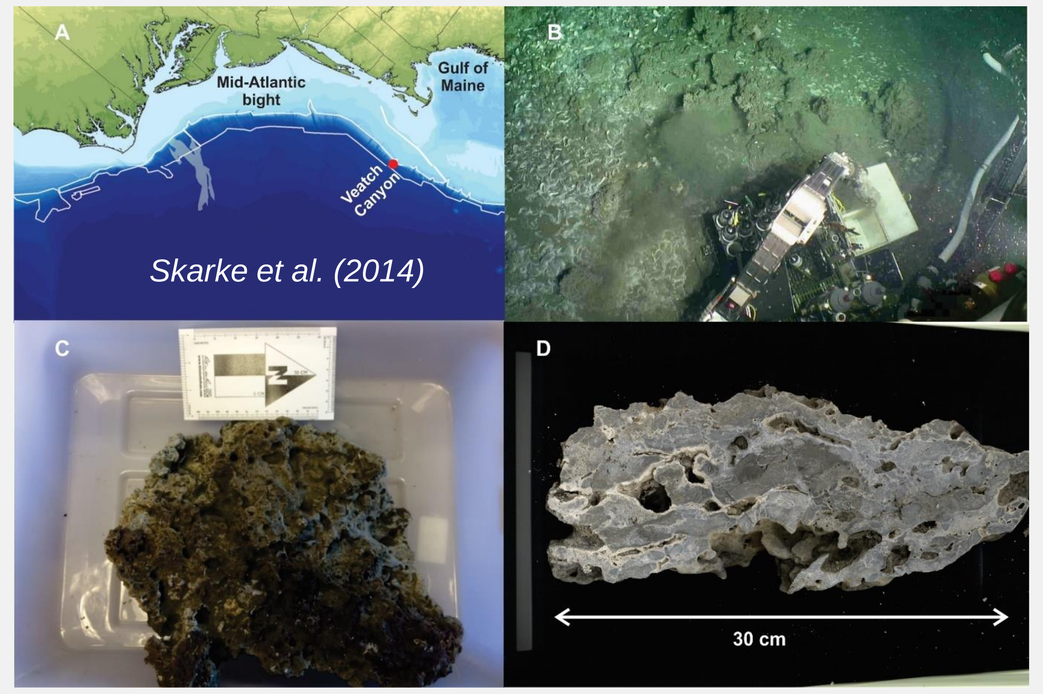
Abstract

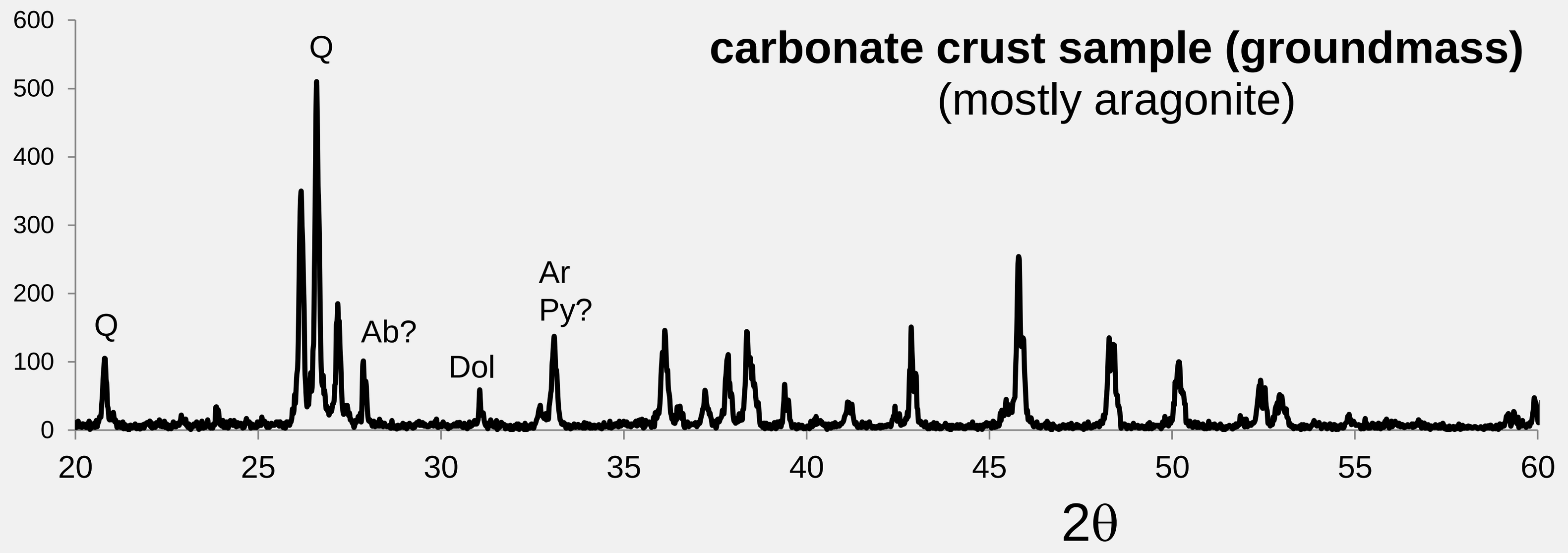
Authigenic carbonate minerals widely occur at the seafloor as carbonate crusts and are often directly linked to microbial activity, about which promotion of carbonate crystal growth and geochemistry are not entirely understood. To evaluate a potential metabolic contribution, studies were conducted on carbonate crust collected from a methane seep and on precipitation experiments which produced inorganic aragonite crystallized at high pressure. The carbonate crust (AD4835 BB4-S22) was collected at Veatch Canyon (39.805860; -69.592593) and at a depth of 1419.6 m. The samples we collected on R/V *Atlantis* cruise AT36 to the US North Atlantic Continental Margin (off of New England) in August 2016. Calcium carbonate minerals were precipitated abiotically at pressures of 1 atm, 110 bars, and 345 bars. The elemental data of carbonate crust compared with the data collected analyzing aragonite crystals precipitated experimentally.

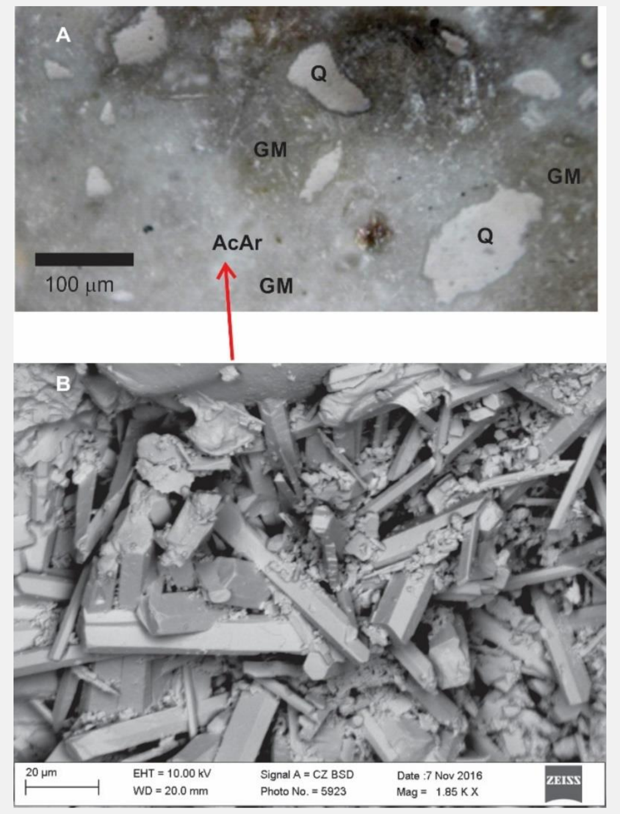
Sample collection and preparation



a) Location
b) Collection of samples.
c) Sample: AD4835-BB4-S22; original location is preserved.
d) Picture of the sliced rock.

XRD pattern





a) Optical micrograph :
GM = groundmass (grey);
ACAr = acicular aragonite (white);
Q = quartz.

b) SEM image of acicular crystals.

Well developed crystal faces suggest abiotic origin of AcAr.

High pressure experiments

In order to simulate high-pressure conditions at the seafloor, several experiments involving aragonite precipitation were conducted using a high pressure apparatus. $CaCO_3$ precipitated by adding of aliquots of Na_2CO_3 to seawater solution (Instant Ocean) at 8°C and 1 atm, 110 bars, 345 bars.

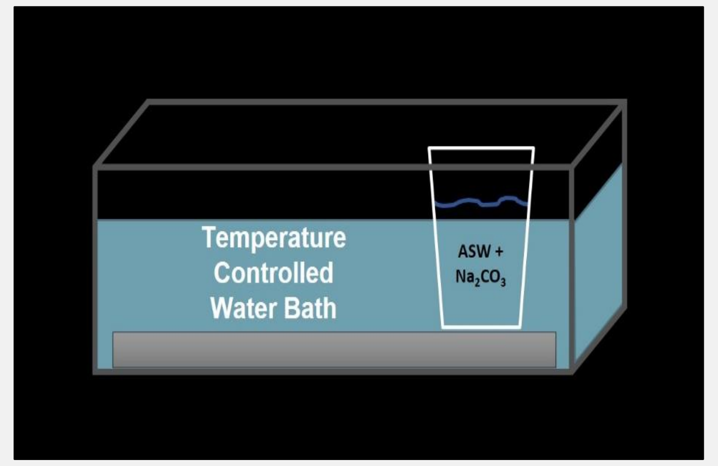


Figure 3. Experimental design for low-pressure experiment.

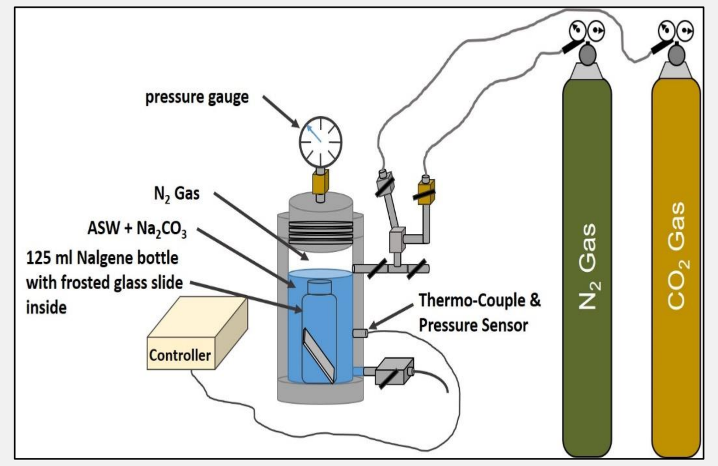


Figure 2. Experimental design for high-pressure experiments. CO2 was used for vessel cleaning from crystals.

Following minerals precipitated at 8°C :

- 1 atm: Aragonite and monohydrocalcite
- 110 bars: Aragonite
- 345 bars: Aragonite with minor monoclinic $CaCO_3$-II

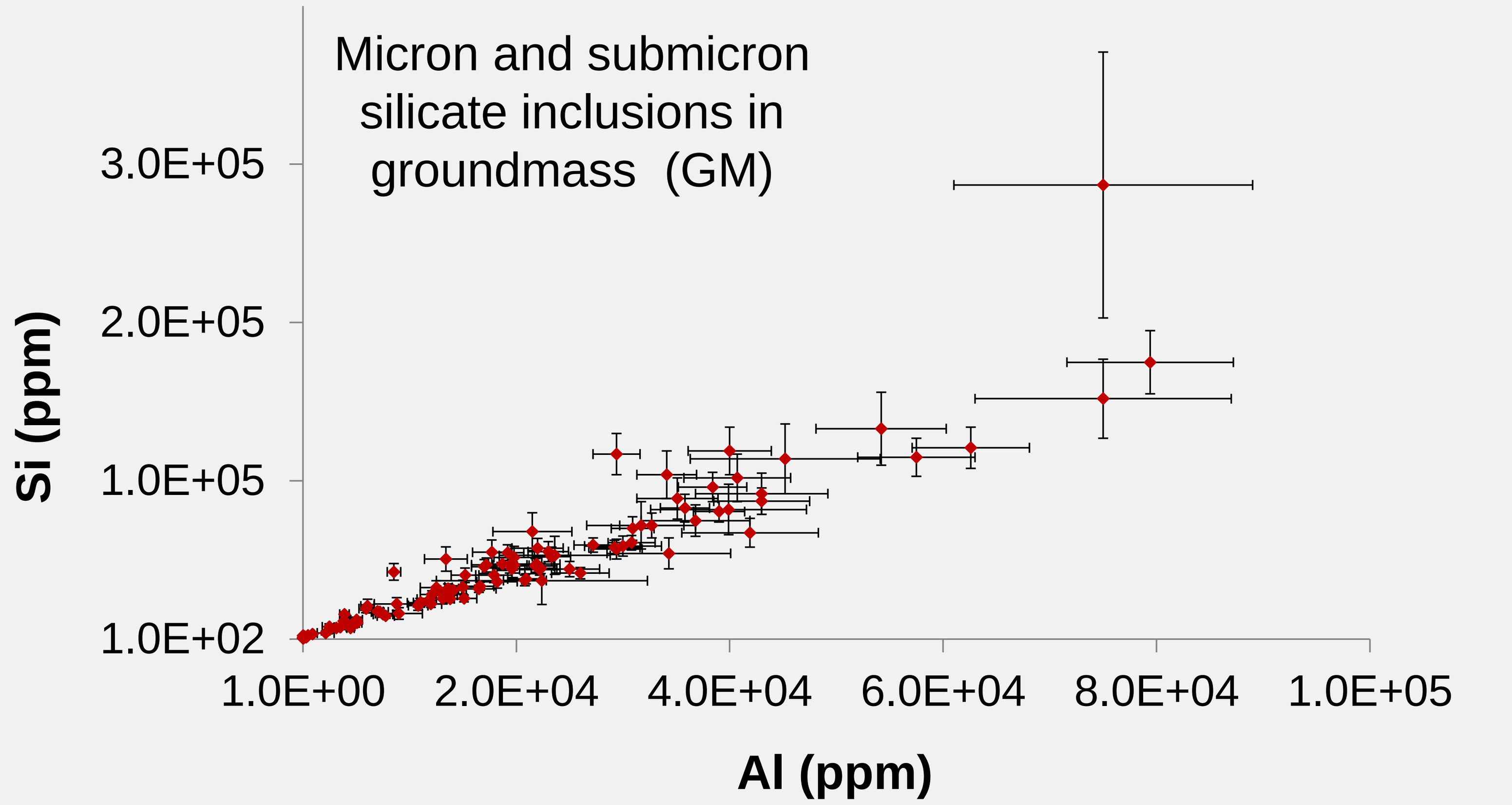
Analyses of aragoniate and fluid with ICP-MS allowed calculating of Doener-Hoskins partition coefficients:

$$K_E = \frac{\log g\left(1 + m_E^{aragonite} / m_E^{fluid}\right)}{\log g\left(1 + m_{Ca}^{aragonite} / m_{Ca}^{fluid}\right)}$$

$m^{aragonite}$ is the total number of moles of element (i.e., Mg, S, Sr, Ba, or U) or Ca in the final precipitate, and m^{fluid} is the total number of moles of element or Ca in the final fluid

Elemental ratios via LA-ICP-MS

Sr/Ca =7.73 - 13.13 mmol/mol (**AcAr** and **GM**).
Mg/Ca = 0.4-2.8 mmol/mol (**AcAr**); Mg/Ca= 2.4-905 (**GM**).
Ba/Ca = 0.4-2.8 µmol/mol; (**AcAr**); Ba/Ca=18.6-389 (**GM**).



Assuming Ca=0.01M and using elemental ratios from uppermost AcAr **porewater concentrations were estimated** at 4°C: Mg=6.23±0.87mM (*53mM*), SO_4=5.35±0.46mM (*28mM*), Sr=0.076±0.009mM (*0.091mM*), Ba=0.035±0.007µM (*0.15µM)*, U=0.010±0.002µM (*0.014µM)*. (*average seawater values*)

Summary

- Aragonite observed: carbonate crust (144 bars, 4°C) and experiment (110 bars, 8°C).
- Micro (nano) alumosilicate inclusions complicates analysis of groundmass.
- Sr (unlike Mg, S, Ba, and U) does not vary between ground mass and inclusion-free acicular aragonite.

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