Supplement

Surface area and Ω-aragonite oversaturation as controls of the runaway precipitation process in ocean alkalinity enhancement

Niels Suitner[1], Jens Hartmann[1], Selene Varliero[2], Giulia Faucher[3], Charly A. Moras[1], and Philipp Suessle[3]

[1]Institute for Geology, University of Hamburg, Bundesstrasse 55, 20146 Hamburg, Germany

[2]Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Milan; Italy

[3]GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstrasse 1-3, 24148 Kiel, Germany

Correspondence: Niels Suitner (niels.suitner@uni-hamburg.de),
Jens Hartmann (geo@hattes.de)

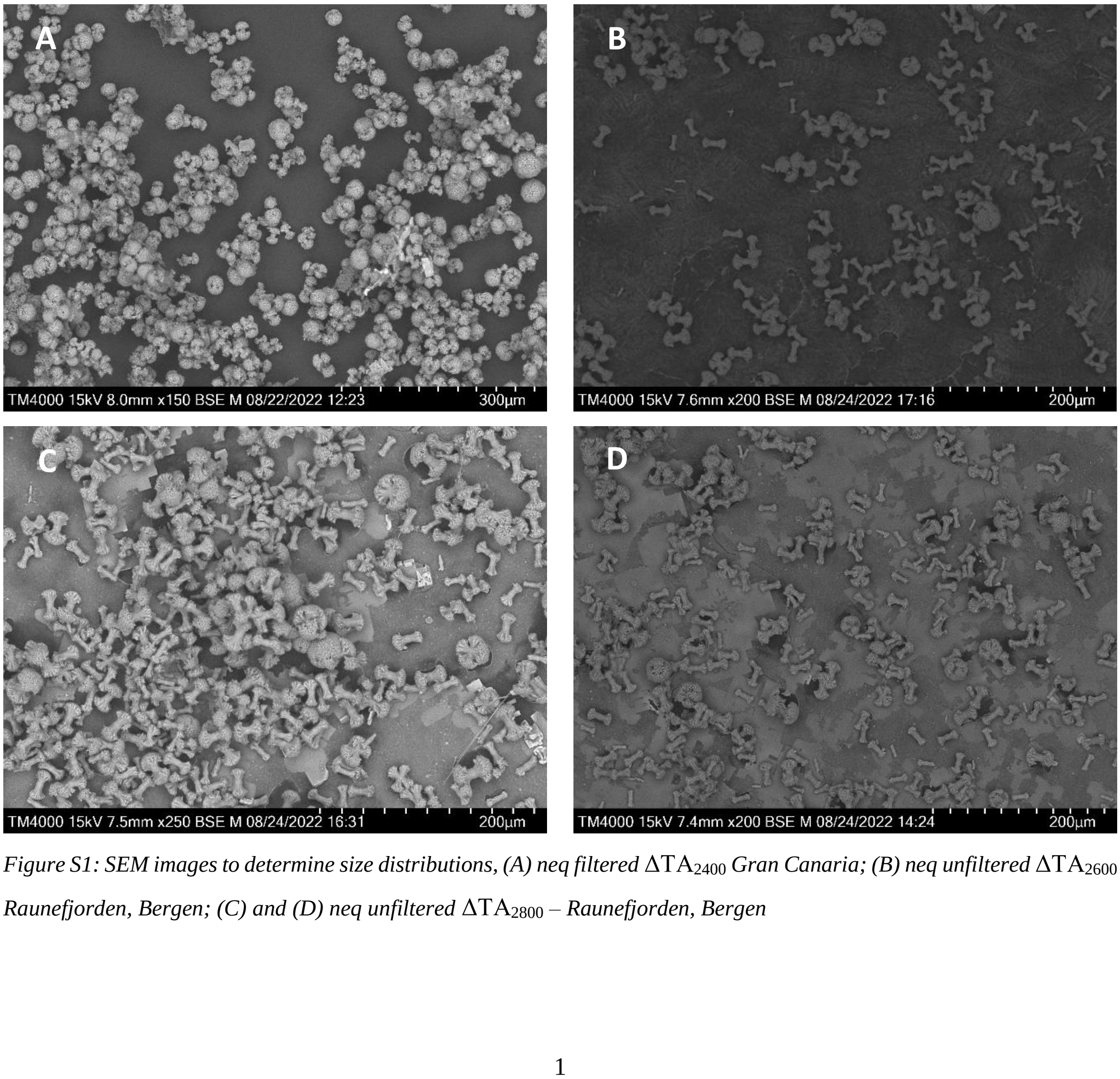

Figure S1: SEM images to determine size distributions, (A) neq filtered ΔTA_{2400} *Gran Canaria; (B) neq unfiltered* ΔTA_{2600} *Raunefjorden, Bergen; (C) and (D) neq unfiltered* ΔTA_{2800} *– Raunefjorden, Bergen*

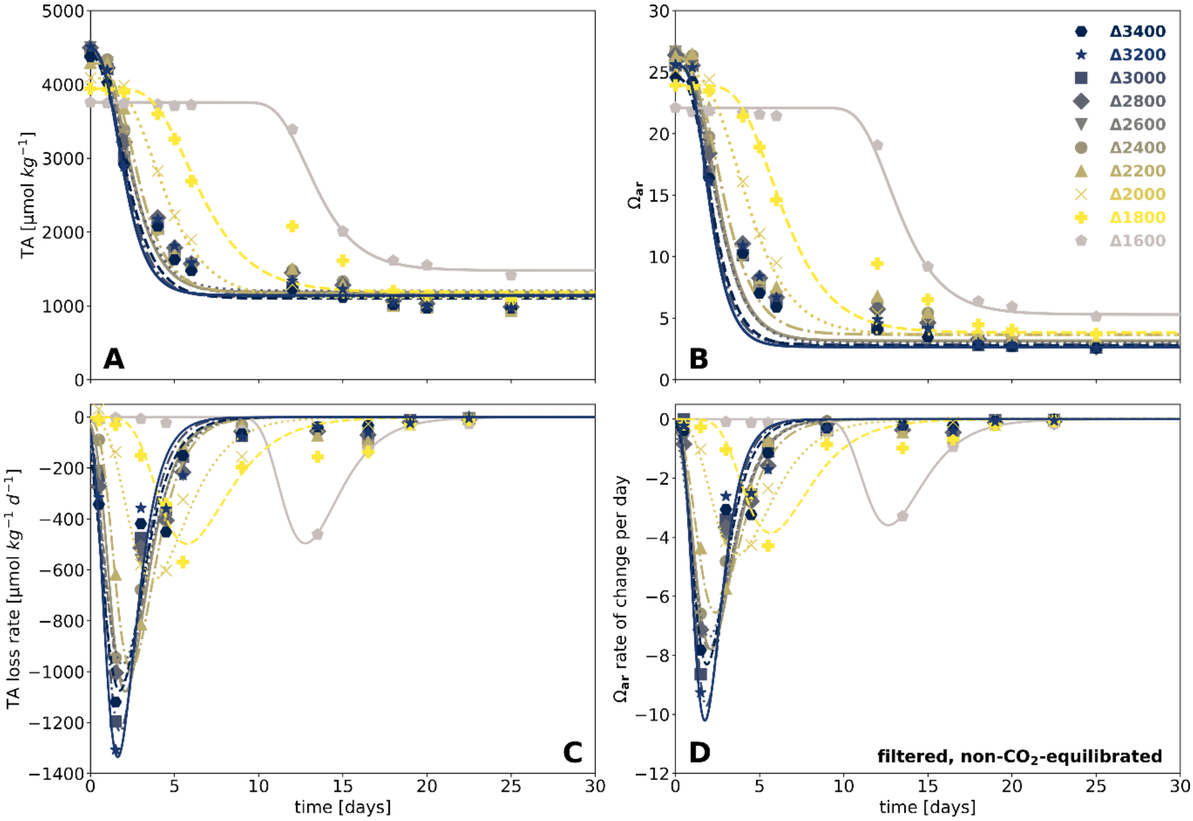

Figure S2: Results of the numerical curve fits – for the filtered neq approach, TA evolution over time (A), Ω_{ar} evolution over time (B), TA-loss rate over time (C), Ω_{ar} rate of change over time (D). line plots: curve-fitted continuous functions, markers: measured data points, also see Figs. 3 and S3

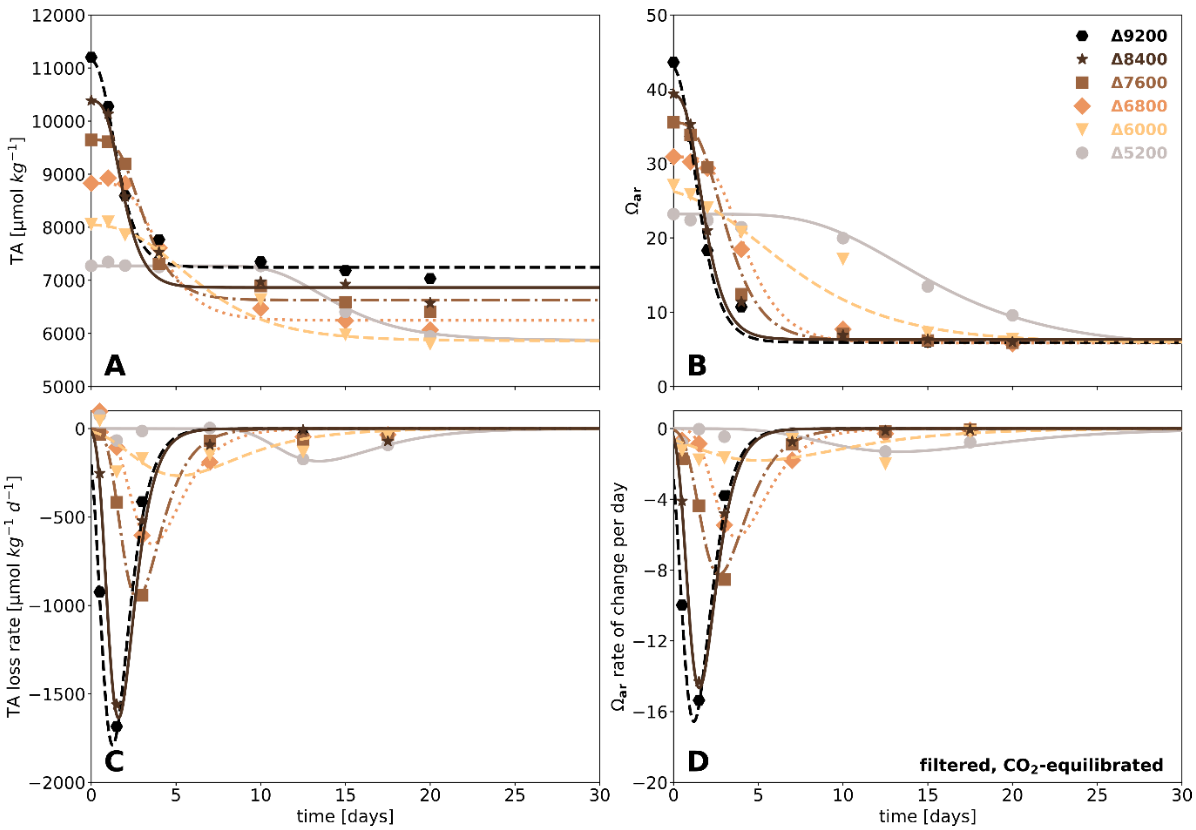

Figure S3: Results of the numerical curve fits – for the filtered eq approach, TA evolution over time (A), Ω_{ar} evolution over time (B), TA-loss rate over time (C), Ω_{ar} rate of change over time (D). line plots: curve-fitted continuous functions, markers: measured data points, also see Figs. 3 and S2

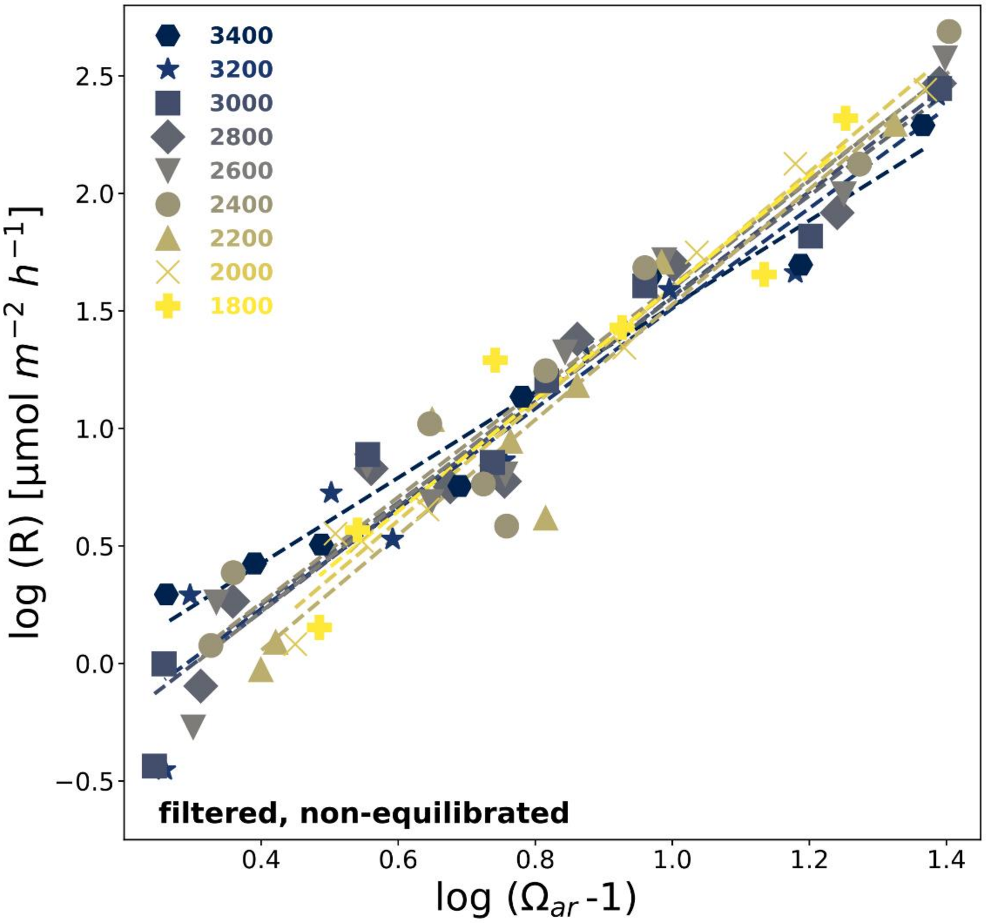

Figure S4: Carbonate precipitation kinetics for filtered neq treatments that entered the APP; see Tab. S1 for related regressions and rate equations.

Table S1: Overview of coefficients and regressions of empirical rate equations for filtered neq treatments, also see Fig. S4

Treatment	$\log(R) = n(\Omega_{ar} - 1) + \log(k)$			
ΔTA	n	log(k)	R^2	$\hat{\sigma}$
3400	1.82	-0.30	0.963	0.080
3200	2.13	-0.62	0.929	0.110
3000	2.24	-0.68	0.955	0.095
2800	2.18	-0.62	0.959	0.080
2600	2.29	-0.70	0.952	0.089
2400	2.25	-0.64	0.924	0.107
2200	2.45	-0.93	0.906	0.100
2000	2.47	-0.88	0.984	0.047
1800	2.38	-0.78	0.924	0.097
all	2.22	-0.66	0.937	0.201

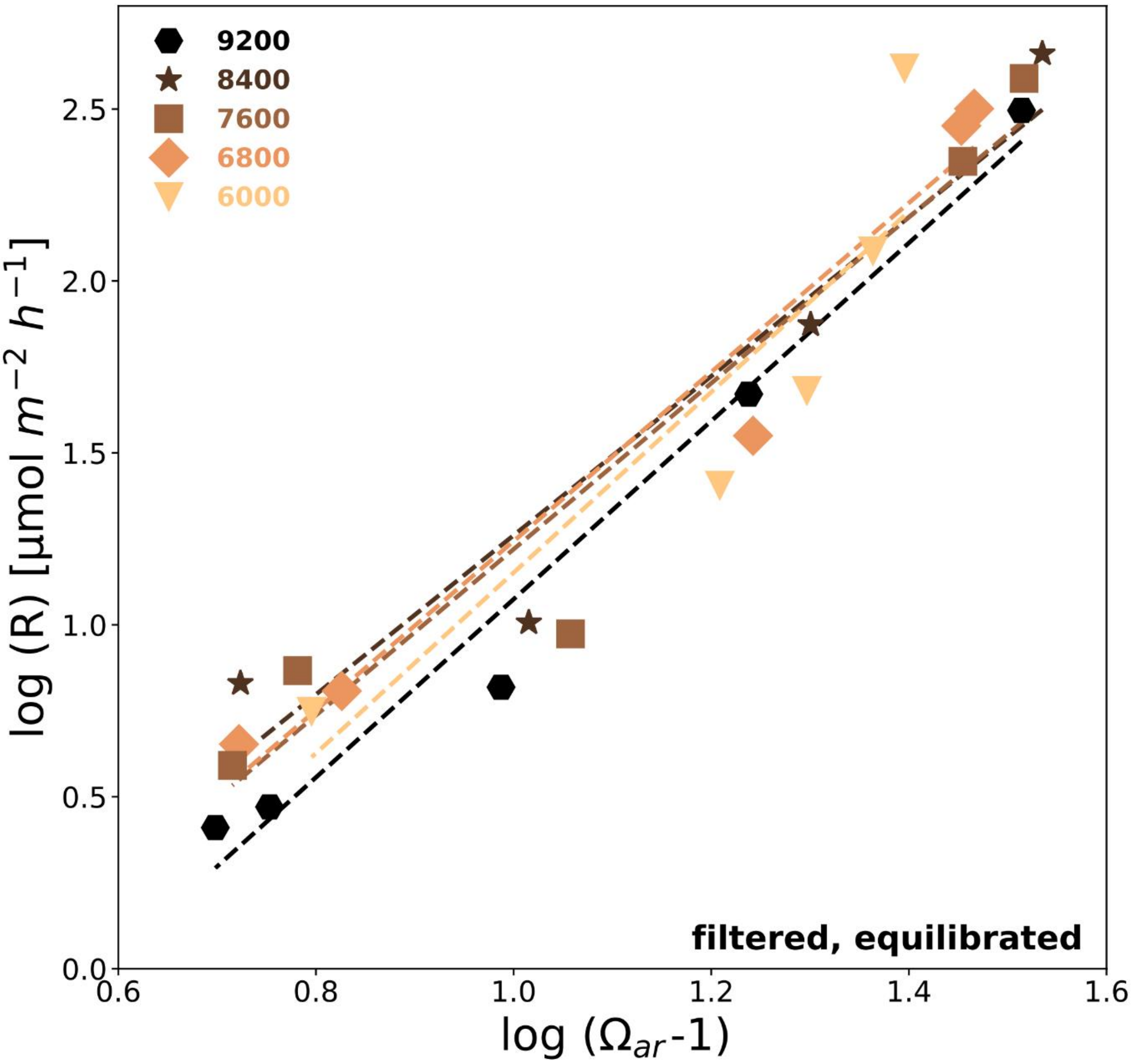

Figure S5: Carbonate precipitation kinetics for filtered eq treatments that entered the APP; see Tab. S2 for related regressions and rate equations.

Table S2: Overview of coefficients and regressions of empirical rate equations for filtered neq treatments, also see Fig. S5

Treatment	$\log(R) = n(\Omega_{ar} - 1) + \log(k)$			
ΔTA	n	log(k)	R^2	$\hat{\sigma}$
9200	2.59	-1.52	0.823	0.118
8400	2.31	-1.05	0.963	0.078
7600	2.41	-1.19	0.942	0.103
6800	2.46	-1.22	0.925	0.118
6000	2.63	-1.47	0.977	0.060
all	2.49	-1.31	0.931	0.214

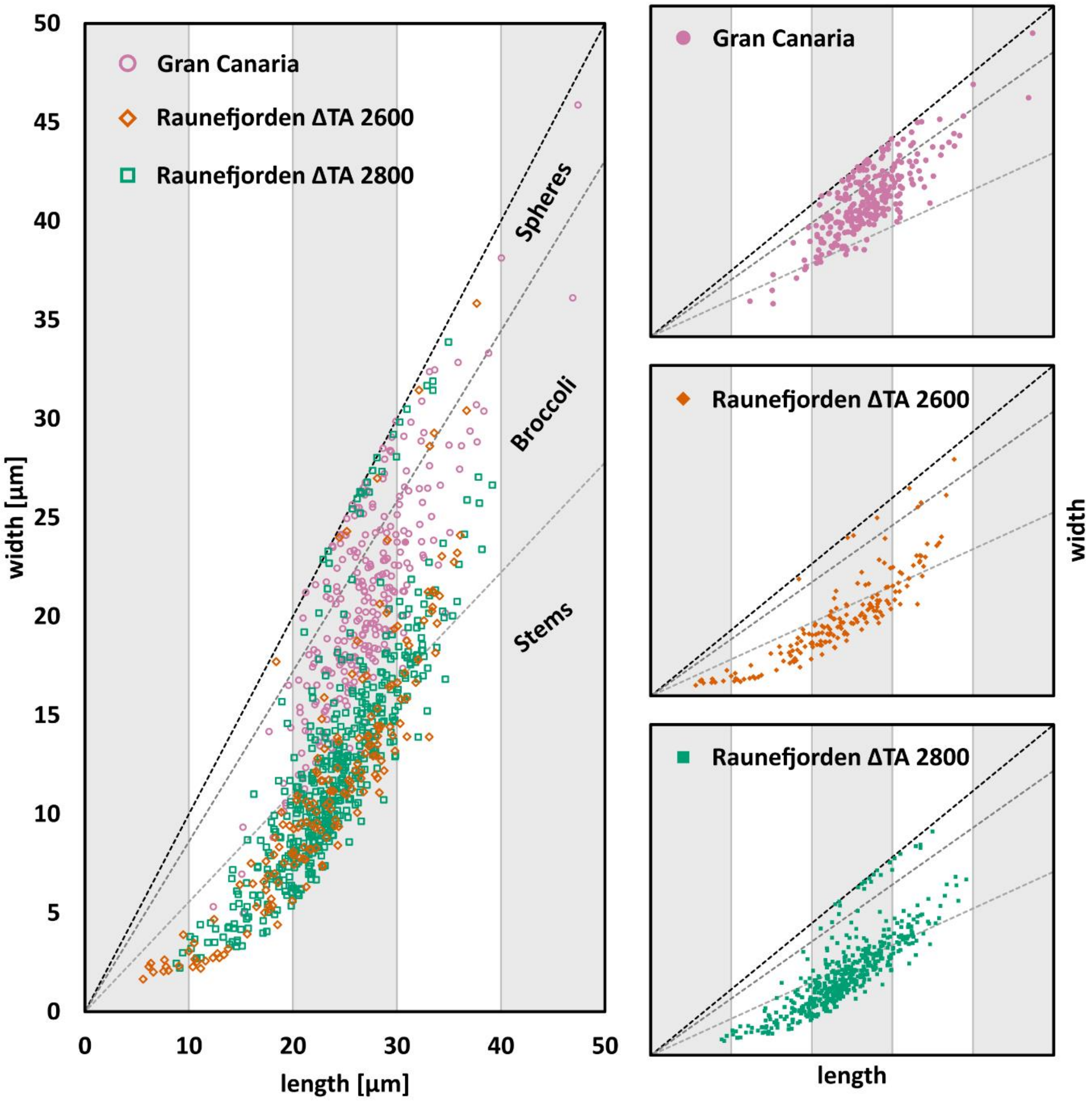

Figure S6: Sizes of precipitated particles during incubation experiments on Gran Canaria (pink circles) (see Hartmann et al., 2023) and in the Raunefjorden, Bergen (see Suitner et al., 2024). Bergen data showcase particles from incubation experiments increasing TA by 2600 (orange diamonds) and 2800 µmol kg^{-1} (green squares); particles where manually counted via SEM images and categorized in three types (spheres, "broccoli" (see Morse et al., 2007 and Suitner et al., 2024), and stems). For a categorization width:length ratios are indicated by dotted lines, sphere (width:length >0.9) – broccoli (width:length 0.5>x>0.9) – stems (width:length >0.5). See Fig. S1 for original SEM images.

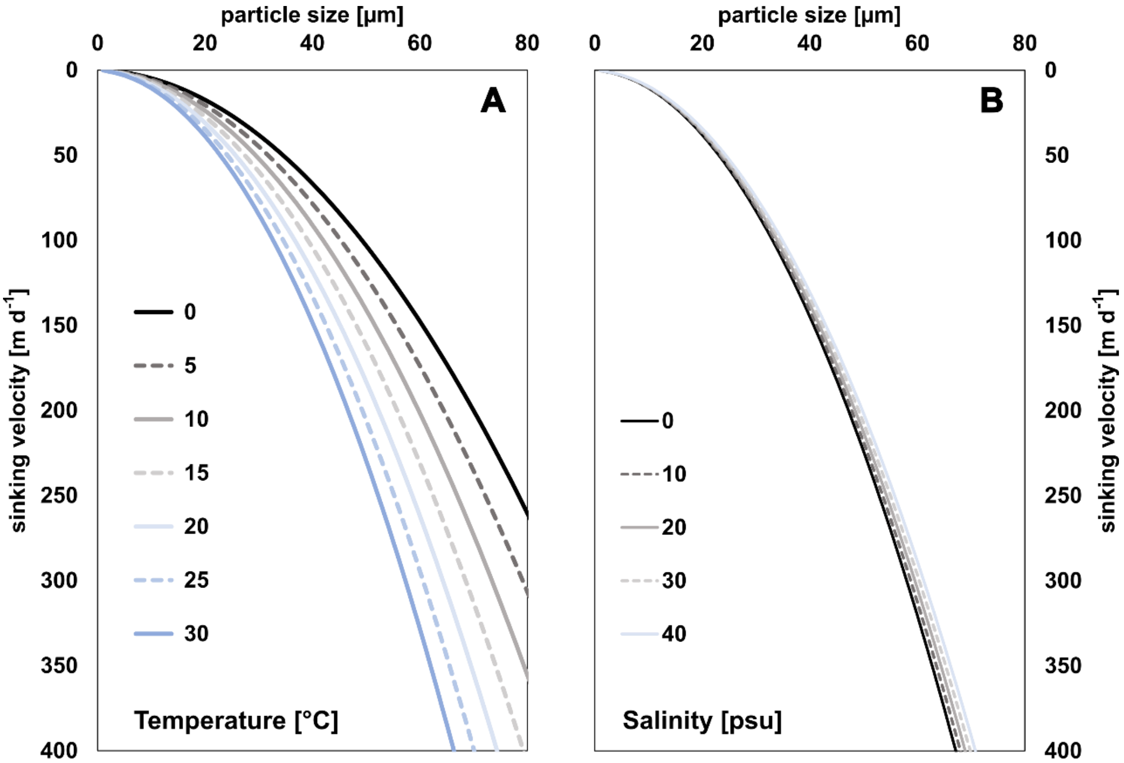

Figure S7: (A) Influence of temperature (Sal. fixed to 35 psu) and (B) salinity (Temp. fixed to 10°C) variations on sinking velocity

30

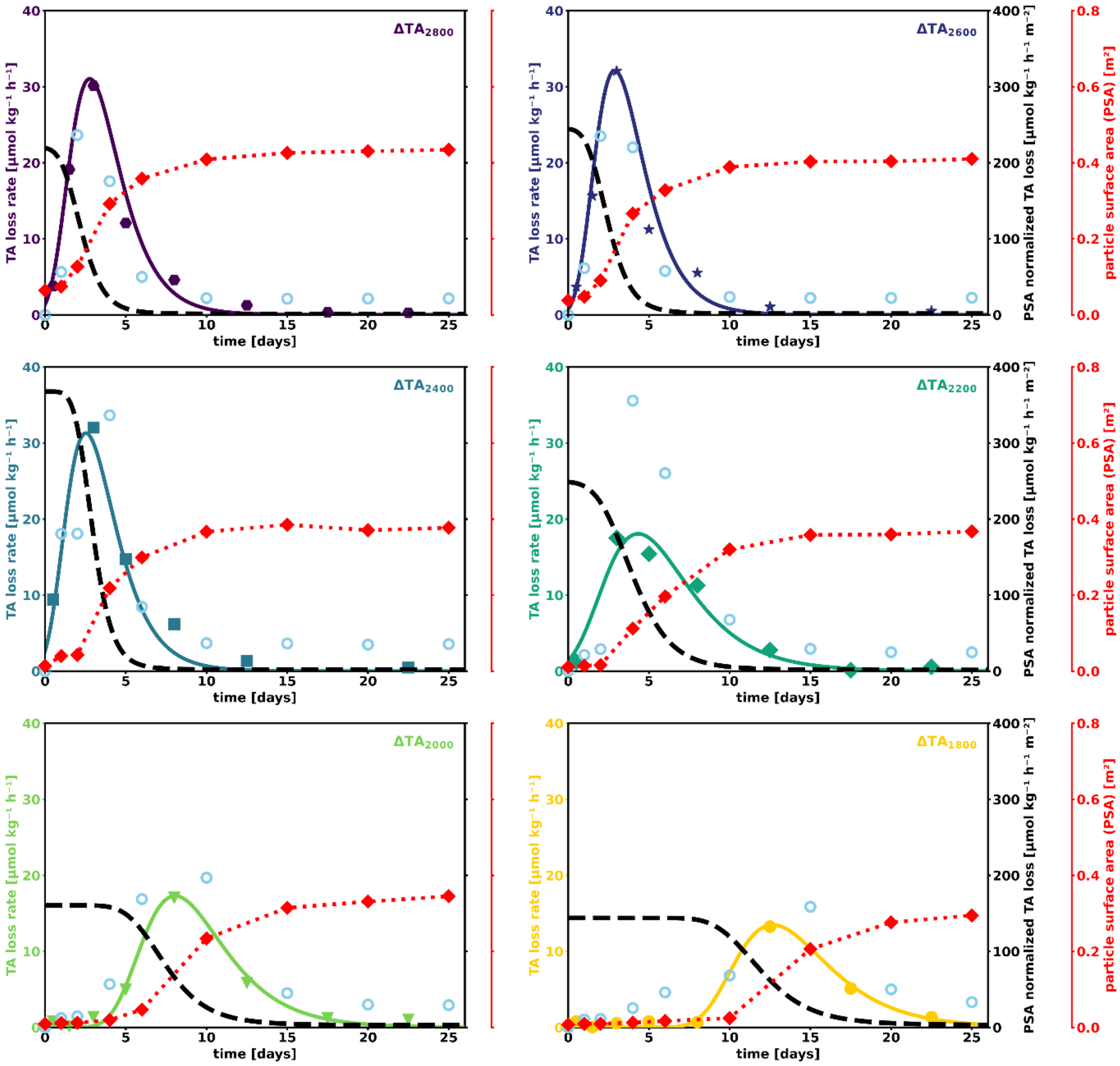

Figure S8: Conceptual figures, showcasing the interplay of Ω_{ar} and particle surface area guiding the theoretical TA-loss rate evolution (dashed graphs) in the unfiltered non-CO_2-equilibrated treatments (Raunefjorden); particle surface area (dotted, red); curve fitted TA-loss rate (solid graphs), measured TA-loss rates are represented by markers of matching colors. Hollow light-blue markers provide the output of the related empirical rate equations (see Tab. 3) for each sampling day.

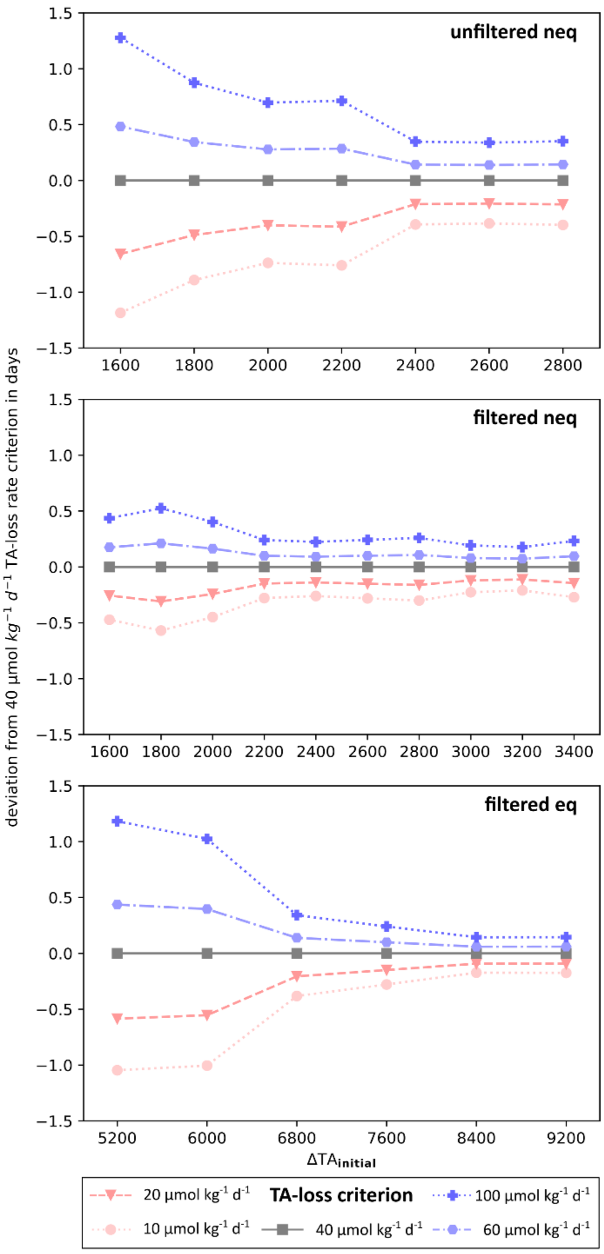

Figure S9: Deviation of onset of the APP with varying TA-loss criteria (see legend) for the unfiltered neq (A), filtered neq (B), and filtered eq (C) experiments.

Conceptual framework to analyze surface area loss during sinking

To estimate the reduction in surface area resulting from the settling of precipitated particles from an assumed alkalized plume of 10 meters, discrete particle diameter size classes were set in increments of 5 µm: specifically, 0-5 µm, 5-10 µm, 10-15 µm, 15-20 µm, 20-25 µm, 25-30 µm, and 30-35 µm. These size classes are based on the distinct particle classifications outlined in section 3.6 and in the study by Suitner et al. (2024). With the known size distributions and aragonite formation rates, treatment level ΔTA_{2800} from the unfiltered non-CO_2-equilibrated experiment (Raunefjorden) was employed as an analogous example to demonstrate the concept of the surface area reduction resulting from particle sinking.

To simplify the calculations, particles were assumed to be spheres with equivalent spherical diameters (ESD) corresponding to the specified size classes. Particles were allowed to transition to the next larger size class in increments of 4 hours, following constant transition factors. Derived from the curve-fitted TA-loss rates, the mass of precipitated aragonite particles is known. When combined with the known size class distribution after 6 days, transition factors and particle counts for each size class can be calculated (see Fig. S10). By assuming uniform sinking velocities for each discrete size class and applying the calculation method outlined in section 3.6, the distance traveled during the sinking process can be calculated for all possible combinations of size class transitions. Based on a set particle surface area of 2.283 $m^2\ g^{-1}$ (see section 2.3), the decrease in available surface area for heterogeneous precipitation can therefore be estimated. Since the available surface area is proportional to the precipitation rate (Eq. 4), the settling of precipitated particles would delay or even stop the precipitation process. Assuming a 10 m alkalized layer, the present example suggests that the available surface area would be reduced by ~35 %, if an export mechanism is incorporated in the treatment level ΔTA_{2800} from the unfiltered non-CO_2-equilibrated experiment.

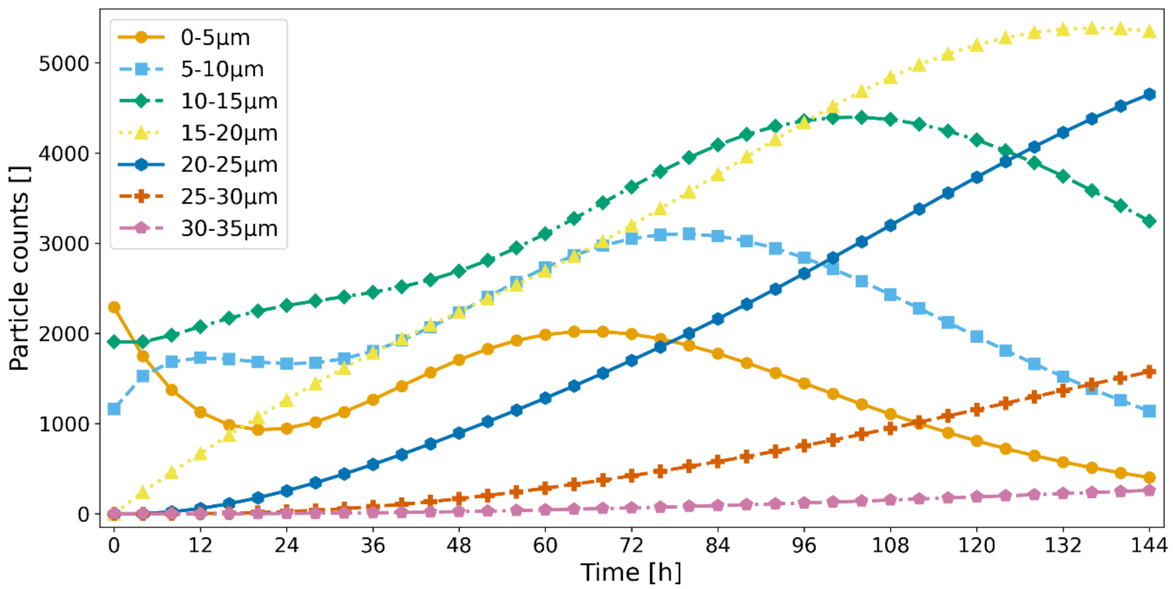

Figure S10: Temporal evolution of particle counts for each designated size class; see text above for details on the calculations and methodology used.