Benthic dunite and calcite weathering as a method for ocean alkalinity enhancement

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Theoretical background:

Weathering of calcite (1) and forsterite (2):

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^- \quad (1)$$
$$Mg_2SiO_4 + 4H_2O + 4CO_2 \rightarrow 2Mg^{2+} + H_4SiO_4 + 4HCO_3^- \quad (2)$$

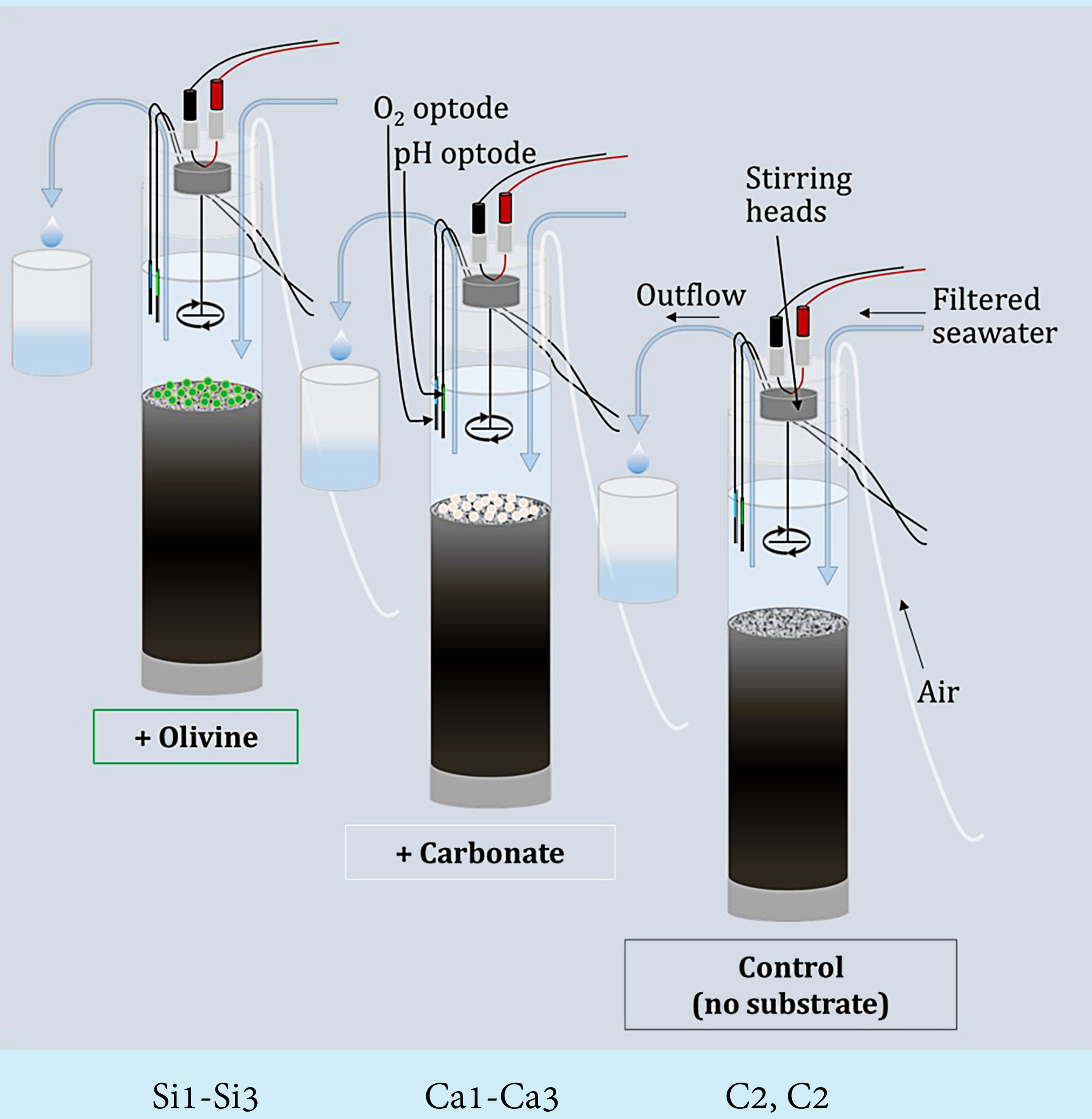
Both reactions increase total alkalinity (TA) via consumption of protons e.g. production of bicarbonate (HCO_3^-). These reactions are coupled to the formation and dissociation of carbonic acid:

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}$$

Thus, CO_2 is consumed and the buffering capacity increased. This has the positive side effect that ocean acidification can be reduced.
Organic rich sediments of the Baltic Sea are governed by low pH values due to oxidation of organic matter via oxic respiration and activity of H_2S oxidizing microbes. Low pH values fuel olivine dissolution directly and lead to saturation states with respect to calcite (Ω_{cal}). These low Ω values again, foster the dissolution of calcite. Thus, these sediments might represent an ideal environment for both dunite/olivine and calcite dissolution.

Experimental set-up:

Oxic incubation:



Results from oxic incubation experiment:

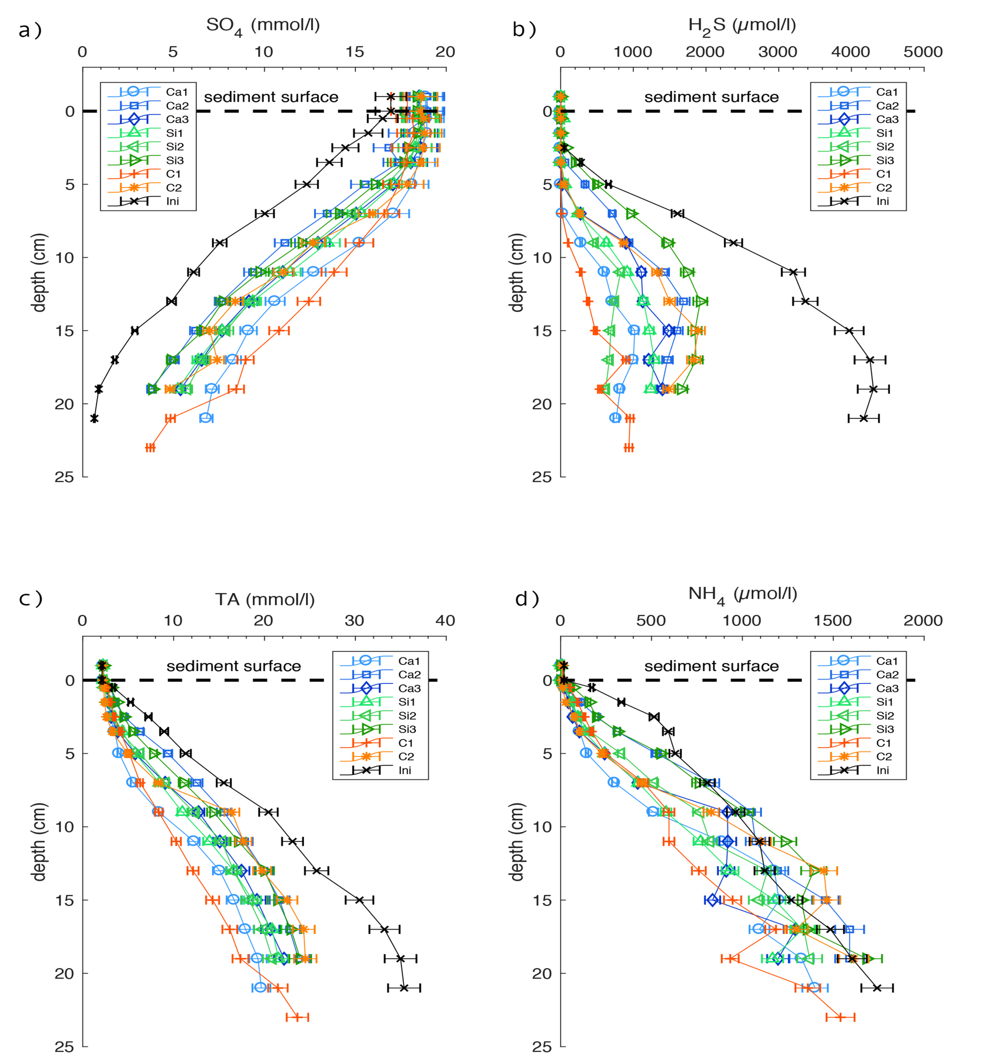


Figure 1: a) SO_4, b) H_2S, c) TA and d) NH_4 concentrations in all sediment cores. Colored markers indicate concentrations in each core at the end of the experiment. Black crosses indicate the concentrations in one exemplary core investigated at the beginning. Horizontal dashed line represents the sediment surface. Error bars are report as relative standard deviation (RSD).

Alterations due to incubation:

- Deeper SO_4^{2-} penetration and lower consumption
- decreased H_2S formation
- lower TA values
- lower NH_4 in upper sediments
- consistent NH_4 in deeper sediments

Explanation:

- ➢ Plugging cut of NH_4 flux from deeper sediments
- ➢ Cut of anaerobic oxidation of methane (AOM)
- ➢ Reduced organic matter degradation in upper sediment due to scarcity of fresh, reactive POC

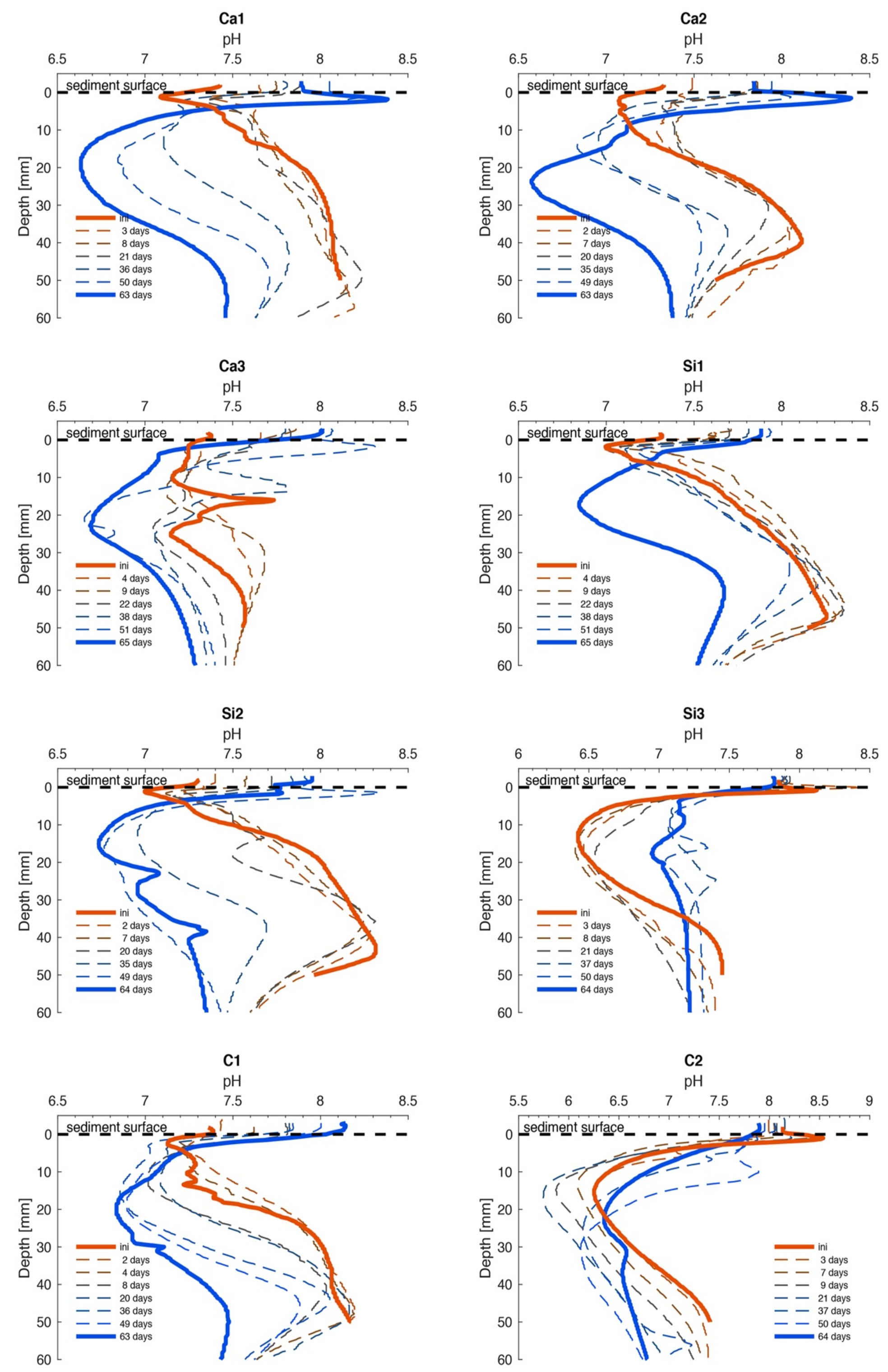


Figure 2: pH-profiles of all cores, observed over the course of the experiment. Solid red lines indicate the first profile taken, solid blue lines show the last profile. Dashed lines represent the profiles taken over time with color coding indicating the chronology after addition of alkaline materials.

Major changes in pH profiles:

- acidification of all cores
- increased bottom water pH
- general change in profile shape

Explanation:

- ➢ chemical and physical changes due to incubation and experimental set-up changed microbial community
- ➢ Different metabolism of now prevailing species changed pH profiles:

Step one: $H_2S + 4H_2O \rightarrow SO_4^{2-} + 8e^- + 10H^+$

Step two: $2O_2 + 8e^- + 8H^+ \rightarrow 4H_2O$

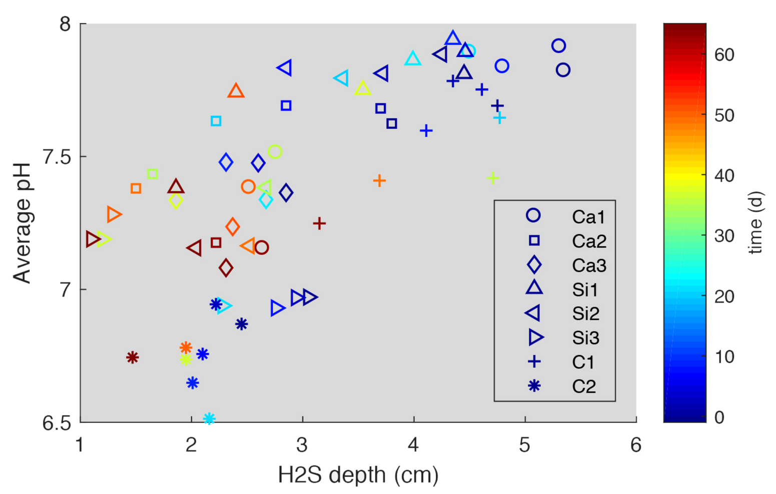


Figure 3: Correlation between H_2S depths and average pH values. different symbols represent different cores. Color coding indicates time after addition of substrates.

Evaluation of weathering effort of oxic incubation experiment:

In order to evaluate benthic weathering, time steps were defined symmetrically around each time a profile was obtained. Subsequently, the average chemistry during these time steps was compared.

Impact of pH on weathering:

$$Diss_{pot} = \int_{z(\Omega<1}^{z(\Omega<1} (1 - \Omega_{cal}(z))\, dz \,/10000$$

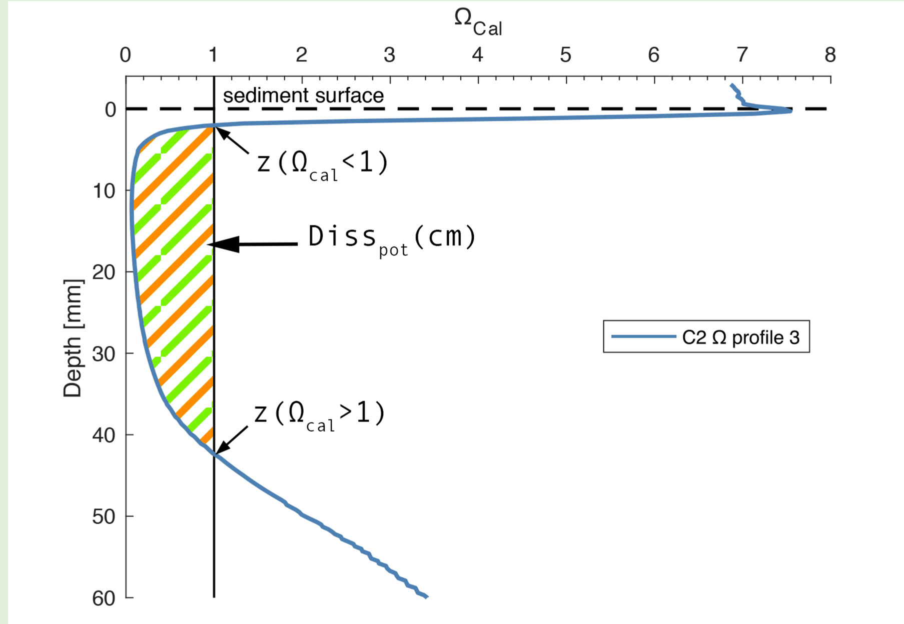


Figure 4: Example for calculation of Disspot on one representative profile (Profile 3, C2). Horizontal dashed line indicates sediment surface. Vertical solid line demarks Ω_{cal}<1. Hatched area depicts the cumulated saturation with respect to calcite ($Diss_{pot}$).

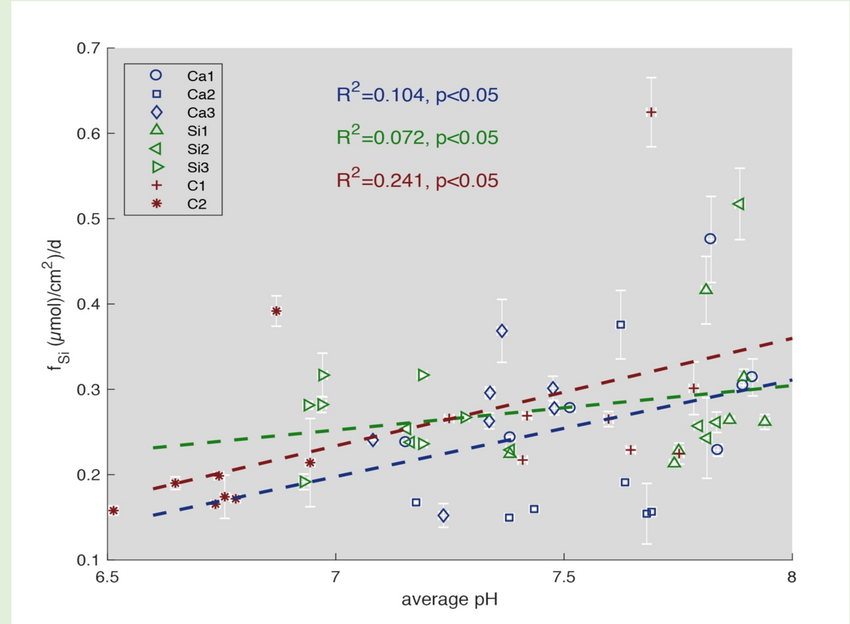


Figure 5: Cumulated [Si] fluxes vi the sediment surface for each time step defined in Table3. Blue symbols represent calcite treated cores, green symbols show dunite treated cores and red symbols represent controls. Dashed lines show linear correlations for each treatment. R^2 values represent the fit of each correlation. Error bars represent SD.

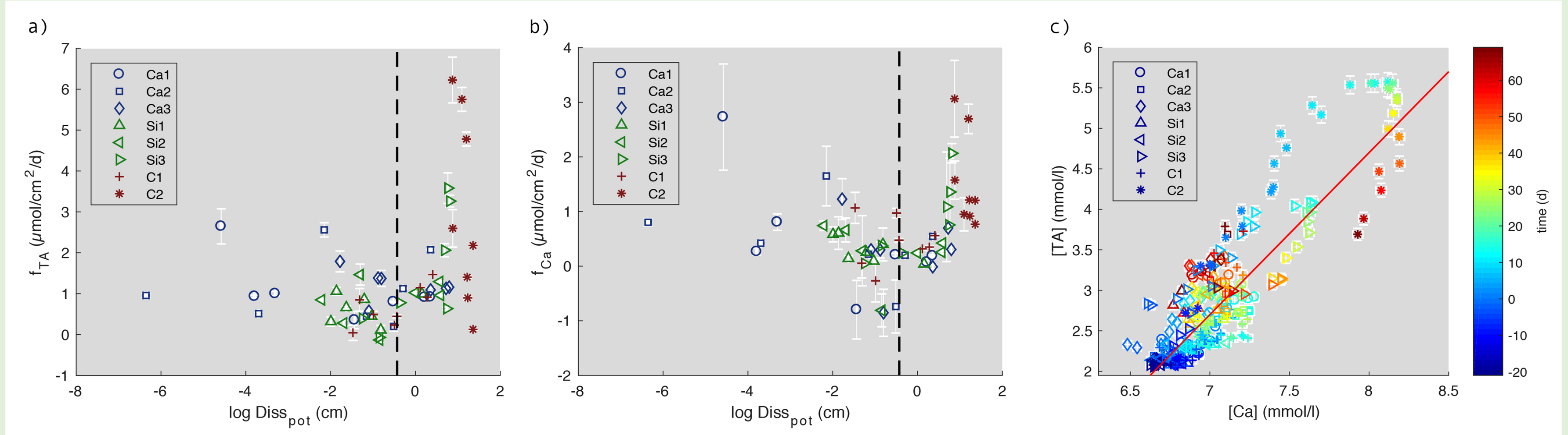


Figure 6: Comparison of $Diss_{pot}$ to TA fluxes (a) and Ca fluxes (b) and [Ca] values to TA values (c). Dashed lines is a and b indicate highest natural $Diss_{tot}$ values. Red solid line (c) demarks TA/Ca ratio of 2. a)and b): Blue markers show values from calcite treated cores, green labels show dunite treated cores and red labels show control cores. Color coding in c) indicates the time at which each sample was taken relative to addition of substrates. Error bars report 2SD.

Table 1: TA, Ca and Si fluxes in different cores averaged over different treatments during comparable time steps. Note that RSD for calcite and dunite treated cores represent RSD between averages of each core. RSD for control experiments derives from only one core and is thus larger.

Treatment	F_{TA} mmol/cm²/d	RSD %	F_{Ca} mmol/cm²/d	RSD %	F_{Si} mmol/cm²/d	RSD %	F_{Ta}/F_{Ca}
Calcite:	1.373	10.31	0.944	34.97	0.247	28.04	1.45
Dunite:	0.634	39.59	0.373	46.34	0.261	4.09	1.70
Control:	0.412	73.48	0.460	125.18	0.329	51.14	0.90

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