Modelling Dissolved CO_2, Mineral Solubilities, and Trace Metal Complexation in Natural Waters Affected by mCDR Activities

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1. Introduction

Proposed approaches to marine carbon dioxide (CO_2) removal (mCDR) include the dissolution of mineral material to increase alkalinity and thereby absorb CO_2. At or near the point of application, the seawater composition (total pH, alkalinity, dissolved Ca^{2+}, Mg^{2+} and other ions) may change considerably, which will affect the values of the acid-base and solubility equilibrium constants: hence **values for ordinary "seawater" may not be accurate**.

The MarChemSpec (Marine Chemical Speciation) acid-base and trace metal complexation model (**marchemspec.org**), for natural waters containing the ions of seawater and GEOTRACES trace metals, has been developed to take such composition changes into account. Here we demonstrate the applications of MarChemSpec to mCDR studies, specifically **alkalinity enhancement** (below), and summarise new features in the model that make it simpler to use. Please see our other poster (OB34C-0880, first author David Turner) for trace metal modelling.

2. Alkalinity enhancement by mineral dissolution

For simplicity, we assume a two step process:

1. Addition to seawater of a mineral that dissolves and increases alkalinity.
2. The seawater then takes up atmospheric CO_2 to attain a new equilibrium and a new composition.

Here are MarChemSpec calculations for several different compounds:

Equilibrium CO_2 Uptake, and Effect on pH, Alkalinity, and Calcite Supersaturation, of Mineral Dissolution in Seawater.

Substance	Added mineral (mmol)	Added mineral (mg)	Alkalinity added (mmol)	pH_T	Calcite sat. ratio	ΔDIC (mmol) (2)	ΔDIC (mol g^{-1}) (3)	pH_T	Calcite sat. ratio
none	-	-	(2.388)	8.102	5.480	-	-	8.102	5.480
Mg_2SiO_4 (1)	0.05	7.034	0.2	8.330	8.530	0.155	0.0222	8.130	6.243
$Ca(OH)_2$	0.1	7.409	0.2	8.334	8.687	0.158	0.0214	8.131	6.313
$Mg(OH)_2$	0.1	5.832	0.2	8.335	8.608	0.159	0.0272	8.131	6.255
$CaCO_3$	0.1	10.01	0.2	8.210	7.188	0.0585	0.00584	8.131	6.313
$(Mg,Ca)_{0.5}CO_3$	0.1	9.22	0.2	8.210	7.155	0.0585	0.00634	8.131	6.284
	Step 1: dissolution of mineral solid					**Step 2**: uptake of atmospheric CO_2			

Notes: all values are for additions to salinity 35 seawater containing 1 kg of pure water (i.e., ~1035 g in total), and calculations are for 25 ºC. The "Step 1" values are those following mineral dissolution (but no CO_2 uptake), and the "Step 2" values are after CO_2 absorption from the atmosphere.
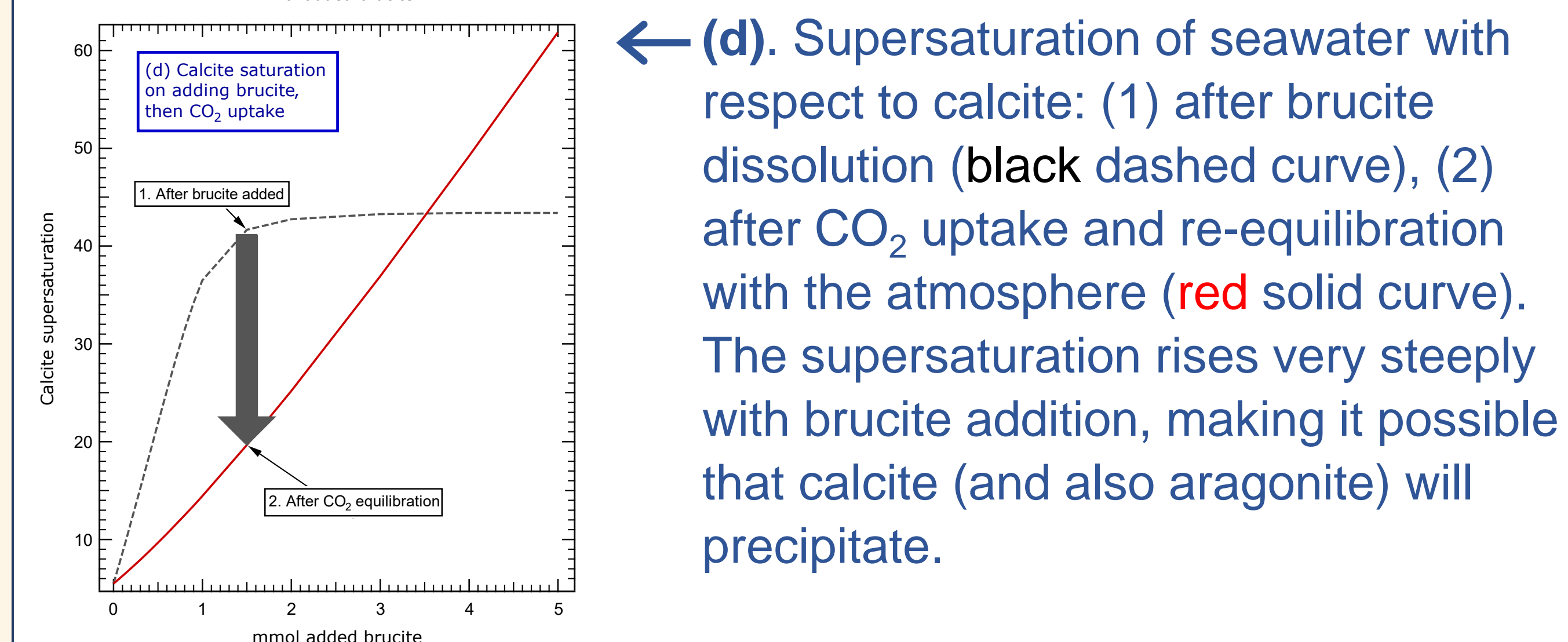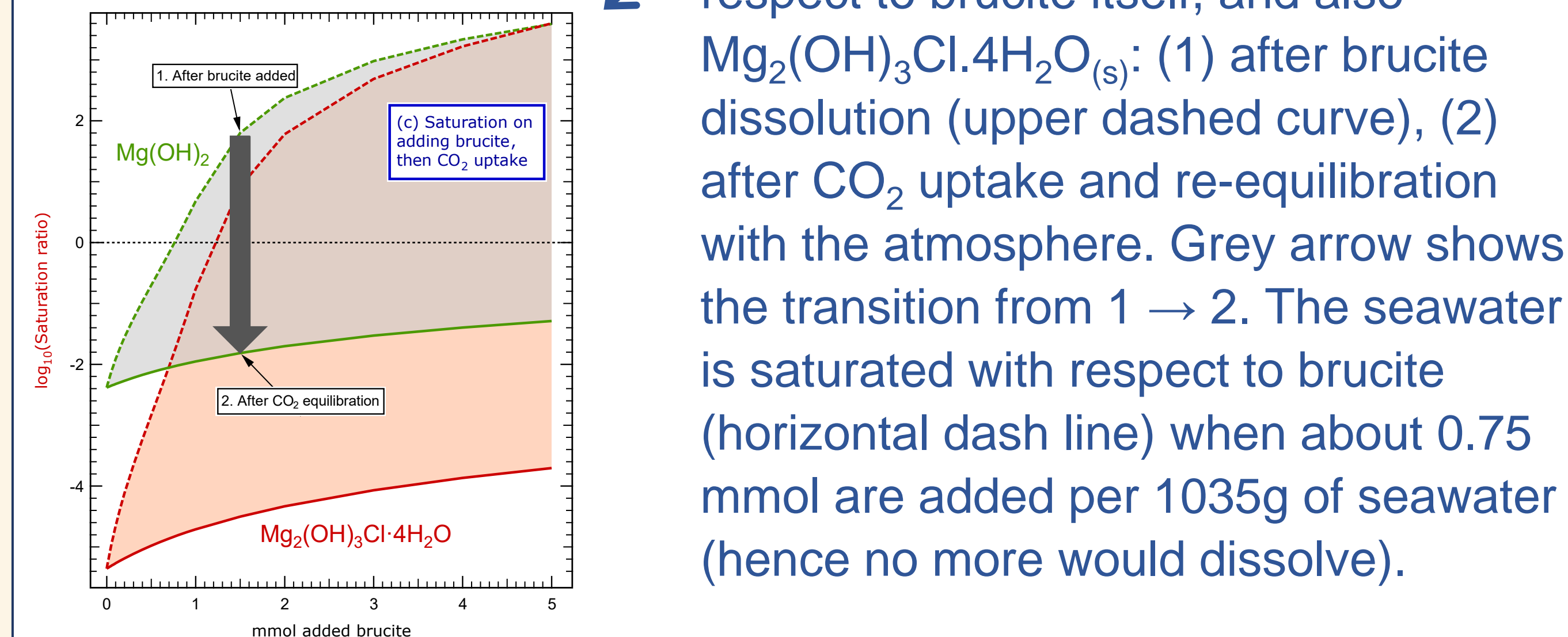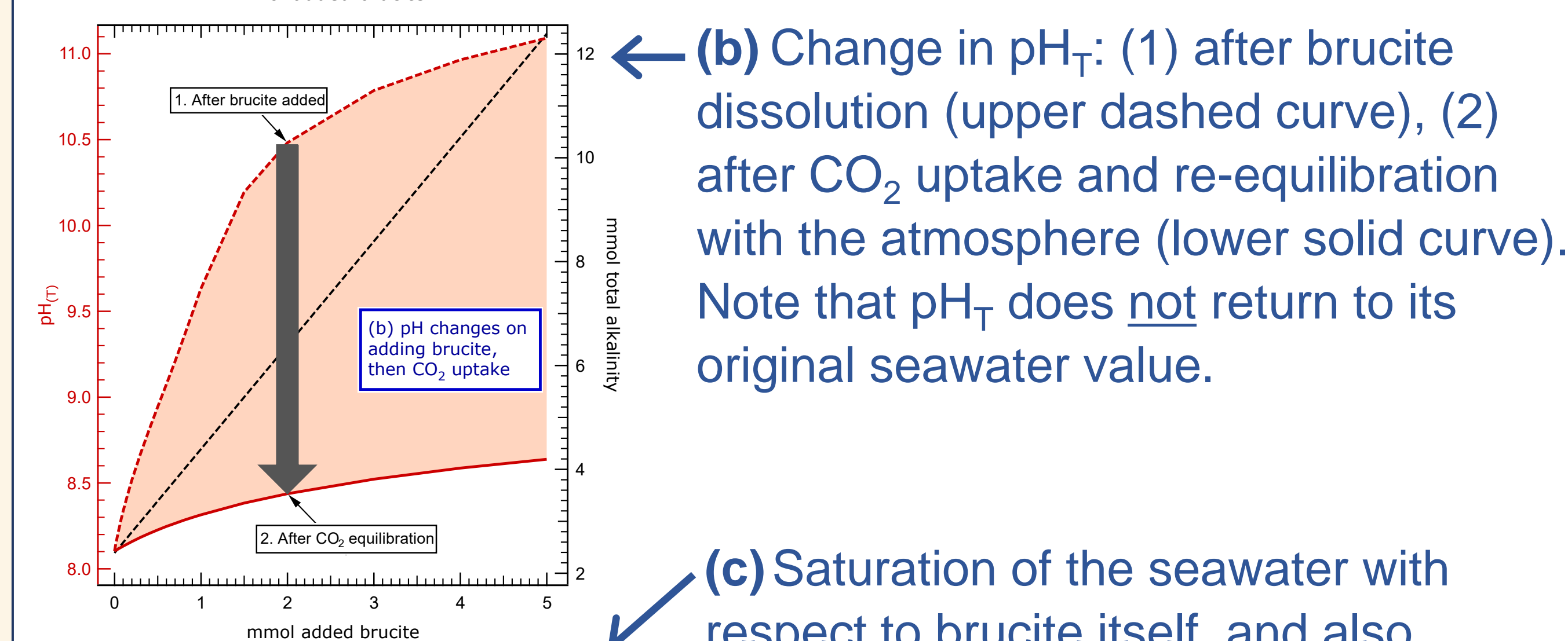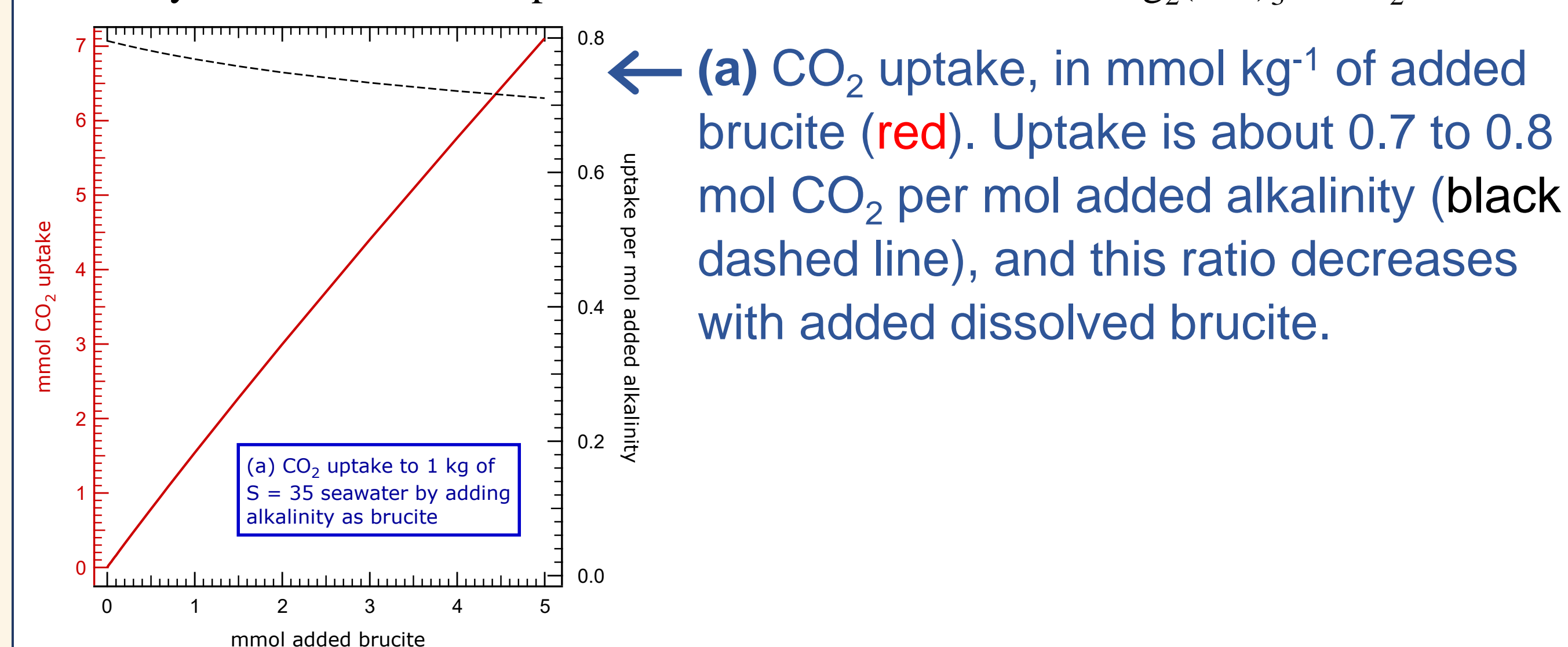
(1) Forsterite (Mg_2SiO_4) is assumed to react with water, yielding $2Mg^{2+}$, $4OH^-$, and $Si(OH)_4$ in solution. (2) The change in total dissolved inorganic carbon due to uptake of CO_2 (i.e., the amount absorbed from the atmosphere to restore equilibrium). (3) Same as (2) above, but per gram of added mineral.

The table shows that the first three compounds are most effective at taking up atmospheric CO_2. However, unless alkalinity is removed in some way (e.g., by precipitation of a CO_3^{2-}- or OH^--containing mineral) the final solution has a slightly elevated pH_T relative to that of unaltered seawater and an increased calcite saturation ratio also.

In the next section we model the effect of varying the amount of dissolved mineral, by using brucite ($Mg(OH)_2$) as an example.

3. Varying the amount of dissolution (brucite)

Here we show the effect at each stage (1 - dissolution; 2 – CO_2 uptake) of varying amounts of brucite dissolution, on: pH_T, alkalinity, CO_2 uptake per mol of added alkalinity, saturation with respect to calcite, brucite itself, and $Mg_2(OH)_3Cl.4H_2O$:

(a) CO_2 uptake, in mmol kg^{-1} of added brucite (red). Uptake is about 0.7 to 0.8 mol CO_2 per mol added alkalinity (black dashed line), and this ratio decreases with added dissolved brucite.

(b) Change in pH_T: (1) after brucite dissolution (upper dashed curve), (2) after CO_2 uptake and re-equilibration with the atmosphere (lower solid curve). Note that pH_T does not return to its original seawater value.

(c) Saturation of the seawater with respect to brucite itself, and also $Mg_2(OH)_3Cl.4H_2O_{(s)}$: (1) after brucite dissolution (upper dashed curve), (2) after CO_2 uptake and re-equilibration with the atmosphere. Grey arrow shows the transition from 1 → 2. The seawater is saturated with respect to brucite (horizontal dash line) when about 0.75 mmol are added per 1035g of seawater (hence no more would dissolve).

(d). Supersaturation of seawater with respect to calcite: (1) after brucite dissolution (black dashed curve), (2) after CO_2 uptake and re-equilibration with the atmosphere (red solid curve). The supersaturation rises very steeply with brucite addition, making it possible that calcite (and also aragonite) will precipitate.

4. The MarChemSpec model

The model calculates equilibrium acid-base, carbonate system, and trace metal speciation of natural waters of arbitrary composition including seawater. It is particularly suited to calculating the effects of *changes* of water composition from normal seawater stoichiometry (such as may occur in mCDR activities). The model uses a state-of-the-art Pitzer treatment of activity coefficients, together with thermodynamic equilibrium constants. Solubility of solids in natural waters – for example calcite, aragonite, $Mg(OH)_2$ and $Ca(OH)_2$ in mCDR-related applications – can readily be calculated.

Inputs: T, and S or individual species compositions of any of the solutes of reference seawater (Na^+,Mg^{2+},Ca^{2+},K^+,Sr^{2+},Cl^-,SO_4^{2-},Br^-,F^-; acid-base carbonate and borate species and HF), and the trace metals Al, Cd, Co, Cu(II), Fe(II), Fe(III), Mn, Ni, Pb or Zn.

Outputs: Speciation of the input solution, together with values of the seawater state parameters (pH (total, free, and seawater scales), alkalinity, DIC, $\{p,f\}CO_2$, and carbonate, sulphate, borate, and fluoride equilibrium constants, and all activity coefficients.

Types of calculation:

1. The equilibrium speciation and properties of the input solution.

2. **NEW FEATURES** in version 1.10: Equilibration of the input solution to fixed (user supplied) values of any single value, or pair, of: pH (total or free), DIC, total alkalinity, pCO_2 or fCO_2. There are 11 different options.

Available codes:

1. Standalone executables (Windows, Linux, macOS)
2. Python function (Windows, Linux)
3. Matlab function (Windows, Linux)
(4. R – we have a draft, would you like to help?)

Note: We have a parallel project to model the pH of Tris buffer solutions, for applications in the calibration of in-situ and other pH sensors. Please ask, if interested.

5. MarChemSpec resources

• Latest news, and links to downloads: **marchemspec.org**
• Recordings of presentations and tutorials: search for **"youtube marchemspec"**
• Zenodo archive of downloads for all model versions: **zenodo.org/records/8373046**
• Description of the model for seawater: there are three papers published in *Marine Chemistry* in 2022 and 2023, and a draft document on trace metal complexation. These are listed at marchemspec.org, and the Zenodo archive.

6. Acknowledgements

How does MarChemSpec work?

1. In the conventional approach to equilibrium constants the dissociation constant of, for example, bicarbonate in seawater (K_2) is equal to:

$$K_2 = [H^+] \cdot [CO_3^{2-}] / [HCO_3^-]$$

The value of K_2 has been measured in seawaters at various temperatures, and represented as a simple function of S and T (e.g., in CO2SYS).

Disadvantages: validity is limited to seawater composition and, mostly, the range of T and S of the measurements.

2. In **MarChemSpec** the same dissociation constant, on a molality basis, is calculated as:

$$K_2 = K_2^o \cdot \gamma HCO_3^- / (\gamma H^+ \cdot \gamma CO_3^{2-})$$

Here K_2^o is the known thermodynamic dissociation constant (i.e., for pure water) which varies with T and P only, and it is multiplied by a term in the *activity coefficients* of the ions (prefix γ). The activity coefficients are functions of the concentrations of all solute species in the aqueous solution, and also T and P. In **MarChemSpec**, as for many/most geochemistry applications, the activity coefficients are calculated using the Pitzer model. The equilibrium state of the solution is determined by Gibbs energy minimisation.

Advantages: not limited to solutions of seawater stoichiometry (so can investigate effects of composition changes); ● can calculate solubility of solids; ● the Pitzer equations conform to thermodynamic relations between solvent and solute activities, and thermal and volumetric properties of solutions. One consequence of this: pressure effects on activity coefficients and therefore equilibrium constants can be determined from density and compressibility measurements of solutions at atmospheric pressure.

Disadvantages: much data for thermodynamic properties of aqueous solutions containing single solutes and simple mixtures is required; ● model building is time consuming.

Go to http://marchemspec.org for information: