

Vademecum for the course

***Climate and Environmental Modelling***

*(SPAT0025 — 2023-2024)*

Guy Munhoven and Louis François

Dept. of Astrophysics, Geophysics and Oceanography  
University of Liège

14th February 2024

Covers: *Guy Munhoven's lectures*

# Preamble

## Purpose and Usage of this Document

Climate and environmental modelling is intrinsically multi-disciplinary, calling upon natural sciences (physics, chemistry, biology, geology, ...), and mathematics. Consequently the amount of material to master is huge. We are aware of this and this document aims at providing you with some guidance through the course material.

The different chapters of this *vademecum* mirror the structure of the lecture slides. Each one first lists the main sections of the lecture chapters. Occasionally extra details are provided. This theme list is followed by a section entitled “What you should have learned here ...” which points that we consider as desirable outcomes, ranked from “Indispensable” to “Important”, “Useful” “Interesting”. In general, we do not expect you to learn many numbers (data) by heart. It is more important to know how and where to find them. However, there are a few of them that we absolutely ask you to remember, since knowing them will help you put things into context.

In general, we expect you to make out links between the different parts of the course.

The learning outcomes presented here should not be seen as exhaustive: we may well ask questions and engage discussion about connected areas, but the stated outcomes should provide a solid base for this purpose.

Please be aware that this document is still evolving. Make sure to always use the latest version, available on <https://www.astro.uliege.be/~munhoven/fr/cours/modenv>. Each version can be identified by the date on its cover page and in the page headings.

# Chapter 1

## Chemical Equilibria and pH Calculations

### 1.1 Carbonate Chemistry

- Carbonate system equilibria
- Equilibrium relationships
- $pK$  values
- Stoichiometric vs. thermodynamic constants
- Chemical composition of seawater
- Activity coefficients
- $pH$  scales
- Carbonate chemistry and speciation
- Special roles of different species; measurables
- State variables of the carbonate system
- Alkalinity: a first tour; exact definition; contributions; examples, contributions; approximations; properties
- $C_T$  and  $Alk_T$  in the oceans

## 1.2 *pH* Calculation

- Carbonate System
  - speciation relationships
  - borate system speciation
- Calculating *pH* From  $\text{Alk}_T$  and  $C_T$ 
  - mathematical properties (monotonicity, limits, ...)
  - numbers of roots
  - root bounds
  - efficient solution method
- General Acid-Base System
  - dissociation reactions and equilibrium relationships
  - speciation relationships
  - example: phosphate system speciation
  - general acid-base system speciation relationships
  - *pH* From  $\text{Alk}_T$  and arbitrary acid-base systems
  - “Some details skipped”: extra and other complications
- *pH*,  $p_{\text{CO}_2}$ ,  $\text{CO}_3^{2-}$  on  $C_T$ – $\text{Alk}_T$  graphs
- Effect of photosynthesis (organic carbon production) and remineralization and of carbonate production and dissolution) on carbonate system species concentrations

## 1.3 Alkalinity: A Conservative Variable?

- Electroneutrality in seawater
- Deriving the Explicit Conservative expression of Alkalinity
- Corollaries

## What you should have learned in this chapter ...

### Indispensable

- Carbonate system equilibria (reactions)
- Equilibrium relationships and  $pK$  values
- Special roles of different species; measurables
- State variables of the carbonate system
- Alkalinity: you should be able
  - to state the definition;
  - to cite the most important contributing species in seawater; (i. e., explicit the  $\text{Alk}_C$ ,  $\text{Alk}_{CB}$  and  $\text{Alk}_{CBW}$  approximations);
  - being given a system of acid-base equilibrium reactions and their respective  $pK$  values, to determine the proton donors and acceptors contributing to  $\text{Alk}_T$ , and their respective strengths.
- You should be able to explain the systematics of  $C_T$  and  $\text{Alk}_T$  distributions in the oceans, being given the graph.
- $pH$  calculation: you should be able
  - to derive the  $pH$  equation for the  $\text{Alk}_{CBW}$  approximation, using the relevant equilibrium relationships;
  - to give its mathematical properties;
  - to suggest numerical methods to solve that equation.

See also Exercise 3.4 in the *Exercise Book*.

- You should be able to explain the effect of photosynthesis (organic carbon production) and organic matter remineralization, and of carbonate production and dissolution on  $pH$ ,  $p\text{CO}_2$ ,  $\text{CO}_3^{2-}$  using  $C_T$ – $\text{Alk}_T$  graphs.
- The Explicit Conservative expression of Alkalinity ( $\text{Alk}_{EC}$ ): you should be able
  - to derive  $\text{Alk}_{EC}$  being given the most important ions in average seawater;
  - to show how  $\text{Alk}_{EC}$  (and thus  $\text{Alk}_T$ ) differs from the charge difference between conservative cations and anions;
  - to deduce that  $\text{Alk}_T$  is a conservative variable.

### **Important**

- Bjerrum plots: what do they show and how are they obtained?
- $pH$  scales

### **Useful**

- Determine the contribution of a general acid-base system to alkalinity.

### **Interesting**

- Everything else...<sup>1</sup>

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<sup>1</sup>What else did you expect?

# Chapter 2

## Isotopes in Environmental Modelling: A Primer

### 2.1 Outline

- Isotope Notation
- Atomic Weights and Abundances of H, C, N, O Isotopes
- Miscellaneous Isotope Facts
- Controls on Isotope Distributions
- Usefulness
- Measuring Isotopic Compositions: Mass Spectrometer
- Nomenclature for Isotopic Data
- Notation
- Reference Standards:  $\delta$  Notation
- Expressing Isotope Abundances: General Definitions and  $^{13}\text{C}$ - $^{12}\text{C}$  Example
- Common Reference Standards
- Distribution of Carbon-13 in Nature (graph)
- Material Balance Relationships
- Mole Fraction vs. Isotope-Number/Isotope-Amount Fraction

- Material Balance Relationships with  $\delta$ 's
- Fractionation: Summary Rules
- Some Physical Properties of Ordinary and Heavy Water
- Equilibrium Fractionation
  - fractionation factor  $\alpha$
  - fractionation constant  $\epsilon$
  - isotopic difference  $\Delta$
  - $\ln \alpha$
- Properties of  $\alpha$ ,  $\epsilon$  and  $\Delta$ , and dependencies
- Caveats regarding usage in the literature
- Non-Equilibrium fractionation
- Mass balance equations
  - typical problem to solve
  - exact and approximate relationships for mass balance variables;  $^{13}\text{C}$  example
  - approximate evolution equation for  $\delta^{13}\text{C}$
  - exact evolution equation for  $x^{13}\text{C}$
  - evolution equations: do's and don'ts
  - alternative: evolution equations for  $^{13}n$  and  $n$

## What you should have learned in this chapter ...

### Indispensable

- Isotopes: what are they? How are they denoted?
- What controls isotope distributions? Why are isotopes useful?
- General nomenclature for isotopic data; commonly adopted notation simplifications.

- $\delta$  notation of isotopic ratios
  - why report  $\delta$ 's rather than  $R$ 's?
  - what is the meaning of the sign of  $\delta$ ;
  - microscopic vs. macroscopic quantities.
- Carbon-13 in nature: you should have an idea of the ranges of  $\delta^{13}\text{C}$  of
  - air  $\text{CO}_2$ , air  $\text{CH}_4$ ,
  - $\text{C}_3$  plants and  $\text{C}_4$  plants,
  - methane,

and how they compare to each other.

See also Exercise 1.3 in the *Exercise Book*.

- Establish the material balance relationships (isotope ratio and  $\delta$  of a multi-component system).  
See also Exercise 1.8 in the *Exercise Book*.
- Quantification of isotope (fractionation) effects
  - definitions of  $\alpha_{(A-B)}$ ,  $\epsilon_{(A-B)}$ ,  $\Delta_{(A-B)}/\text{std}$ ;
  - usefulness of  $\ln \alpha_{(A-B)}$  and relationship to  $\epsilon_{(A-B)}$ ;
  - quality of the approximation  $\epsilon_{(A-B)} = \Delta_{(A-B)}/\text{std}$ .
- Mechanisms of non-equilibrium fractionation
- Mass Balance Equations
  - typical problem to solve
  - exact and approximate relationships for mass balance variables;  
 $^{13}\text{C}$  example
  - approximate evolution equation for  $\delta^{13}\text{C}$
  - exact evolution equation for  $x^{13}\text{C}$
  - evolution equations: do's and don'ts

**Important**

- H, C, N, O Isotopes: have a rough idea of the fractional abundance of the most abundant isotope of each of these four elements (of the order of 99 to 99.99 %).
- Name a few commonly used reference standards: you should know for which isotope ratios they are used, but you do not have to learn their isotope ratios!
- Fractionation: summary rules of Bigeleisen (helpful to understand why there may be isotope effects at equilibrium).
- Mass balance equations:
  - do's and don'ts
  - evolution equations for  $^{13}n$  and  $n$  directly (alternative to equations for  $\delta^{13}C$  and  $^{13}x$ ).

**Useful**

- How are isotopic compositions measured?

**Interesting**

- Physical properties of ordinary and heavy water.
- Most of the rest.

# Chapter 3

## The Ocean Carbon Cycle

### 3.1 Box-model of the Global Ocean: Phosphorus, Alkalinity, Carbon

- Phosphate Distribution in the Ocean
  - profiles for major basins of the World Ocean
  - link to biological activity and thermohaline circulation
- Model Structure
  - Reservoir delimitations
  - Residence times of water in the different basins
- DIC ( $C_T$ ) and  $Alk_T$  distributions in the World Ocean
- Dissolved  $O_2$  distributions in the World Ocean

### 3.2 Pre-industrial model

- Phosphorus
  - productivity control
  - pre-industrial steady-state solution
  - comparison with data
- Carbon and Alkalinity
  - link to the phosphorus model

- surface, thermocline and deep reservoirs
- pre-industrial steady-state solution for alkalinity and comparison with data
- pre-industrial steady-state solution for carbon and comparison with data

### 3.3 Evolution during the industrial period

- Forcing of the Model.
- Evolution of Dissolved Inorganic Carbon.
- Evolution of  $pH$  in the Surface Reservoirs.
- Flux Balance of Atmospheric  $CO_2$ .
- Atmospheric  $CO_2$  Budget 1980–1990.

### 3.4 $^{13}C$ Isotopic Evolution

- Average Abundances of Naturally Occurring Carbon Isotopes.
- Isotopic Evolution Equation (see chapter 2 in this *Vademecum*).
- Pre-Industrial Steady-State Solution ( $\delta^{13}C$ ).
- Evolution of  $\delta^{13}C$  During the Industrial Period (coupled ocean-atmosphere-biosphere model).

## What you should have learned in this chapter ...

### Indispensable

- Phosphate, DIC, alkalinity and oxygen distributions in the World Oceans: explain the general characteristics (gradients), being given the graphs.
- Reservoir model of the ocean carbon cycle:
  - model structure: reservoirs and residence times; (please refer also to the chapter on *Reservoir Models*);

- organic matter processing from the surface through the intermediate (thermocline) to the deep reservoirs;
  - critical evaluation of the model results;
  - rationale of the flux balance of atmospheric CO<sub>2</sub> (industrial simulation with atmospheric pCO<sub>2</sub> prescribed)
- You should be able to explain the evolutions of the different reservoirs' concentrations during the industrial period, being given the graphs

**Important, Useful, Interesting**

- Rationale of the Atmospheric CO<sub>2</sub> Balance for 1980–1990.
- Redfield C:P ratio value (molar ratio).
- Carbonate-C:Organic-C ratio (rain ratio).

# Chapter 4

## Seafloor Sediments – Interaction with the Ocean and Early Diagenesis

### 4.1 The Seafloor and its Sediments

- A First Exploration
  - bathymetry
  - surface sediment %CaCO<sub>3</sub> distribution
  - surface sediment %opal distribution
  - surface sediment %TOC (total organic carbon) distribution
  - non-biogenic components
- Archives of the Earth's History:  $\delta^{18}\text{O}$ , dating, ...
- Role of Sediments in Biogeochemical Cycling
- Concentration Gradients: Ocean vs. Surface Sediment
- Acidification: Perturbation of the Ocean-Sediment Exchange

### 4.2 Modelling

- Preludes: Geometric Setting
- General Continuity Equation
- General Continuity Equation for Interfaces

- Sediments: Two Phases and Multiples Constituents
  - porosity
  - link between total concentrations and phase concentrations
- One-Dimensional Model
  - flux types: advection, diffusion
  - mixing processes relevant for the solid phase (bioturbation, biodiffusion)
  - reaction rate law expressions
  - boundary conditions
- A First Simple Carbonate Diagenesis Model
- Organic Matter Remineralization
  - remineralization pathways (sequence)
  - porewater solute zonation
- Improved Carbonate Diagenesis Model
  - general characteristics (extent, components, reactions)
  - reaction terms: organic matter and oxygen
  - reaction terms: calcite
  - reaction terms: dissolved inorganic carbon
    - notice: although ‘1/2’ in  $r_{1/2}$  has a meaning—the stated reaction combine the 1<sup>st</sup> and 2<sup>nd</sup> dissociation reactions of the carbonate system—this is irrelevant here.
  - elimination of the fast reactions
  - typical  $\text{CO}_3^{2-}$  profiles in the porewater above and below the CSH
    - note: CSH is the *Calcite Saturation Horizon*, i. e., the depth at which the water is saturated with respect to calcite; CCD is the *Calcite Compensation Depth* or *Carbonate Compensation Depth*, i. e., the depth at which the deposition rate of calcite and the total dissolution rate in the sediment column are equal.

## What you should have learned in this chapter ...

### Indispensable

- You should be able to state the general diagenesis equation (general continuity equation) and the continuity equation at an interface.
- You should know the different flux type expressions.
- Boundary conditions (you may skip the two starred slides)
- Organic matter remineralization: you should be able to explain the importance of
  - the sequence of oxidation-reduction (redox) pathways for the remineralization of organic matter
  - and its role in explaining the porewater solute zonation
- Improved Carbonate Diagenesis Model
  - reaction rate law expressions
  - links between solids' and solutes' reaction rates

You should be able to explain the rationale behind the elimination of the fast interconversion reactions from the partial differential equation system.

### Important

- Transport in the solid phase: mixing processes and their characteristics (thickness of the mixed-layer throughout the ocean; absence of bioturbation in anoxic environments; ...)

### Useful

- General characteristics of the surface sediment composition
- Derivation of the general continuity equation and the continuity equation at an interface
- The first simple carbonate diagenesis model: outline and insufficiencies

### Interesting

- Difference between interphase and intraphase bioturbation

# **Chapter 5**

## **Continent-Ocean Interaction: the Role of Weathering**

### **5.1 Carbon Cycle**

- Processes
- Time scales
- Modelling: Why?

### **5.2 Model Development: General Principles**

- The Essence of Modelling: Linking Theory and Data to Interpret or Make Predictions
- The Four Stages of Model Development

### **5.3 Illustration: Simple Carbon Cycle Model**

- Model Formulation: Hypotheses and Simplifications
- Processes Considered
- Carbonate Chemistry in Seawater
- Fluxes Considered
- Conservation Equations

- sources and sinks of DIC and alkalinity in the ocean
- typical weathering reactions for silicate minerals
- systematics of weathering  $\text{CO}_2$  consumption and  $\text{HCO}_3^-$  production rates
- global balance of DIC and alkalinity in the Ocean-Atmosphere System
- Model Resolution
  - relationship between  $\text{CO}_2$  emissions by volcanic and hydrothermal activity and  $\text{CO}_2$  consumption by silicate weathering
  - analysis of the river  $\text{HCO}_3^-$  partitioning
  - solution and interpretation
- Connecting the Carbon and Alkalinity Budgets:
  - non steady-state
  - constraints on time scales  $> 1$  Myr
  - constraints on time scales  $< 1$  Myr: generalized silicate weathering constraint
  - sensitivity analysis: variable silicate weathering, variable carbonate weathering
- Model Sensitivity Analysis of the Impact of Weathering Flux Changes on Time Scales of 10 to 100 kyr
  - MBM – Ocean-Atmosphere Carbon Cycle Model
  - MEDUSA – Early Diagenesis Model
  - Pre-industrial Surface Sediment % $\text{CaCO}_3$
  - Bicarbonate production rate and  $\text{CO}_2$  consumption rate scenarios
  - $\text{pCO}_2$  and Calcite Saturation Horizon variations

## What you should have learned in this chapter ...

### Indispensable

- The Essence of Modelling: How to Link Data and Theory: scheme (please notice that this is a replicate from the *Introduction* by Louis François)
- The four stages of model development

- You should be able to reproduce the showcase application, with emphasis on the four development stages:
  - state the hypotheses made and the simplifications adopted
  - schematic of the carbon cycle model, DIC and alkalinity exchange fluxes
  - systematics of weathering  $\text{CO}_2$  consumption and  $\text{HCO}_3^-$  production rates (no obligation to learn the silicate mineral reactions),
  - relationships between DIC and alkalinity fluxes
  - deduction of the relationship between  $\text{CO}_2$  emissions by volcanic and hydrothermal activity and  $\text{CO}_2$  consumption by silicate weathering
  - resolution by use of the given riverine  $\text{HCO}_3^-$  analysis
  - interpretation (comparison with anthropogenic  $\text{CO}_2$  emissions)

### **Important**

- Interpretation of the model results: secondary result regarding the sedimentary flux  $C_{\text{sed}}$  (carbonate burial)
- Generalization of the silicate weathering  $\text{CO}_2$  constraint for non steady-state

### **Useful**

- Carbon cycle scheme: it is always useful to have a rough idea of reservoir sizes and flux estimates, and also of the current anthropogenic  $\text{CO}_2$  emission rate
- One or two silicate mineral reactions
- Meaning of “congruent” and “incongruent” dissolution
- Qualitative analysis of the possible impacts of variable  $\text{HCO}_3^-$  production and  $\text{CO}_2$  consumption rates
- Quantitative analysis of the impacts of variable  $\text{HCO}_3^-$  production and  $\text{CO}_2$  consumption rates with a coupled ocean carbon cycle–surface sediment model

### **Interesting**

- The rest (if anything left)