Exercise and Problem Collection for the Course

Climate and Environmental Modelling

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(Version 0.8.1 – **DRAFT** – 15th May 2023)

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Introduction

Usage of this document

This exercise collection is meant to contribute to improve the students' mastering of the material of the course SPAT0025 (*Climate and Environmental Modelling*) at the University of Liège as of the academic year 2022-2023.

Each chapter in this problem collection covers one theme, broadly following those covered in the theoretical lectures. The order may be different, but this should not be a hindrance, as the different chapters are only loosely interdependent, a fact that is taken into account here as well as in the order adopted for the theoretical lectures.

Each chapter starts with a *Review Questions* section that includes short questions whose answers can be directly found in the lecture slides and presentations (you *did* attend the lectures, didn't you?).

There is a data collection in a section at the end, where some of the physical data required to solve the different problems can be found. Some problems, clearly identified as such, require a literature research to be performed in order to gather the required information. Unless this is the case, all of the data is made available in the problem collection book, or in the slide collection of the course made available to the student enrolled in the course.

In some instances, we might ask you to solve, write and hand your solution for selected problems.

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Chapter 1

Isotopes

Review Questions

1. What do all oxygen isotopes have in common?

2. Why are isotopes abundances expressed in terms of isotope ratios, instead of elemental fractions?

3. What is the δ notation and why is it used? What is the theoretically possible range of δ?

4. What is isotope fractionation and why does it arise?

Problems and Exercises

Exercise 1.1 READY

What is the $\delta^{13}C$ with respect to VPDB of a sample whose carbon is

1. pure ^{12}C?

2. half ^{12}C, half ^{13}C?

3. 99 % ^{12}C, 1 % ^{13}C?

4. twice the ratio of the standard.

Please use the classical $R_{std} = 0.0112372$ determined for PDB by Craig (1957), and adopted for VPDB when this latter replaced PDB. [1]

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[1] This ratio has been repeatedly re-evaluated to a significantly smaller value over the past years. One of the most recent figures is 0.011125 ± 0.000043 (Fleisher et al., 2021).

Answer 1. $-1000\,‰$ **2.** $88000\,‰$ **3.** $-101.1\,‰$ **4.** $1000\,‰$

Exercise 1.2 *READY*

What are the D/H (^{2}H/^{1}H) isotope ratios of a mixture of

1. 1 g pure D_2O and 1 g pure ^1H_2O,

2. 1 ml pure D_2O and 1 ml pure ^1H_2O,

at 25 °C and 1013.25 hPa?
    Suppose that we use the first mixture as a working standard. What would be the $\delta(D/H)_{mix\,2/mix\,1}$ of the second mixture?

Answer 1. 0.89952805(33)   **2.** 0.996428(68)   **3.** 107.723(76)$\,‰$

Exercise 1.3 *READY*

Please range the following materials according to their $\delta^{13}C$ isotopic signature, from the most depleted to the most enriched:

1. atmospheric CO_2

2. terrestrial C_4 plant material

3. terrestrial C_3 plant material

4. surface ocean DIC;

5. deep-sea DIC

Answer $(3) < (2) < (1) < (5) < (4)$

Exercise 1.4 *READY*

Ice core data provide the following carbon isotopic compositions of atmospheric CO_2 for three periods over the past 25,000 years:

1. preindustrial: $\delta^{13}C = -6.5\,‰$

2. 12–16 kyr BP: $\delta^{13}C = -6.65\,‰$

3. Last Glacial Maximum (LGM): $\delta^{13}C = -6.6\,‰$

What are the corresponding isotopic ratios R, assuming that these $\delta^{13}C$ values are expressed relative to PDB scale ($^{13}R_{PDB} = 0.0112372$)?

(Data sources: Craig (1957) for $^{13}R_{PDB}$; Francey et al. (1999) for pre-industrial $\delta^{13}C$; Schmitt et al. (2012) for pre-industrial $\delta^{13}C$; Lourantou et al. (2010) for LGM $\delta^{13}C$).

Answer **1.** 0.0111642 **2.** 0.0111625 **3.** 0.0111630

Exercise 1.5 (✳✳) <mark>*ALMOST READY*</mark>

When we established the differential equations that control the evolution of the ^{13}C signature of a reservoir, we assumed that $DI^{12}C \simeq DIC$ and that $^{12}F \simeq F$ to simplify the conversion of total carbon concentrations and total carbon fluxes to the corresponding ^{13}C concentrations and ^{13}C fluxes, knowing the respective ^{13}R.

1. Write the exact relationship between $n(^{13}C)$ and $C = n(^{12}C) + n(^{13}C)$.

2. Use this relationship to derive an estimate of the relative error between the exact and the approximate concentration or flux *value*. It is assumed that the standard isotope ratio is representative of the isotope ratio of the material.

3. Repeat the same exercise for oxygen with its three stable isotopes ^{16}O, ^{17}O and ^{18}O.

Exercise 1.6 <mark>*READY*</mark>

Define $\delta^{11}B$, for the ^{10}B–^{11}B pair (^{10}B being used as the reference).

Literature search

1. Look up the value of the $^{11}B/^{10}B$ ratio of the standard used for marine boron isotopic measurements. Please provide a trusted source (link to official certification data sheet or an original reference to the peer-reviewed literature).

2. There is a fundamental difference between the $^{11}B/^{10}B$ ratio and other used commonly isotopic ratios such as D/H, $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$. What is it and what implications does this have for modelling equations?

3. What is $\delta^{11}B$ used for as a proxy? What is the rationale behind this usage?

Answer $\delta^{11}\text{B} = \left(\left(\frac{^{11}\text{B}}{^{10}\text{B}}\right)_{\text{sample}} - \left(\frac{^{11}\text{B}}{^{10}\text{B}}\right)_{\text{std}}\right) / \left(\frac{^{11}\text{B}}{^{10}\text{B}}\right)_{\text{std}}$

1. NIST SRM 951; **2.** Light isotope less abundant than the heavy one; **3.** pH proxy.

Exercise 1.7 `READY`

By definition, the fractionation constant ε for a reaction

$$\text{A}^{\text{n}}\text{X} + \text{B}^{\text{m}}\text{X} \longrightarrow \text{A}^{\text{m}}\text{X} + \text{B}^{\text{n}}\text{X}$$

by which AX and BX exchange two isotopes $^{\text{n}}\text{X}$ and $^{\text{m}}\text{X}$ of X, is related to the fractionation factor α by

$$\varepsilon = \alpha - 1,$$

for $\alpha = \frac{R_B}{R_A}$. If δ_A and δ_B denote the X-isotopic signature of AX and BX (where X could, e. g., be any of C, O, ...), it is generally assumed that $\varepsilon \simeq \delta_B - \delta_A$.

1. Under which conditions is this approximation valid?

2. What would be the exact value of δ_B, as a function of δ_A and ε?

Answer **1.** $|\delta_A| \ll 1$; **2.** $\delta_B = \delta_A + \varepsilon(1 + \delta_A)$.

Exercise 1.8 `READY`

Calculate the $\delta^{13}\text{C}$ of atmospheric CO_2 in $\sim$230 years from now (i. e., 500 years after the start of industrialisation in 1750), resulting from the emission of 4000 GtC of anthropogenic carbon, of which 25 % get absorbed by the terrestrial biosphere and 60 % taken up by the ocean and the rest staying in the atmosphere. It is assumed that deep-sea carbonate dissolution has not yet contributed significantly and will only start to become significant afterwards.

The characteristics of the three system components (compartments) at pre-industrial are as follows:

- atmosphere: $C_{a0} = 600$ GtC with $\delta_{a0} = -6.4‰$;

- ocean: $C_{o0} = 38{,}000$ GtC with $\delta_{o0} = 0.0‰$;

- terrestrial biosphere: $C_{b0} = 2000$ GtC.

Anthropogenic CO_2 is assumed to have a $\delta^{13}\text{C}$ of $\delta_f = -28‰$.

The difference between the global average oceanic and the atmospheric $\delta^{13}\text{C}$ is supposed to remain constant; fractionation by the terrestrial biosphere is supposed to remain constant at $-18‰$ on global average.

Answer $\delta_a = -8.28\%o$.

To learn more...

- Sharp (2017): "Principles of Stable Isotope Geochemistry," (2nd edition).

Chapter 2

Box-Models

Review Questions

1. Please state the three different time scales that characterise a reservoir. How are they related to each other in a steady state regime?

2. Why does a closed system of reservoirs have a zero eigenvalue? Please provide a short mathematical proof.

Problems and Exercises

Exercise 2.1 READY

Rivers transport on average each year about $39\,000$ and $44\,700\,\text{km}^3$ of water to the oceans (Munhoven, 2002). Convert this flux of water to Sverdrup ($1\,\text{Sv} = 10^6\,\text{m}^3\,\text{s}^{-1}$). How does this flux compare with a North-Atlantic Deep-Water (NADW) formation rate of $14\,\text{Sv}$ (Schmitz, 1995)?

Answer $1.24 - 1.42\,\text{Sv}$, i. e., one order of magnitude less than NADW formation.

Exercise 2.2 (–/∗∗) READY

Figure 2.1 shows the scheme of a classical box model of the phosphorus cycle (Lerman et al., 1975). The phosphorus cycle model shown in class was derived from this one.

1. Is this cycle balanced? If not, please try to balance it, by making the least possible relative change(s).
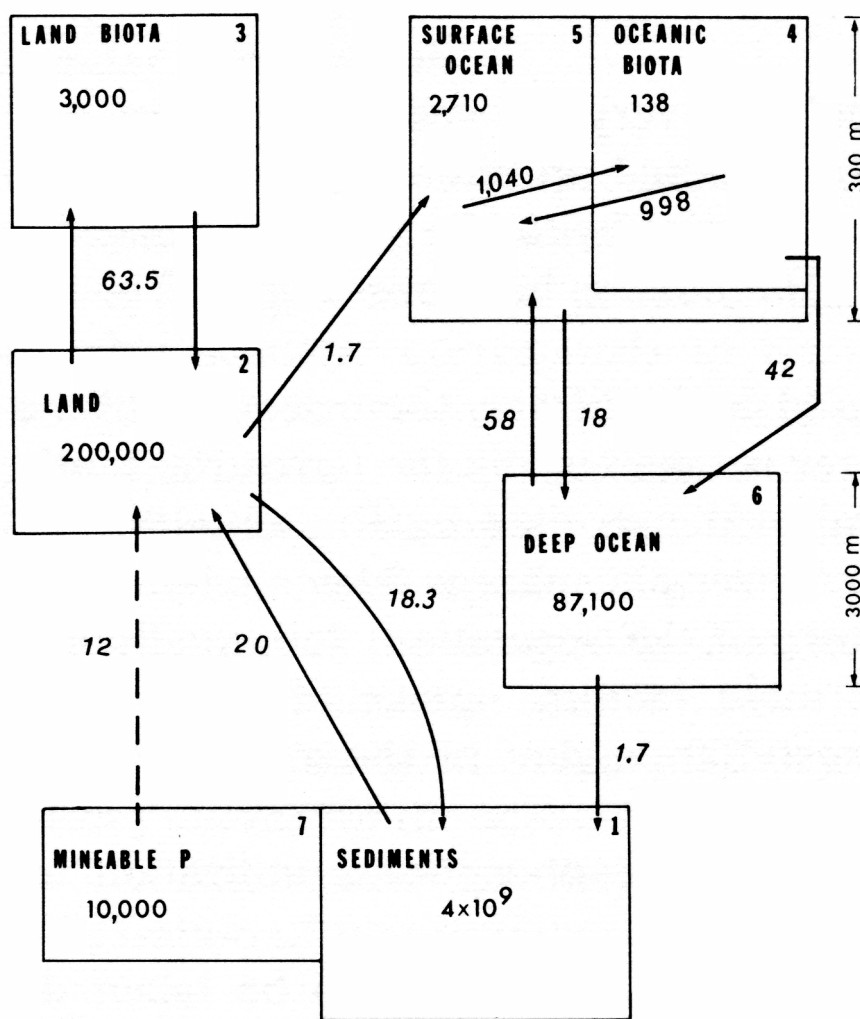
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Figure 2.1: Box model of the phosphorus cycle (Lerman et al., 1975). Upright numbers in the middle of the boxes give the reservoir contents in Mt P, numbers in italics close to the arrows give the exchange fluxes between reservoirs in Mt P yr^{-1}.

2. Calculate the residence time of P in each reservoir (disregarding the perturbation from "Minable P").

3. What is the residence time of P in the combined "Land"–"Land biota" reservoirs?

4. What is the residence time of P in the combined "Surface ocean"–"Oceanic biota" reservoirs? of the combined oceanic reservoirs?

5. (∗∗) Write a Python script to determine the eigenvalues and eigenvectors of the system:

   - Construct the exchange coefficient matrix K(you will first have to determine the exchange coefficients from the scheme).

   - Calculate the eigenvalues and eigenvectors of K: the eig function from numpy.linalg does this in one call.[1]

   - Calculate the response times.

   - Additionally, you may try to recalculate the coefficients of the exponentials for the perturbation presented in the lecture: first calculate the coefficients c required for the linear combination of basis functions to represent the perturbed initial state (use solve from numpy.linalg to do this) and then apply these with the adequate components of the eigenvectors to get the coefficient of the linear combination of exponentials that describe the content of Reservoir 2.

Answer   **1.** Increase F_{64} from 58 to 58.3 Mt P yr^{-1} **2.** $\tau_{0,1} = 200 \times 10^6$ Myr, $\tau_{0,2} = 2395$ yr; $\tau_{0,3} = 47$ yr; $\tau_{0,4} = 0.125$ yr; $\tau_{0,5} = 2.56$ yr; $\tau_{0,6} = 1450$ yr **3.** $\tau_{0,2+3} = 10150$ yr   **4.** $\tau_{0,4+5} = 47.3$ yr; $\tau_{0,4+5+6} = 52900$ yr   **5.** $\tau_1 = 52863$ yr; $\tau_2 = 10150$ yr; $\tau_3 = 46.5$ yr; $\tau_4 = 45.9$ yr; $\tau_5 = 0.126$ yr $= 46.2$d.

Exercise 2.3 (–/∗∗) <mark>*READY*</mark>

Figure 2.2 shows the scheme of an eight-box model of the nitrogen cycle (Chameides and Perdue, 1997).

1. Calculate the residence time of N in each reservoir.

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[1]Feel free to check out `https://pythonnumericalmethods.berkeley.edu/notebooks/chapter15.04-Eigenvalues-and-Eigenvectors-in-Python.html` or any other similar introduction to see how (easily) this can be done.
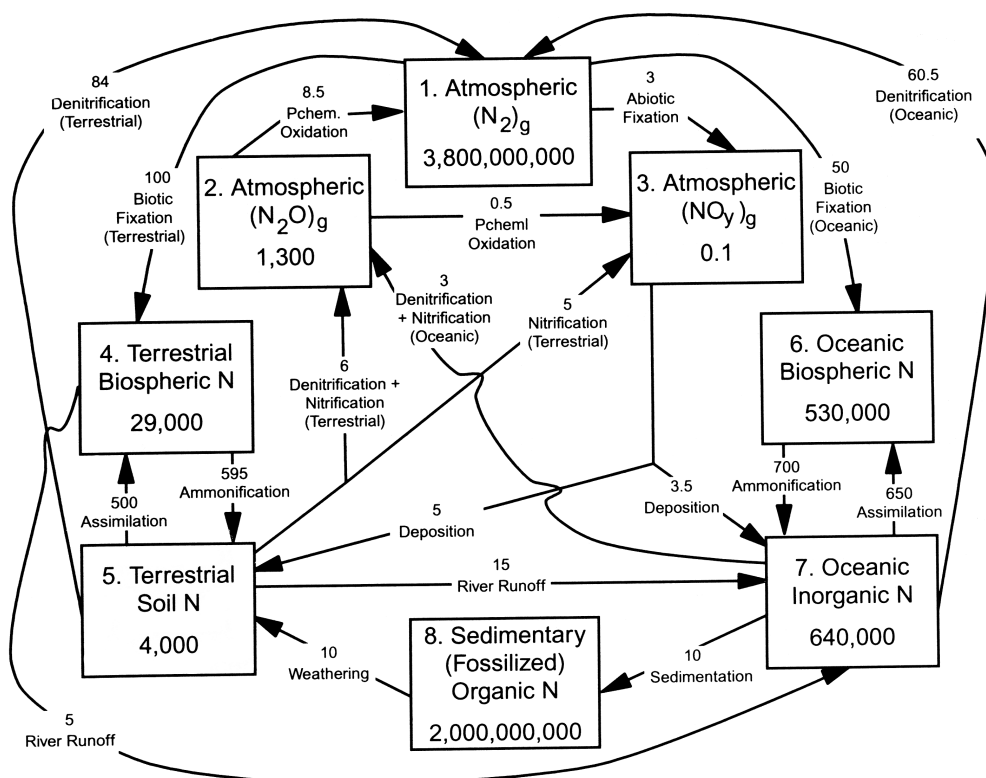
Figure 2.2: Eight-box model of the nitrogen cycle (Chameides and Perdue, 1997). Units are Tg N for the reservoir contents and Tg N yr^{-1} for the fluxes.
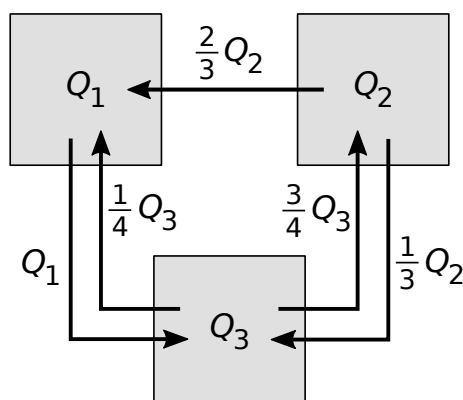
Figure 2.3: Three-box model.

2. What is the residence time of N in the combined "Terrestrial Biospheric N"–"Terrestrial Soil N" reservoirs? of the combined "Terrestrial Biospheric N"–"Terrestrial Soil N"–"Atmospheric $(N_2)_g$" reservoirs?

3. What is the residence time of P in the combined "Oceanic Biospheric N"–"Oceanic Inorganic N" reservoirs?

4. (**) Write a Python script (or adapt that developed for exercise 2.2) to determine the eigenvalues and eigenvectors of the system as in Exercise 2.2 in order to derive the response times. Additionally, calculate the coefficients of the exponentials for a perturbation of the content of Reservoir 5, resulting from the addition of 100 Tg N.

Answer **1.** $\tau_{0,1} = 24.8 \times 10^6$ Myr, $\tau_{0,2} = 144$ yr; $\tau_{0,3} = 0.00118$ yr $= 4.3$ d; $\tau_{0,4} = 48.3$ yr; $\tau_{0,5} = 6.56$ yr; $\tau_{0,6} = 757$ yr; $\tau_{0,7} = 885$ yr; $\tau_{0,8} = 200 \times 10^6$ Myr **2.** $\tau_{0,4+5} = 287$ yr; $\tau_{0,1+4+5} = 135 \times 10^6$ Myr **3.** $\tau_{0,6+7} = 15918$ yr **4.** $\tau_1 = 134.57 \times 10^6$ yr; $\tau_2 = 15756$ yr; $\tau_3 = 419$ yr; $\tau_4 = 295$ yr; $\tau_5 = 144$ yr; $\tau_6 = 5.9$ yr; $\tau_7 = 0.0118$ yr $= 4.3$ d

Exercise 2.4 (**) <mark>*READY*</mark>

Figure 2.3 shows a scheme of a generic three-box model.

1. What are the turnover times of the three reservoirs?

2. Write the exchange coefficient matrix of the depicted model.

3. Calculate the eigenvalues of the matrix and the corresponding eigenvectors, either by hand (recommended) or with a Python script. What is particular about this model?

4. Write the general solution of the reservoir contents.

5. Application: apply this general solution with $Q(0) = (1, 2, 3)$. What are the steady-state contents of the reservoirs?

Answer **1.** $\tau_{0,1} = \tau_{0,2} = \tau_{0,3} = 1$ **3.** $\lambda(\lambda^2 + 3\lambda + \frac{5}{2}) = 0$, with roots $\lambda_0 = 0$, $\lambda_1 = \frac{1}{2}(-3+i)$, $\lambda_2 = \frac{1}{2}(-3-i)$. **5.** $\vec{Q}_\infty = [1.8, 1.8, 2.4]$

Exercise 2.5 (–/∗∗) `READY`

Consider the general exchange coefficient matrix of a three-box model:

$$A = \begin{bmatrix} -k_{11} & k_{21} & k_{31} \\ k_{12} & -k_{22} & k_{32} \\ k_{13} & k_{23} & -k_{33} \end{bmatrix}$$

with $k_{ij} \geq 0$ for $i \neq j$, and $k_{jj} = \sum_{i \neq j} k_{ij}$, $k_{jj} > 0$, for $j = 1, 2, 3$.

1. Show that the eigenvalue equation for this matrix can be written as

$$\lambda(\lambda^2 + B\lambda + D - E) = 0$$

where

- $B = k_{11} + k_{22} + k_{33} > 0$
- $D = k_{11}k_{22} + k_{22}k_{33} + k_{33}k_{11} > 0$
- $E = k_{12}k_{21} + k_{23}k_{32} + k_{31}k_{13} \geq 0$

2. What are the conditions that B, D and E have to fulfil so that the two non-zero eigenvalues are complex (with a non-zero imaginary part)?

3. What can be said about the real part of such complex eigenvalues?

4. The theoretical developments seen in the lecture apply without modifications for complex eigenvalues, and will thus involve exponentials with complex arguments. How does the exponential basis solution for a complex eigenvalue write?
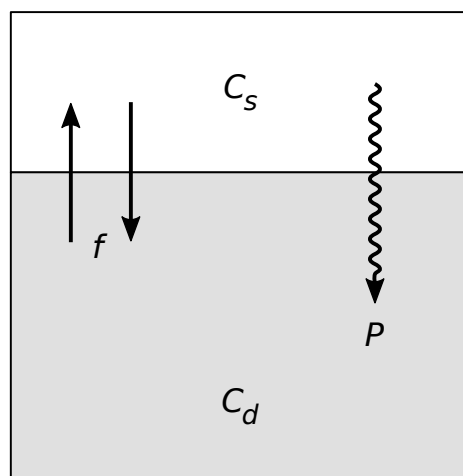
Figure 2.4: Two-box ocean model. f: physical exchange between surface and deep boxes; C_s and C_d: average surface and deep concentrations; P: particulate rain of PO_4 (Broecker and Peng, 1982; Sarmiento, 1986, 1992).

5. Such a complex exponential involves thus two response times. Do we now have to expect four different response times in the solution of the model above? What are the response times τ_e of the exponential and τ_t of the trigonometric part for the particular problem defined by the matrix A above?

6. (∗∗) Show that $\tau_t > \tau_e$.

Answer **2.** $\Delta = B^2 - 4(D - E) < 0$, i. e., $4(D - E) > B^2$. **3.** $\mathcal{R}(\lambda_1) = \mathcal{R}(\lambda_2) = -\frac{B}{2} < 0$. **4.** For $\lambda = a + ib$: $\exp(\lambda t) = \exp(at) \times (\cos bt + i\sin(bt))$. **5.** No. $\tau_e = 2/B$, $\tau_t = 2/\sqrt{-\Delta}$. **6.** This results from $4(D - E) < 4D$ and $B^2 > 2D$.

Exercise 2.6 <mark>READY</mark>

This "Tale of two (box-)models" was inspired by Sarmiento et al. (1988) and Sarmiento (1992) and is about the importance of the saying that "Everything should be as simple as it can be but not simpler!"[2]

1. Two-box model

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[2] Attributed to Albert Einstein by Roger Sessions in a *New York Times* article on 8th January 1950 (see https://quoteinvestigator.com/2011/05/13/einstein-simple, last accessed on 30th August 2022).

Figure 2.4 shows a two-box model representation of the ocean. The two boxes exchange material via ocean circulation and via the export of organic matter, here expressed in terms of the corresponding PO_4 flux P. All the organic matter exported to the deep sea remineralizes there.

1. Consider that C_s and C_d represent PO_4 concentrations. Write the steady-state balance equation for PO_4 in the deep reservoir and express P/f as a function of the surface and deep concentrations of PO_4

2. Next, consider that C_s and C_d represent O_2 concentrations. O_2 gets consumed in the deep sea during organic matter remineralisation at a rate $r_{O_2/P}P$, where $r_{O_2/P}$ is the ratio of O_2 consumed to PO_4 released during remineralization.

   Write the steady-state balance equation for O_2 in the deep reservoir and use the expression for P/f derived in the previous step to express the deep-sea O_2 concentration, $[O_2]_d$ as a function of the other concentrations.

   Evaluate $[O_2]_d$ using the following data, derived from observations:

   - $[PO_4]_s = 0.0\ \mu\text{mol kg}^{-1}$
   - $[PO_4]_d = 2.2\ \mu\text{mol kg}^{-1}$
   - $[O_2]_s = 240\ \mu\text{mol kg}^{-1}$
   - $r_{O_2/P} = 172\ \text{mol}\,O_2/\text{mol}\,P$ (Takahashi et al., 1985)

   How realistic is this result? Can it be rescued by using the classical Redfield $r_{O_2/P}$ of 138 mol O_2/mol P? What might have gone wrong?

2. Going for three

Figure 2.5 shows a revised version of the failing two-box model ocean where the surface has been subdivided into a low-latitude and a high-latitude reservoir.

1. Consider again the steady-state balance equation for PO_4 in the deep reservoir and adapt the procedure used above to derive and appropriate production/transport ratio.

2. Next, write again the steady-state balance equation for O_2 in the deep reservoir and use the information derived in the previous step to express the deep-sea O_2 concentration, $[O_2]_d$ as a function of the other concentrations.

   Re-evaluate $[O_2]_d$ using the same data as above, and the following extra ones:
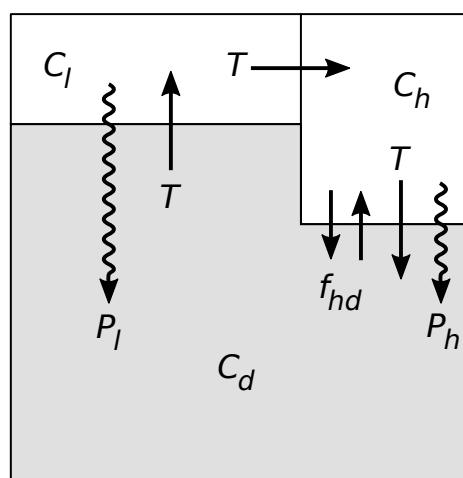
Figure 2.5: Three-box ocean model, with separate high-latitude (index 'h') and low-latitude (index 'l') surface boxes. f_{hd}: exchange flux between high-latitude surface and the deep box. T transport by thermohaline overturning. P_h and P_l: particulate rain of PO_4 out of the high- and the low-latitude boxes (Sarmiento and Toggweiler, 1984; Sarmiento, 1986, 1992).

- $[PO_4]_h = 1.2 \ \mu\text{mol kg}^{-1}$
- $[O_2]_h = 340 \ \mu\text{mol kg}^{-1}$

How realistic is the result now, knowing that the observed global average deep-sea O_2 concentration is about $166 \ \mu\text{mol kg}^{-1}$? What are the critical differences between this set-up and the previous one?

Answer **1.** Unrealistic. **2.** More realistic.

Exercise 2.7 (∗) <mark>READY</mark>

Please notice that this problem requires some knowledge of the chapter on *Chemical Equilibria and pH Calculations*.

Why can the linear box-model approach (i. e., using constant exchange coefficients) not be used for the CO_2 exchange between the atmosphere and the (surface) ocean?

Answer The CO_2 flux from the ocean to the atmosphere is not linear in C_T.

Exercise 2.8 (∗/∗∗∗) <mark>READY</mark>

Phase lag and amplitude shift for a reservoir with a periodic forcing.

1. Write the ordinary differential equation, ODE, describing the evolution of the content M of a reservoir submitted to

   - a periodical source $F_{in} = \bar{F} + f \sin(\omega t)$
   - a linear sink $F_{out} = kM$

   where ω [rad s^{-1}] and k [s^{-1}] are constants.

2. Solve this equation:

   (a) Solve the homogeneous equation (i. e., the previous equation, where only the time derivative and the term proportional in M are considered).

   (b) Use the method of *variation of parameters* (also known as *variation of constants*, i. e. assume that the solution of the general ODE can be written in the form of the solution to the homogeneous equation, and further assume that the integration constant (let us denote it a) of the homogeneous solution, is a function of t: $a \equiv a(t)$. Introduce this formal solution into the complete ODE for $M(t)$ and derive an ODE for $a(t)$.

   (c) Solve the resulting ODE for $a(t)$.

   (d) The solution of this equation contains a term in $k \sin(\omega t) - \omega \cos(\omega t)$. Define a φ to transform this expression to the form $\sin(\omega t - \varphi)$, making appear φ as a phase lag.[3] What are the lowest and highest φ to expect? For what values of the parameters ω and k, or combination thereof?

3. Determine the time lag constant, which is related to the phase lag φ.
   (∗∗∗) What is the minimum time lag? What is the maximum time lag? For what extreme (limit) values of the parameters ω and k would these be reached?

4. Application (Wollast, 1986): impact of seasonal and diurnal fluctuations on the mass of silica in the siliceous skeletons (opal) in the surface water. For this application, we adopt an annual mean opal production of 400 Tmol Si yr^{-1} and a removal rate constant $k = 1.67$ yr^{-1}.

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[3]Hint: use the fact that for any a and b such that $a^2 + b^2 = 1$, there exists φ such that $\cos \varphi = a$ and $\sin \varphi = b$; then use the trigonometric formula for $\sin(x - y)$.

- Translate the average annual mean production to appropriate $\bar{F}$ and f values to apply the periodic F_{in} forcing formulation, assuming a minimum productivity of $0\ \text{Tmol Si yr}^{-1}$. Calculate the mean opal content of the surface waters, the amplitude of its variation during the year, the phase lag and the time lag.

- How do these results change if it is assumed that the minimum production is $25\,\%$ of the maximum?

Answer **1.** $\frac{dM}{dt} = \bar{F} + f\sin(\omega t) - kM$; **2.** $M(t) = \frac{\bar{F}}{k} + \frac{f}{\sqrt{k^2+\omega^2}}\sin(\omega t - \varphi) + \left(M_0 - \frac{\bar{F}}{k} + \frac{f\omega}{k^2+\omega^2}\right)\exp(-kt)$; **3.** The minimum time lag is zero and the maximum time lag is $\tau/4 = \pi/(2\omega)$ for ω fixed and $1/k$ for k fixed.

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Chapter 3

Chemical Equilibria
and pH Calculations

Review Questions

1. Define pH.

2. Why are there different pH scales used in marine geochemistry? How do they differ?

3. How many measurables are there to characterize the carbonate system in seawater? Please name them and indicate, if possible, a method of measuring. How many of them are required to completely determine the speciation of the carbonate system?

4. What are the relative abundances of dissolved CO_2, HCO_3^- and CO_3^{2-} at a typical ocean pH?

5. What does DIC stand for and what does it represent?

6. What is alkalinity (in general terms)?

7. Which are the main alkalinity contributors in seawater by order of importance?

8. What is a conservative variable and why is it useful?

9. Why are pH and $p\mathrm{CO}_2$ not conservative variables?

Problems and Exercises

Exercise 3.1 READY

Calculate the fractional change of $[H^+]$ (i. e., $\frac{\Delta[H^+]}{[H^+]}$) for

1. a pH increase of 0.1;

2. a pH decrease of 0.1;

3. a pH decrease of 0.4.

Answer   **1.** $-20.57\,\%$ **2.** $25.89\,\%$ **3.** $151.19\,\%$

Exercise 3.2 READY

Atmospheric CO_2 concentrations are sometimes given in ppm (i. e., as a mixing ratio, denoted xCO_2), and sometimes in μatm (i. e., as a partial pressure, pCO_2). Knowing that the mixing ratio is always measured in dry air, whereas pCO_2 is given for moist air, how are the two related to each other?

Answer $pCO_2 = xCO_2 \times (p_{atm} - pH_2O)$

Exercise 3.3 READY

How is alkalinity affected by

1. the precipitation of 1 mmol of gypsum $(CaSO_4)$

2. the dissolution of 1 mmol of ammonium dihydrogen phosphate (ADP – $(NH_4)(H_2PO_4)$), a fertilizer ingredient also known as biphosphammite or mono-ammonium phosphate

3. the dissolution of 1 mmol of disodium phosphate (Na_2HPO_4)

4. the dissolution of 1 mmol of boric acid $(B(OH)_3)$

in 1 kg of seawater? Use both A_T and A_{EC} to justify your answers.

Answer   **1.** $0\,\text{meq kg}^{-1}$ **2.** $0\,\text{meq kg}^{-1}$ **3.** $1\,\text{meq kg}^{-1}$ **4.** $0\,\text{meq kg}^{-1}$

Exercise 3.4 (∗/∗∗) READY

In the following, it is assumed that A_T, C_T and B_T are given (fixed) and that K_1, K_2, K_B and K_W are known constants. H is used as a shorthand for $[H^+]$ to simplify the notation.

1. Prove that
$$A_C(H) \equiv \frac{K_1 H + 2K_1 K_2}{H^2 + K_1 H + K_1 K_2} C_T$$
   is a strictly decreasing function of H ($H > 0$). What are the lower and upper bounds of A_C?

2. Prove that
$$A_B(H) \equiv \frac{K_B}{H + K_B} B_T$$
   is a strictly decreasing function of H ($H > 0$). What are the lower and upper bounds of A_B?

3. Prove that
$$A_W(H) \equiv \frac{K_W}{H} - H$$
   is a strictly decreasing function of H ($H > 0$). What are the lower and upper bounds of A_W?

4. (∗∗) In the light of the previous findings, what *a priori* statements can be made about the equation $E(H) = 0$ and its root(s), where
$$E(H) \equiv \frac{K_1 H + 2K_1 K_2}{H^2 + K_1 H + K_1 K_2} C_T + \frac{K_B}{H + K_B} B_T + \frac{K_W}{H} - H - A_T,$$
   for C_T, B_T and A_T fixed?

5. Consider the auxiliary equation
$$\frac{K_W}{H} - H + A_{Cinf} + A_{Binf} - A_T = 0$$
   where A_{Cinf} and A_{Binf} denote the lower bounds of $A_C(H)$ and $A_B(H)$, resp. Show that it has exactly one positive root, which we denote by H_{inf}. What can be said about $E(H_{inf})$?

6. Consider the analogue auxiliary equation using the upper bounds A_{Csup} and A_{Bsup}. Show that this equation also has exactly one positive root, which we denote by H_{sup}. What can be said about $E(H_{sup})$?

7. Which quantitative conclusions can be drawn regarding the root(s) of the equation $E(H) = 0$? Can you outline a robust and efficient numerical method to solve that equation?

Answer **1.** $dA_C/dH < 0$ and $0 < A_C < 2C_T$. **2.** $dA_B/dH < 0$ and $0 < A_B < B_T$. **3.** $dA_W/dH < 0$ and $-\infty < A_W < +\infty$ **4.** $dE/dH < 0$ and $E(H)$ decreases from $+\infty$ in $H = 0^+$ to $-\infty$ for $H \to +\infty$. $E(H) = 0$ has exactly one positive root. **5.** $E(H_{\text{inf}}) > 0$ **6.** $E(H_{\text{sup}}) < 0$ **7.** The root of $E(H) = 0$ is bracketed by H_{inf} and H_{sup}.

Exercise 3.5 READY

The speciation relationships of the carbonate system can be strongly simplified by introducing $h = [H^+]/K_2$ and $k = K_2/K_1$.

Rewrite the speciation relationships for **1.** $[CO_2]/C_T$, **2.** $[HCO_3^-]/C_T$, and **3.** $[CO_3^{2-}]/C_T$ in terms of h and k and calculate estimates, using the following typical values:

- surface cold: $h = 15$ and $k = 5.4 \times 10^{-4} = 1/1852$;

- surface temperate: $h = 7$ and $k = 7.8 \times 10^{-4} = 1/1282$;

- deep cold: $h = 23$ and $k = 4.8 \times 10^{-4} = 1/2083$.

- average surface: $h = 11$ and $k = 6.6 \times 10^{-4} = 1/1515$;

In addition: **4.** express the ratio A_C/C_T in terms of h and k.

Answer **1.** $[CO_2]/C_T = kh^2/(kh^2 + h + 1)$; **2.** $[HCO_3^-]/C_T = h/(kh^2 + h + 1)$; **3.** $[CO_3^{2-}]/C_T = 1/(kh^2 + h + 1)$; **4.** $A_C/C_T = (h+2)/(kh^2 + h + 1)$.

Exercise 3.6 READY

It has been shown in class that A_C can be expressed as a function of C_T and $H = [H^+]$ as

$$A_C(C_T, H) = \frac{K_1 H + 2K_1 K_2}{H^2 + K_1 H + K_1 K_2} C_T.$$

Derive the expressions for A_C as a function of

1. $a = [CO_2]$ and H;

2. $b = [HCO_3^-]$ and H;

3. $c = [CO_3^{2-}]$ and H.

Hint: use the expressions for the fractions a/C_T, b/C_T and c/C_T, respectively.

Answer **1.** $A_C(a,H) = \frac{K_1 H + 2K_1 K_2}{H^2} a$; **2.** $A_C(b,H) = (1 + \frac{2K_2}{H}) b$;
3. $A_C(c,H) = (\frac{H}{K_2} + 2) c$.

Exercise 3.7 READY

Express $H = [H^+]$ as a function of C_T and either one of

1. $a = [CO_2]$,

2. $b = [HCO_3^-]$,

3. $c = [CO_3^{2-}]$.

Answer **1.** $H = 2K_2/(\sqrt{1 + 4\frac{K_2}{K_1}(\frac{C_T}{a} - 1)} - 1)$; **2.** $H_\pm = \frac{1}{2}(K_1(\frac{C_T}{b} - 1) \pm \sqrt{\Delta})$
for $\Delta \equiv \left(\frac{C_T}{b} - 1\right)^2 K_1^2 - 4K_1 K_2 \geq 0$; **3.** $H = \frac{1}{2}(-K_1 + \sqrt{K_1^2 + 4K_1 K_2(\frac{C_T}{c} - 1)})$.

Exercise 3.8 READY

It has been shown in class that A_T is not changed when CO_2 is dissolved in sea-water. How does carbonate alkalinity, A_C, change when CO_2 is dissolved?

Answer A_C increases when CO_2 is dissolved.

Exercise 3.9 (–/∗∗∗) READY

Please characterize

1. the lines of equal pH;

2. (∗∗∗) the lines of equal pCO_2 (or equivalently, of equal $[CO_2]$);

3. (∗∗∗) the lines of equal $[CO_3^{2-}]$.

on a C_T–A_T graph. Give equations, and, if possible, slope, threshold values etc.

Answer **1.** Lines of equal pH are straight lines with a positive slope, which is greater than 1 if pH $> (pK_1 + pK_2)/2$.

Exercise 3.10 : Worked Out Problem (∗∗)

Revelle buffer factor: how to calculate it

$$\beta = \frac{\partial \ln p\mathrm{CO}_2}{\partial \ln C_\mathrm{T}}\bigg|_{A_\mathrm{T}} = \left(\frac{\partial p\mathrm{CO}_2}{p\mathrm{CO}_2} \bigg/ \frac{\partial C_\mathrm{T}}{C_\mathrm{T}} \right)_{A_\mathrm{T}}$$

Application/programming practice: use pySolveSAPHE to calculate and plot β as a function of C_T (surface seawater ranges, different temperatures) for given A_T. Same for a range of $p\mathrm{CO}_2$.

Solution

Following the approach of Zeebe and Wolf-Gladrow (2001) using differentials, but swapping here the roles of C_T and s (using s as the function, and C_T as the independent variable, since we are interested in deriving $\frac{ds}{dC_\mathrm{T}}$)

With independent variables $C = C_\mathrm{T}$ and $H = [\mathrm{H}^+]$ we may express $[\mathrm{CO}_2] = a(C,H)$ and $A_\mathrm{T} = A_\mathrm{T}(C,H)$. Differentiation of these two functions leads to

$$da = \left(\frac{\partial a}{\partial C} \right)_H dC + \left(\frac{\partial a}{\partial H} \right)_C dH$$

$$dA_\mathrm{T} = \left(\frac{\partial A_\mathrm{T}}{\partial C} \right)_H dC + \left(\frac{\partial A_\mathrm{T}}{\partial H} \right)_C dH$$

The exchange of CO_2 does not alter A_T, and therefore $dA_\mathrm{T} = 0$, which leads to

$$\frac{dH}{dC} = - \left(\frac{\partial A_\mathrm{T}}{\partial C} \right)_H \bigg/ \left(\frac{\partial A_\mathrm{T}}{\partial H} \right)_C$$

(Alternatively and equivalently: apply the implicit function theorem on $A_\mathrm{T}(C,H) = A_\mathrm{T0}$.) Since

$$\frac{da}{dC} = \left(\frac{\partial a}{\partial C} \right)_H + \left(\frac{\partial a}{\partial H} \right)_C \frac{dH}{dC}$$

we get

$$\frac{da}{dC} = \left(\frac{\partial a}{\partial C} \right)_H - \left(\frac{\partial a}{\partial H} \right)_C \left(\frac{\partial A_\mathrm{T}}{\partial C} \right)_H \bigg/ \left(\frac{\partial A_\mathrm{T}}{\partial H} \right)_C$$

The definition of $a(C,H)$ can be directly derived from the speciation relationship for $[\mathrm{CO}_2]/C_\mathrm{T}$:

$$a(C,H) = \frac{H^2}{H^2 + K_1 H + K_1 K_2} C.$$

Hence

$$\left(\frac{\partial a}{\partial C}\right)_H = \frac{H^2}{H^2 + K_1 H + K_1 K_2} = \frac{a}{C}$$

and

$$\left(\frac{\partial a}{\partial H}\right)_C = \frac{K_1 H^2 + 2 K_1 K_2 H}{(H^2 + K_1 H + K_1 K_2)^2} C = \frac{A_C}{H}\frac{a}{C}.$$

The expression for $A_T(C,H)$ directly derives from the alkalinity-pH equation. We thus have

$$\left(\frac{\partial A_T}{\partial C}\right)_H = \frac{K_1 H + 2 K_1 K_2}{H^2 + K_1 H + K_1 K_2} = \frac{A_C}{C}.$$

and

$$\left(\frac{\partial A_T}{\partial H}\right)_C = \left(\frac{\partial A_C}{\partial H}\right)_C + \left(\frac{\partial A_B}{\partial H}\right)_{B_T} + \cdots - \frac{K_W}{H^2} - \frac{1}{s}.$$

All the terms on the right-hand side of the previous equation are negative; since the other three partial derivatives making up $\frac{da}{dC}$ are all strictly positive, we may already conclude that $\frac{da}{dC} > 0$.

Finally,

$$\beta = 1 - \frac{A_C}{H}\frac{A_C}{C_T} \bigg/ \left(\frac{\partial A_T}{\partial H}\right)_{C_T}$$

Application: for each $C_T - A_T$ pair in the range, first calculate the corresponding H, then evaluate A_C and $\left(\frac{\partial A_T}{\partial H}\right)_C$.

Exercise 3.11 `READY`

Buffer factor for CO_3 at constant A_T: Carbonate exchange buffer factor for $[CO_3^{2-}]$

$$\beta_{CO_3} = \frac{\partial \ln [CO_3^{2-}]}{\partial \ln C_T}\bigg|_{A_T} = \left(\frac{\partial [CO_3^{2-}]}{[CO_3^{2-}]} \bigg/ \frac{\partial C_T}{C_T}\right)_{A_T}$$

Knowing this buffer factor will allow to test the claim of Broecker and Peng (1982, p. 522) that

- $pCO_2 \times [CO_3^{2-}] = (pCO_2)_0 \times [CO_3^{2-}]_0$

- $\Delta C_T = -\Delta [CO_3^{2-}]$

during (fossil fuel) CO_2 uptake because, allegedly, CO_2 is mainly neutralised by CO_3^{2-} ions following $CO_2 + CO_3^{2-} + H_2O \rightarrow 2\,HCO_3^-$. To what extent are these two approximations valid?

Exercise 3.12 <mark>*READY*</mark>

Similarly to β and β_{CO_3}, define β_{HCO_3} and show that $\beta_{HCO_3} = \frac{1}{2}(\beta + \beta_{CO_3})$.

Answer   Eliminate $[H^+]$ between the two equilibrium relationships of the carbonate system and derive both sides of the combined relationship with respect to C_T.

Chapter 4

Seafloor Sediments – Interaction with the Ocean and Early Diagenesis

Review Questions

1. Why is it important to study sea-floor sediments?

2. Please name the three most important biogenic components of sea-floor sediment. What are their respective typically observed ranges of abundances?

3. What are the main controls on carbonate preservation in deep-sea sediment?

4. What do CSH and CCD stand for?

5. What is the sequence of oxidants for organic matter oxidation? Why are not all oxidants of equal importance?

Problems and Exercises

Exercise 4.1 <mark>*READY*</mark>

Calculate the fraction of %CaCO$_3$ in the surface sediment as a function of the deposition rates of CaCO$_3$ and clay, and the fraction of CaCO$_3$ deposited that gets dissolved. We adopt rain rates of $9\,\mathrm{g\,CaCO_3\,m^{-2}\,yr^{-1}}$ and $1\,\mathrm{g\,clay\,m^{-2}\,yr^{-1}}$.

Answer Please see Solution.

Table 4.1:

f_{CaCO_3} dissolved (%)	F_{CaCO_3} buried (g m^{-2} yr^{-1})	F_{Clay} buried (g m^{-2} yr^{-1})	%CaCO$_3$ sediment (%)
0	9.00	1.00	90
25			
50			
75			
89			
95			
98			
99			

Chapter 5

Atmosphere and Climate

Review Questions

1. How constant or variable is the solar constant?

2. What is the effective or emission temperature of a planet?

3. Please name the main types of climate models (acronyms and meaning, number of dimensions).

4. What is a parametrization? Why are parametrizations used in climate (and other) models?

Problems and Exercises

Exercise 5.1 *READY*

What are the roles of the following gases in the atmosphere: **1.** N_2; **2.** O_2; **3.** H_2O; **4.** Ar; **5.** CO_2; **6.** O_3.

Answer   All are transparent in the visible. N_2 and O_2 are also transparent in the IR and provide heat capacity. H_2O, CO_2, and O_3 absorb in the IR (contribute to the greenhouse effect). H_2O, CO_2, and O_2 exchange with the biosphere. O_2 and O_3 absorb in the UV. Ar has no role.

Exercise 5.2 *READY*

Calculate the emission (effective, equilibrium) temperatures of the terrestrial planets, using the physical data in Tab. 5.1. Comment on the differences between the

Table 5.1: Physical data for the terrestrial planets

	Mercury	Venus	Earth	Mars
albedo	0.068	0.77	0.306	0.250
semimajor axis (AU)	0.387099	0.723332	1.00000	1.52366
avg. surface temp. (K)	440	737	288	∼210
irradiance (W m^{-2})			1361	

Source: Planetary Fact Sheets for Mercury, Venus, Earth and Mars.

Table 5.2: Albedo and latitude bands.

Latitude band / Albedo	$0\,° - 10\,°$N	$40\,°$N $- 50\,°$N	$80\,°$N $- 90\,°$N
0.25			
0.40			
0.75			

calculated temperatures and the actually observed ones.

Answer Mercury: $S = 9083$ W m^{-2}, $T_{\text{eff}} = 440$ K; Venus: $S = 2601$ W m^{-2}, $T_{\text{eff}} = 227$ K; Earth: $S = 1361$ W m^{-2}, $T_{\text{eff}} = 254$ K; Mars: $S = 586.2$ W m^{-2}, $T_{\text{eff}} = 209.8$ K.

Exercise 5.3 (∗)

The global energy balance for the Earth writes

$$(1 - \alpha)S = 4\sigma T^4$$

where α is the average albedo, σ the Stefan-Boltzmann constant and T the effective (or emission) temperature.

Establish this same energy balance for a latitude band delimited by latitudes λ_{N} at its northern and λ_{S} at its southern boundary.

Calculate the emission temperatures for each albedo-latitude-band combination given in Table 5.2. The diagonal elements give the realistic combinations (characteristic albedo values as a function of latitude esimated from (Marzeion, 2021, Fig. 1).

Answer **1.** $4\pi \cdot \cos\left(\frac{1}{2}(\lambda_N + \lambda_S)\right) \cdot \sin\left(\frac{1}{2}(\lambda_N - \lambda_S)\right)$ **2.** $R^2\left((\lambda_N - \lambda_S) + \cos(\lambda_N + \lambda_S) \cdot \sin(\lambda_N - \lambda_S)\right)$

Exercise 5.4 `READY`

Calculate the amount of heat required to heat the atmosphere by 1 K. The mass of the atmosphere is 5.1480×10^{18} kg (Trenberth and Smith, 2005), the specific heat capacity of air (at constant pressure here, since the volume of the atmosphere is not fixed) is $C_p = 1000$ J kg^{-1} K^{-1}.

Determine the thickness of the uppermost ocean layer that could be warmed by 1 K by this same amount of heat energy. The density of seawater is 1025 kg m^{-3} and its specific heat capacity is $C_p = 3986$ J kg^{-1} K^{-1}. The surface area of the oceans is 361.9×10^6 km^2.

Answer Heat required: 5.1480 ZJ; surface layer thickness: 3.5 m.

Exercise 5.5

1. In the 34 years from 1977 to 2011, the ocean heat content has increased by about 260 ZJ. Calculate the corresponding global average (i. e., averaged over the whole globe) radiative forcing (in W m^{-2}).

2. During the 11 last years of that period (from 2000 to 2011), the increase was 125 ZJ. Calculate the corresponding radiative forcing.

Estimates derived from Rhein et al. (2013, Box 3.1, Fig. 1)

Answer **1.** 0.48 W m^{-2} **2.** 0.71 W m^{-2}.

Exercise 5.6 (∗) `READY`

According to the hydrostatic equilibrium equation, the vertical pressure and air density profiles in the atmosphere are related to each other by

$$\frac{\partial p}{\partial z} = -\rho g.$$

1. Solve this equation for $p = p(z)$ in an isothermal atmosphere by using the ideal gas equation for dry air.
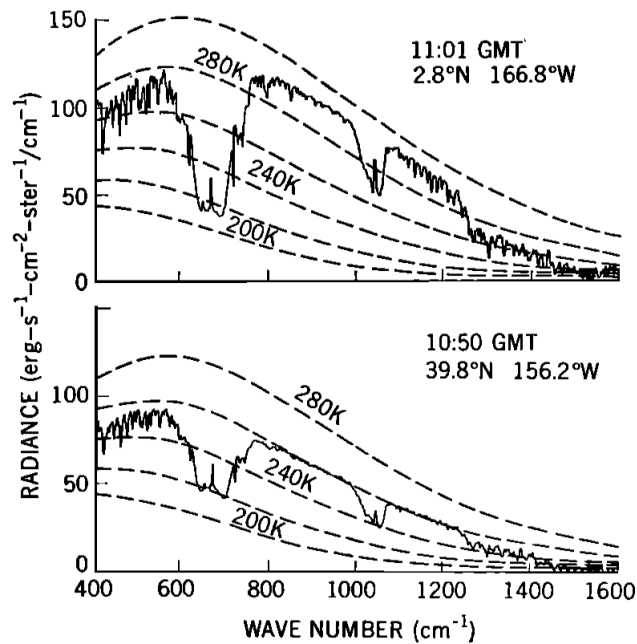
Figure 5.1: Nimbus-4 IRIS spectra over the western Pacific Ocean. Dashed lines show blackbody radiances for different temperatures (in K). Source: (Hanel et al., 1972).

2. Adopt a constant vertical temperature gradient such that $T(z) = T_{\text{surf}} + az$ and solve the resulting equation. Calculate the relative deviation of the isothermal from the latter solution at the surface, at mid-troposphere height and at the tropopause, using the temperature at the mid-troposphere as the isothermal temperature. Look up other required data in the U. S. Standard Atmosphere 1976 (COESA, 1976).

Answer **1.** $p(z) = p_{\text{surf}} \times \exp\left(-\frac{M_{\text{air}}g}{RT_{\text{iso}}}z\right);$ **2.** $p(z) = p_{\text{surf}} \times \left(\frac{T_{\text{surf}}+az}{T_{\text{surf}}}\right)^{-\frac{M_{\text{air}}g}{aR}}.$

Exercise 5.7 (–/∗/∗∗) READY

Figure 5.1 shows two spectra obtained with the Infrared Interferometric Spectrometer (IRIS) aboard Nimbus-4 in 1970, orbiting at altitudes of 1092 to 1108 km.

1. Wave lengths on the horizontal axis are reported as *wave numbers*, in cm^{-1}. How are these units related to the more common wave length units μm?

2. The peak at about $667\,\mathrm{cm}^{-1}$ and valley around it correspond to a well-known absorption band. Use the previously established relationship to determine which one it is. And what about that at $1040\,\mathrm{cm}^{-1}$? Where is the infrared window located?

3. (∗) Can you give an estimate of the ground temperature for the top spectrum? Assuming a lapse rate of $6.25\,\mathrm{K\,km}^{-1}$ and a tropopause height of $16\,\mathrm{km}$, can you give estimates of the emission heights of the bottom of the valleys around $667\,\mathrm{cm}^{-1}$ and $1040\,\mathrm{cm}^{-1}$? How can the temperature increase witnessed by the central peak at $667\,\mathrm{cm}^{-1}$ be explained?

4. (∗∗) Repeat the previous questions for the spectrum in the bottom panel.

5. Check your answers with MODTRAN Infrared Light in the Atmosphere, a web-interface to MODTRAN3 by David Archer at the University of Chicago. MODTRAN simulates the emission and absorption of infrared radiation in the atmosphere. Please test different altitudes, always looking down.

Answer **1.** Waves at $n\,\mathrm{cm}^{-1}$ correspond to $\lambda = 10^4/n$ in μm. **2.** $667\,\mathrm{cm}^{-1}$: $15\,\mu$m CO_2 absorption band; $1040\,\mathrm{cm}^{-1}$: $9.6\,\mu$m O_3 absorption band; infrared window (8–$12\,\mu$m): 830–$1250\,\mathrm{cm}^{-1}$. **3.** Ground temperature: $290\,\mathrm{K}$; valley bottom emission temperature: $215\,\mathrm{K}$, i. e.,$12\,\mathrm{km}$ in the troposphere. **4.** — **5.** Try 0, 5, 10, 12, 14, 16, 20, 25 and $70\,\mathrm{km}$.

To learn more...

- The Climate Laboratory, by Brian E. J. Rose (University at Albany), a truly hands-on experience to climate physics and climate modeling

- METEO 300: Fundamentals of Atmospheric Science at Penn State University

- Climate and Carbon Cycle Models, as supporting web applications for David Archer's book *Global Warming: Understanding the Forecast*

- How Atmospheric Warming Works, part of the Climate Science Toolkit of the American Chemical Society.

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Chapter 6

Continental Biosphere

Review Questions

1. What is the difference between autotrophic and heterotrophic respiration?

2. What do the acronyms NPP, NEE, NEP and NBP stand for? How are they related to each other?

3. What are the two limiting factors in the photosynthetic assimilation model of Farquhar et al. (1980), seen in class?

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Chapter 7

Continent-Ocean Interaction

Review Questions

1. Name the four stages of model development.

2. Prognostic or diagnostic model: what is the difference?

Chapter 8

Data, Software Codes and Project Protocols: Mining the Internet

Exercise 8.1 : Data

Find data sets and gather information about reading them. Also secure the original literature references for them.

- ice core data

- SSP, RCP climate scenario data

- CMIP5, CMIP6

- PMIPx.y data

- CO_2 emission data (historical)

- Mauna Loa (CO_2, $\delta^{13}C$, . . .) – also South Pole, etc.

- Sea Surface Temperature Data

- Arctic sea ice cover

- Seafloor surface sediment composition

- isotopic records for $\delta^{13}C$, $\delta^{18}O$

- Paleo sea-level data

Exercise 8.2 : Source Codes

Get software codes for the following programs:

- SolveSAPHE pH calculation software (Fortran 90 and Python)

- CO2SYS carbonate speciation software (MATLAB, Excel, Python)

- Seacarb carbonate speciation software (R)

- mocsy 2.0 carbonate speciation software (Fortran 90)

- GENIE-2 Earth System Model (Fortran 90)

- Loveclim Earth System Model (FORTRAN77)

- CESM

- NEMO Ocean physics and biogeochemistry

- Planet Simulator

- MITgcm

- CANDI (C-CANDI) early diagenesis models

- LPJ vegetation model

Exercise 8.3 : Protocols

Get intercomparison project protocol specifications.

- PMIP

- OCMIP

- OMIP

- ISIMIP

- …

Miscellaneous Data and Constants' Values

Table 8.1: Earth Data

Surface area of the Earth	510.072×10^{12} m^2	(1)
Volume of the Oceans	1.335×10^{18} m^3 ($\pm\,1\,\%$)	(1)
Surface area of the Oceans	361.9×10^{12} m^2 ($\pm\,0.1\,\%$)	(1)
Mass of the atmosphere	5.1480×10^{18} kg	(2)
$-$ mass of dry air	5.1352×10^{18} kg	(2)
$-$ mean mass of water vapour	0.0127×10^{18} kg	(2)
Solar constant	1361 W m^{-2}	(3)

(1) Eakins and Sharman (2010) and Amante and Eakins (2009); (2) Trenberth and Smith (2005) (3) Kopp and Lean (2011).

Table 8.2: Physical Constants

Stefan-Boltzmann constant	σ	$5.670374419 \times 10^{-8}$ W m^{-2} K^{-4}	(1)
Avogadro number	N_{A}	$6.02214076 \times 10^{23}$ mol^{-1}	(1)
Boltzmann constant	k_{B}	1.380649×10^{-23} J K^{-1}	(1)
Gas constant	R	$8.314462618\ldots$ J K^{-1} mol^{-1}	(1)
Specific heat capacity of air	C_{P}	1000 J kg^{-1} K^{-1}	
Specific heat capacity of seawater	C_{P}	3986 J kg^{-1} K^{-1}	(2)

(1) CODATA (Tiesinga et al., 2021); (2) Brewer and Peltzer (2019).

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Bibliography

C. Amante and B. W. Eakins. ETOPO1 1 arc-minute global relief model: Procedures, data sources and analysis. Technical Report NESDIS NGDC-24, National Geophysical Data Center, Boulder (CO), March 2009. URL `http://www.ngdc.noaa.gov/mgg/global/relief/ETOPO1/docs/ETOPO1.pdf`.

P. G. Brewer and E. T. Peltzer. The molecular basis for the heat capacity and thermal expansion of natural waters. *Geophys. Res. Lett.*, 46(22):13227–13233, 2019. doi: 10.1029/2019GL085117.

W. S. Broecker and T.-H. Peng. *Tracers in the Sea*. Lamont-Doherty Geological Observatory of Columbia University, Palisades (NY), 1982. URL `https://www.ldeo.columbia.edu/~broecker/Home_files/TracersInTheSea_searchable.pdf`.

W. L. Chameides and E. M. Perdue. *Biogeochemical Cycles: A Computer-Interactive Study of Earth System Science and Global Change*. The Computer-Based Earth System Science Series. Oxford University Press, New York (NY), 1997. ISBN 0-19-509279-1.

COESA. U. S. standard atmosphere, 1976. Technical Report NOAA-S/T 76-1562, National Oceanic and Atmospheric Administration, Washington (DC), October 1976. URL `https://www.ngdc.noaa.gov/stp/space-weather/online-publications/miscellaneous/us-standard-atmosphere-1976/us-standard-atmosphere_st76-1562_noaa.pdf`.

H. Craig. Isotopic standards for carbon and oxygen and correction factors for mass-spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Ac.*, 12 (1/2):133–149, 1957. doi: 10.1016/0016-7037(57)90024-8.

R. E. Criss. *Principles of Stable Isotope Distribution*. Oxford University Press, New York (NY), 1999. ISBN 978-0-19-511775.

B. W. Eakins and G. F. Sharman. Volumes of the world's oceans from ETOPO1, 2010. URL `http://www.ngdc.noaa.gov/mgg/global/etopo1_ocean_volumes.html`. Last access: 25th August 2022.

A. J. Fleisher, H. Yi, A. Srivastava, O. L. Polyansky, N. F. Zobov, and J. T. Hodges. Absolute ^{13}C/^{12}C isotope amount ratio for Vienna PeeDee Belemnite from infrared absorption spectroscopy. *Nature Physics*, 17(8):889–893, 2021. doi: 10.1038/s41567-021-01226-y.

R. J. Francey, C. E. Allison, D. M. Etheridge, C. M. Trudinger, I. G. Enting, M. Leuenberger, R. L. Langenfelds, E. Michel, and L. P. Steele. A 1000-year high precision record of δ^{13}C in atmospheric CO_2. *Tellus*, 51B(2):170–193, 1999. doi: 10.3402/tellusb.v51i2.16269.

R. A. Hanel, B. J. Conrath, V. G. Kunde, C. Prabhakara, I. Revah, V. V. Salomonson, and G. Wolford. The Nimbus 4 infrared spectroscopy experiment : 1. Calibrated thermal emission spectra. *J. Geophys. Res.*, 77(15):2629–2641, 1972. doi: 10.1029/JC077i015p02629.

G. Kopp and J. L. Lean. A new, lower value of total solar irradiance: Evidence and climate significance. *Geophys. Res. Lett.*, 38(1):L01706, 2011. doi: 10.1029/2010GL045777.

A. Lerman, F. T. Mackenzie, and R. M. Garrels. Modeling of geochemical cycles : Phosphorus as an example. In E. H. T. Whitten, editor, *Quantitative studies in the Geological Sciences*, volume 142 of *Geol. Soc. Am. Mem.*, pages 205–218. Geological Society of America, 1975. doi: 10.1130/MEM142-p205.

A. Lourantou, J. V. Lavrič, P. Köhler, J.-M. Barnola, D. Paillard, E. Michel, D. Raynaud, and J. Chappellaz. Constraint of the CO_2 rise by new atmospheric carbon isotopic measurements during the last deglaciation. *Global Biogeochem. Cy.*, 24(2):GB2015, 2010. doi: 10.1029/2009GB003545.

I. Marinov and J. L. Sarmiento. The role of the oceans in the global carbon cycle : An overview. In M. Follows and T. Oguz, editors, *The Ocean Carbon Cycle and Climate*, volume 40 of *NATO Science Series IV:Earth and Environmental Sciences*, pages 251–295. Kluwer Academic Publishers, Dordrecht (NL), 2004. doi: 10.1007/978-1-4020-2087-2_8.

B. Marzeion. ESD ideas: A weak positive feedback between sea level and the planetary albedo. *Earth System Dynamics*, 12(4):1057–1060, 2021. doi: 10.5194/esd-12-1057-2021.

G. Munhoven. Mathematics of the total alkalinity-pH equation – pathway to robust and universal solution algorithms: the SolveSAPHE package v1.0.1. *Geosci. Model Dev.*, 6(4):1367–1388, 2013. doi: 10.5194/gmd-6-1367-2013. URL https://gmd.copernicus.org/articles/6/1367/2013.

G. Munhoven. Glacial-interglacial changes of continental weathering : estimates of the related CO_2 and HCO_3^- flux variations and their uncertainties. *Global Planet. Change*, 33(2-3):155–176, 2002. doi: 10.1016/S0921-8181(02)00068-1.

G. Munhoven. SolveSAPHE-r2 (v2.0.1): revisiting and extending the Solver Suite for Alkalinity-PH Equations for usage with CO_2, HCO_3^- or CO_3^{2-} input data. *Geosci. Model Dev.*, 14(7):4225–4240, 2021. doi: 10.5194/gmd-14-4225-2021. URL https://gmd.copernicus.org/articles/14/4225/2021.

M. Rhein, S. R. Rintoul, S. Aoki, E. Campos, D. Chambers, R. A. Feely, S. Gulev, G. C. Johnson, S. A. Josey, A. Kostianoy, C. Mauritzen, D. Roemmich, L. D. Talley, and F. Wang. Observations : Ocean. In T. F. Stocker, D. Qin, G.-K. Plattner, M. M. B. Tignor, S. K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex, and P. M. Midgley, editors, *Climate Change 2013 : The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, chapter 3, pages 255–315. Cambridge University Press, Cambridge (UK), 2013. ISBN 978-1-107-66182-0. URL https://www.ipcc.ch/site/assets/uploads/2018/02/WG1AR5_Chapter03_FINAL.pdf.

J. L. Sarmiento. Modeling oceanic transport of dissolved constituents. In P. Buat-Ménard, editor, *The Role of Air-Sea Exchange in Geochemical Cycling*, volume 185 of *NATO ASI Series C : Mathematical and Physical Sciences*, pages 65–82. Reidel, Dordrecht, 1986. ISBN 90-277-2318-4. doi: 10.1007/978-94-009-4738-2_3.

J. L. Sarmiento. Biogeochemical ocean models. In K. E. Trenberth, editor, *Climate System Modeling*, chapter 16, pages 519–551. Cambridge University Press, Cambridge, 1992.

J. L. Sarmiento and J. R. Toggweiler. A new model for the role of the oceans in determining atmospheric p_{CO_2}. *Nature*, 308:621–624, 1984. doi: 10.1038/308621a0.

J. L. Sarmiento, J. R. Toggweiler, and R. Najjar. Ocean carbon-cycle dynamics and atmospheric p_{CO_2}. *Philos. T. R. Soc. Lond. A*, 325:3–21, 1988. doi: 10.1098/rsta.1988.0039.

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J. Schmitt, R. Schneider, J. Elsig, D. Leuenberger, A. Lourantou, J. Chappel-laz, P. Köhler, F. Joos, T. F. Stocker, M. Leuenberger, and H. Fischer. Carbon isotope constraints on the deglacial CO_2 rise from ice cores. *Science*, 336: 711–714, 2012. doi: 10.1126/science.1217161.

W. J. Schmitz, Jr. On the interbasin-scale thermohaline circulation. *Rev. Geophys.*, 33(2):151–173, 1995. doi: 10.1029/95RG00879.

Z. Sharp. *Principles of Stable Isotope Geochemistry*. University of New Mexico, 2 edition, 2017. doi: 10.25844/h9q1-0p82. URL `https://digitalrepository.unm.edu/unm_oer/1`.

T. Takahashi, W. S. Broecker, and S. Langer. Redfield ratio based on chemical data from isopycnal surfaces. *J. Geophys. Res.*, 90(C4):6907–6924, 1985. doi: 10.1029/JC090iC04p06907.

E. Tiesinga, P. J. Mohr, D. B. Newell, and B. N. Taylor. CODATA recommended values of the fundamental physical constants : 2018. *Reviews of Modern Physics*, 93(2):025010, 2021. doi: 10.1103/RevModPhys.93.025010.

K. E. Trenberth and L. Smith. The mass of the atmosphere : A constraint on global analyses. *J. Climate*, 18(6):864–875, 2005. doi: 10.1175/JCLI-3299.1.

R. G. Williams and M. J. Follows. *Ocean Dynamics and the Carbon Cycle : Principles and Mechanisms*. Cambridge University Press, Cambridge (UK), 2011. ISBN 978-0-521-84369-0. doi: 10.1017/CBO9780511977817.

R. Wollast. Basic concepts in geochemical modelling. In P. Buat-Ménard, editor, *The Role of Air-Sea Exchange in Geochemical Cycling*, volume 185 of *NATO ASI Series C : Mathematical and Physical Sciences*, pages 1–34. Reidel, Dordrecht, 1986. ISBN 90-277-2318-4. doi: 10.1007/978-94-009-4738-2_1.

R. E. Zeebe and D. Wolf-Gladrow. *CO_2 in seawater : Equilibrium, kinetics, isotopes*, volume 65 of *Elsevier Oceanography Series*. Elsevier, Amsterdam (NL), 2001. ISBN 978-0-444-50579-8. URL `http://www.sciencedirect.com/science/bookseries/04229894/65`.

Appendix A

Sources

Isotopes

Exercise 1.1: original exercise

Exercise 1.2: original exercise, inspired by Criss (1999)

Exercise 1.3: adapted from exercice 21 of the homework collection to lecture 16 of the *Marine Chemistry* developed by Adina Paytan at Stanford University (spring 2006 – last access 05th January 2023)

Exercise 1.4: original exercise

Exercise 1.5: original exercise

Exercise 1.6: original exercise, inspired by the recommendation of Zeebe and Wolf-Gladrow (2001) to start isotope system studies with ^{10}B–^{11}B pair

Exercise 1.7: original exercise

Exercise 1.8: original exercise

Box-Models

Exercise 2.1: original exercise

Exercise 2.2: original exercise, based upon (Lerman et al., 1975, Fig. 2)

Exercise 2.3: original exercise, based upon Chameides and Perdue (1997, Fig. 8.6)

Exercise 2.4: original exercise

Exercise 2.5: original exercise

Exercise 2.6: original exercise, based upon a series of classical papers (Broecker and Peng, 1982; Sarmiento and Toggweiler, 1984; Sarmiento, 1986; Sarmiento et al., 1988; Sarmiento, 1992; Marinov and Sarmiento, 2004)

Exercise 2.7: original exercise

Exercise 2.8: theoretical part – original exercise; practical application – Wollast (1986), with original extension.

Chemical Equilibria and pH Calculations

Exercise 3.1: original exercise

Exercise 3.2: TBD (from textbook)

Exercise 3.3: original exercise

Exercise 3.4: original exercise (following Munhoven, 2013)

Exercise 3.5: original exercise

Exercise 3.6: original exercise

Exercise 3.7: original exercise (see, however, Munhoven, 2021)

Exercise 3.8: original exercise (following erroneous statement in the literature pretending that A_C does *not* change upon dissolution of CO_2)

Exercise 3.9: original exercise

Exercise 3.10: inspired by Zeebe and Wolf-Gladrow (2001), but original solution

Exercise 3.11: original exercise

Exercise 3.12: original exercise

Seafloor Sediments – Interaction with the Ocean and Early Diagenesis

Exercise 4.1: classical problem (see, e. g., Broecker and Peng, 1982)

Atmosphere and Climate

Exercise 5.1: inspired by the contents of the table in Section 4.1 of the *Fundamentals of Atmospheric Physics* (METEO 300) course at Penn State University

Exercise 5.2: classical application

Exercise 5.3: original exercise, loosely inspired from Williams and Follows (2011, Q2.2c)

Exercise 5.4: inspired from Williams and Follows (2011, Q2.1)

Exercise 5.5: original exercise

Continental Biosphere

—None—

Continent-Ocean Interaction

—None—

Data, Software Codes and Project Protocols: Mining the Internet

Exercise 8.1: original exercise

Exercise 8.2: original exercise

Exercise 8.3: original exercise

Appendix B

Acronyms and Abbreviations

CESM Community Earth System Model

CMIP5 Coupled Model Intercomparison Project Phase 5

CMIP6 Coupled Model Intercomparison Project Phase 6

CODATA Committee on Data of the International Science Council

COESA U. S. Committee On Extension to the Standard Atmosphere

DAE Differential-Algebraic Equation

DBL Diffusive Boundary Layer

DOI Digital Object Identifier

EBM Energy Balance Model

EPICA European Project for Ice Coring in Antarctica

ESA European Space Agency

ESGF Earth System Grid Federation

GFDL Geophysical Fluid Dynamics Laboratory

ICSU International Council for Science (previously: International Council of Scientific Unions; merged with ISSC→ to form ICS→)

IIASA International Institute for Applied Systems Analysis

IPCC Intergovernmental Panel on Climate Change

IPSL Institut Pierre-Simon Laplace

IR Infrared

ISC International Science Council (merger of ICSU and ISSC)

ISSC International Social Science Council (merged with ICSU→ to form ICS→)

ISIMIP Inter-Sectoral Impact Model Intercomparison Study

IUPAC International Union of Physical and Applied Chemistry

LGM Last Glacial Maximum

NASA National Aeronautic and Space Administration

    GISS Goddard Institute for Space Sciences

    GSFC Goddard Space Flight Institute

    JPL Jet Propulsion Laboratory

    NSSDCA NASA Space Science Data Coordinated Archive

NBS National Bureau of Standards (now NIST→)

NCAR National Center for Atmospheric Research

NEMO Nucleus for European Modelling of the Ocean

NGDC National Geophysical Data Center

NIST National Institute of Standards and Technology (formerly NBS→)

NOAA National Oceanic and Atmospheric Administration

    NCEI National Centers for Environmental Information

    NESDIS National Environmental Satellite, Data, and Information Service

    STAR Center for Satellite Applications and Research

OCMIP Ocean Carbon-Cycle Model Intercomparison Project

ODE Ordinary Differential Equation

OMIP Ocean Model Intercomparison Project

OLR Outgoing Longwave Radiation

PDB Pee Dee Belemnite

PMIP Paleo-Modelling Intercomparison Project

SLAP Standard Light Antarctic Precipitation

SMOW Standard Mean Ocean Water

SRM Standard Reference Material

TOA Top Of the Atmosphere

UCAR University Corporation for Atmospheric Research

UV Ultraviolet

VPDB Vienna-PDB

VSMOW Vienna Standard Mean Ocean Water

WDC World Data Centre

WDS World Data Service