Early Diagenesis Modelling with MEDUSA

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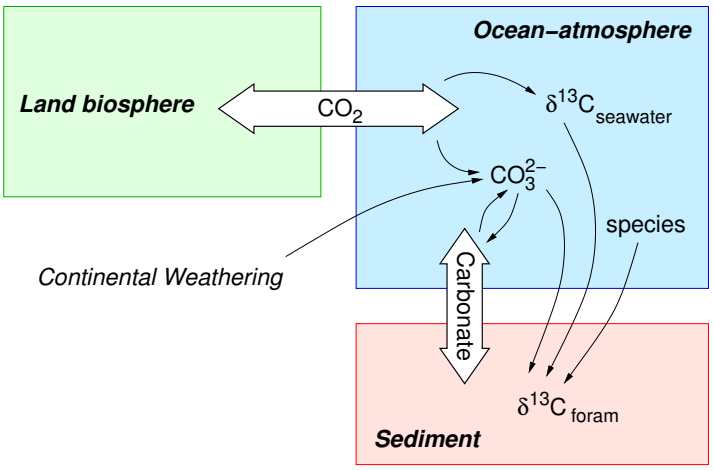
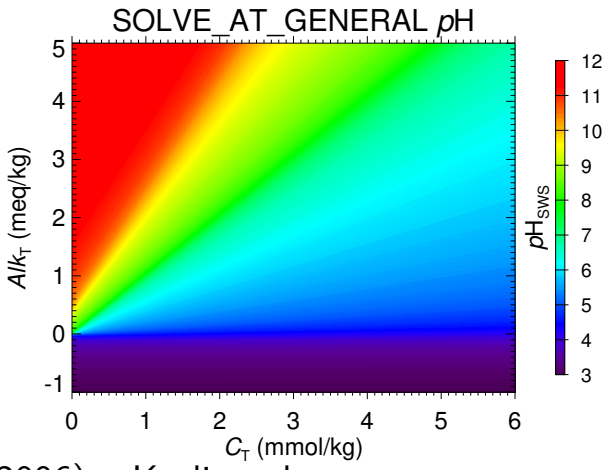
Terrestrial Atmosphere and Carbon Cycle

- Atmosphere ↔ ocean
- Continent ↔ ocean-atmosphere
- Ocean ↔ seafloor sediment
- **Global** scale
- **1 – 100 kyr** time scales
  - atmospheric lifetime of fossil-fuel CO_2
  - glacial-interglacial atmospheric CO_2 variations
  - ocean acidification impact on sea-floor sediments
- **Mechanistic understanding**



Model Theory, Mathematical Methods and Development

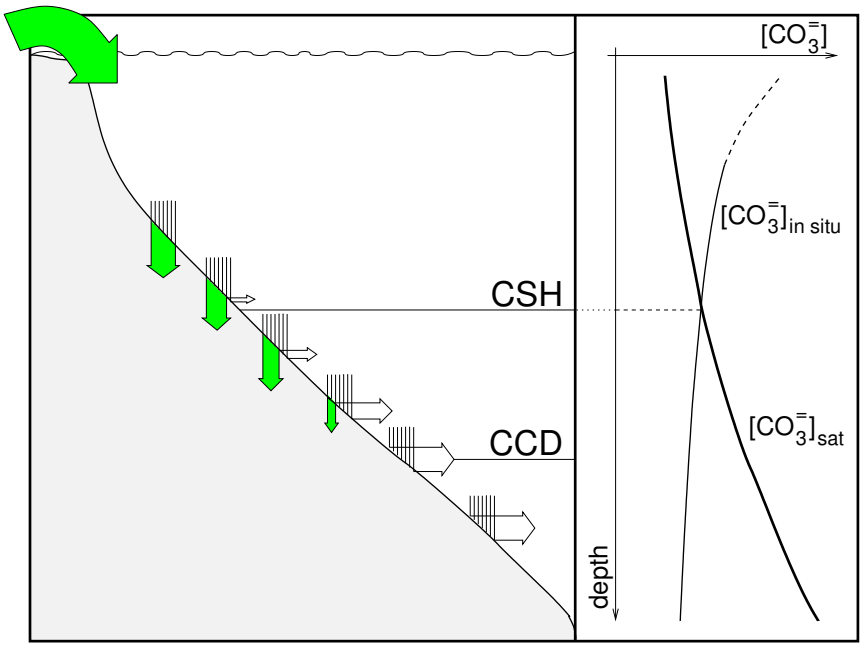
- Basic research
  - resolution methods
  - properties and limitations
  - reliability
  - extension of existing methods



- Noteworthy outcomes
  - Köhler et al. (Biogeosciences 2006) – Keeling plots
  - Munhoven (Geoscientific Model Development 2013) – solving the pH-alkalinity equation (SolveSAPHE methods and library), adopted as the workhorse in MOCSY 2.0, to be used in the upcoming CMIP6 Ocean Model Intercomparison Project (OMIP)

Acidification: Perturbation of the ocean-sediment exchange

Marine carbonates: ocean-sediment exchange



Model Description

MBM – *Multi-Box Model* of ocean-atmosphere carbon cycle

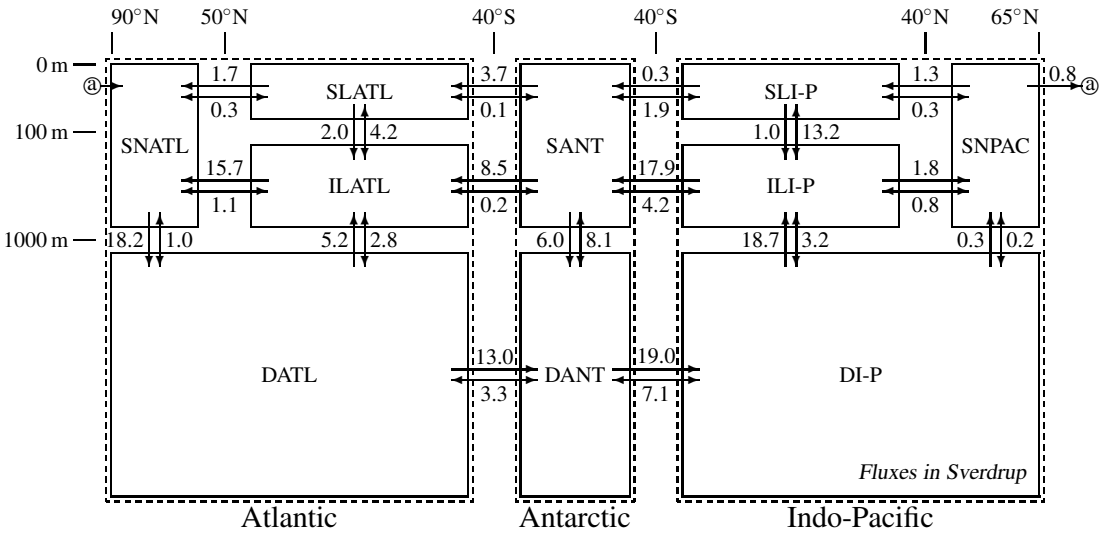
- ten oceanic and one atmospheric reservoirs
- realistic hypsometry
- fully coupled to . . . 304 copies of

MEDUSA *Model of Early Diagenesis in the Upper Sediment (A)*

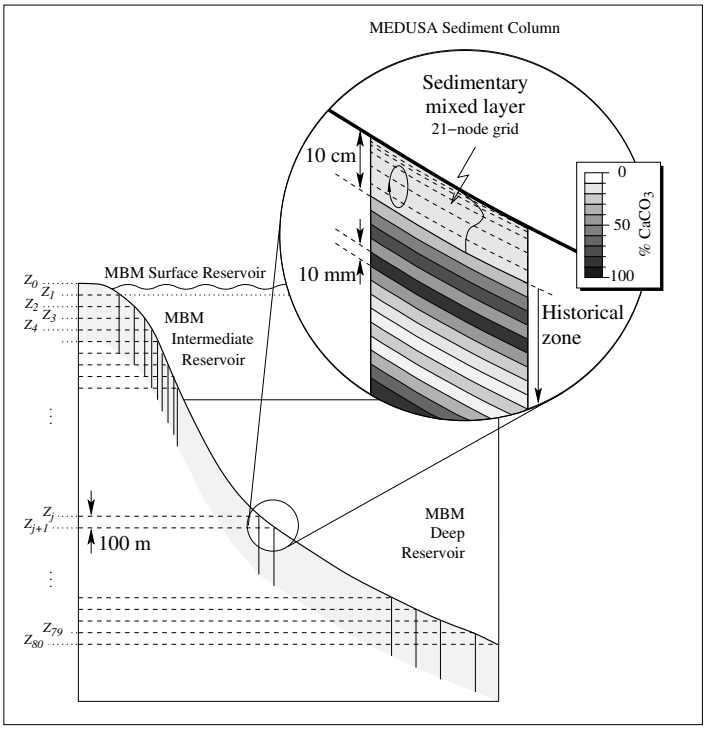
- bioturbated mixed-layer with 21 grid-points
  on top of a stack of thin layers (sediment core)
- solves time-dependent transport-reaction equations
- solids: calcite, aragonite, POM, clay
- solutes: CO_2, HCO_3^-, CO_3^{2-}, O_2
- fully bi-directional exchange between the two zones

Full description: Munhoven, Deep-Sea Res. II (2007)

Ocean Carbon Cycle Model MBM



Coupling MBM and MEDUSA



Sediment Model MEDUSA (Version 1)

MEDUSA-v1 (Munhoven, 2007)

- Solids: clay, calcite, aragonite and organic matter
- Porewater solutes: CO_2, HCO_3^-, CO_3^{2-} and O_2

Unpublished #1

- Solids: clay, calcite, aragonite, opal and organic matter
- Porewater solutes: CO_2, HCO_3^-, CO_3^{2-}, O_2 and H_4SiO_4

Unpublished #2

- Solids: clay, calcite, aragonite, opal and organic matter; ^{13}C-calcite, ^{13}C-aragonite, ^{13}C-organic matter
- Porewater solutes: CO_2, HCO_3^-, CO_3^{2-}, O_2 and H_4SiO_4; $^{13}CO_2$, $H^{13}CO_3^-$, $^{13}CO_3^{2-}$

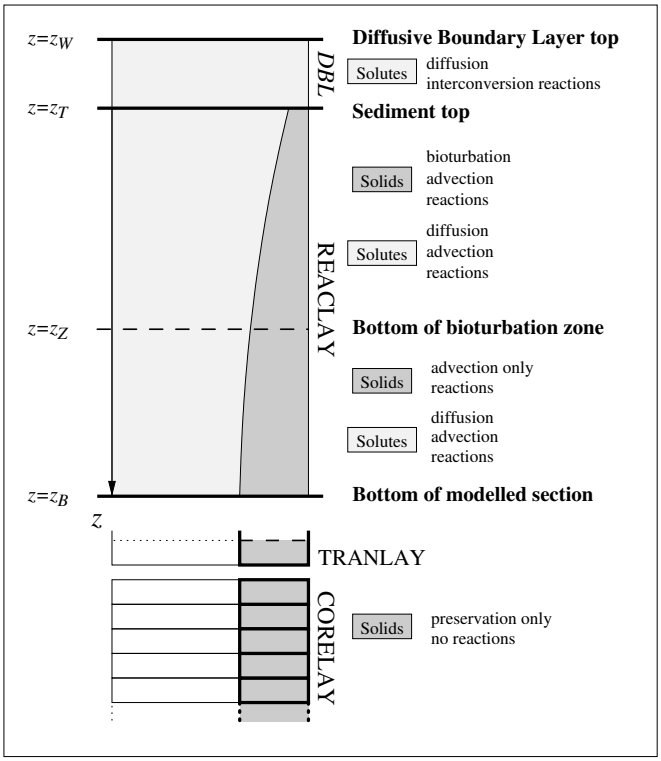
Sediment Model MEDUSA (Version 1 to Version 2)

- Configurations assembled and selected by pre-processor directives
- Pre-processor directives cumbersome to use for complex code configuration
- Code became difficult to manage and extend with time
- Develop a scheme to have the code built from description files
- Similar to BRNS (Regnier et al., U. Utrecht, V. U. Brussels) or MEDIA (Meysman, NIOZ Yerseke)

Sediment Model MEDUSA (Version 2)

- Flexible configuration
  - composition: solid and solute components
  - processes: includes extensible library of rate laws
  - equilibria: includes extensible library of equilibrium relationships
- Configuration and descriptions based upon XML files
  - extensible and flexible format
  - uses Fortran 95 library μXML to read XML files
- Code generator MEDUSACOCOGEN (also in Fortran 95)

Partitioning of the Model Sediment



General Diagenesis Equation

$$\frac{\partial \hat{C}_i}{\partial t} + \frac{\partial \hat{J}_i}{\partial z} - \hat{S}_i = 0$$

- t is time
- z depth below the sediment-water interface
- $\hat{C}_i$ is the concentration of i per unit volume of total sediment (solids plus porewater)
  - in moles for solutes
  - in kg for solids
- $\hat{C}_i$ related to phase-specific concentrations C_i^{s} (for solids) and C_i^{f} (for solutes) by $\hat{C}_i = (1-\varphi)C_i^{\mathrm{s}}$ and $\hat{C}_i = \varphi^{\mathrm{f}} C_i^{\mathrm{f}}$
- $\hat{J}_i$ is the local transport (advection and diffusion), per unit surface area of total sediment

General Diagenesis Equation

$$\frac{\partial \hat{C}_i}{\partial t} + \frac{\partial \hat{J}_i}{\partial z} - \hat{S}_i = 0$$

- $\hat{S}_i = \hat{R}_i + \hat{r}_i + \hat{Q}_i$ is the net source-minus-sink balance for constituent i, per unit volume of total sediment
- $\hat{R}_i = \hat{P}_i - \hat{D}_i$ is the net reaction rate, i.e., the difference between
  - $\hat{P}_i \geq 0$, production rate
  - $\hat{D}_i \geq 0$, destruction or decay rate
- $\hat{r}_i$ is the net fast reaction rate, filtered out by an equilibrium consideration
- $\hat{Q}_i$ is the non-local transport (considered only for solutes).

Transport

Solids

$$\hat{J}_i = -D_i^{\text{inter}} \frac{\partial (1-\varphi) C_i^{\text{s}}}{\partial z} - (1-\varphi) D_i^{\text{intra}} \frac{\partial C_i^{\text{s}}}{\partial z} + (1-\varphi) w C_i^{\text{s}}$$

Solutes: local

$$\hat{J}_i = -\varphi \frac{D_i^{\text{sw}}}{\theta^2} \frac{\partial C_i^{\text{f}}}{\partial z}.$$

Solutes: non-local

$$\hat{Q}_i(z) = \alpha(z) \varphi^{\text{f}}(z) (C_i^{\text{oc}} - C_i^{\text{f}}(z))$$

Transport

- Common framework:
  - evaluating transport terms
  - compiling equation system and Jacobian
  - solving the system (fully implicit in time, upwind biased in space)
- Application specific parts added by the Medusa Configuration and Code Generation tool MEDUSACOCOGEN
  - Components (solids and solutes)
  - Processes (chemical reactions)
  - Chemical equilibria

Solid Definition File: Calcite

```
<?xml version="1.0"?>

<Solid type="normal">

   <Names>
      <Generic>Calcite</Generic>
      <Long>Calcite</Long>
      <ShortID>calc</ShortID>
   </Names>


   <PhysicalProperties>
      <Density units="kg/m3">2700</Density>
      <MolWeight units="kg/mol">0.1000869</MolWeight>
   </PhysicalProperties>

```

Solid Definition File: Calcite

```
17
18    <ChemicalComposition>
19       <Ca>1</Ca>
20       <C> 1</C>
21       <O> 3</O>
22    </ChemicalComposition>
23
24
25    <CodeBits>
26       <SolubilityProduct units="mol^2/m^6">
27          <Fortran requireslibrary="libthdyct"
28                   requires="wtmpk, wsalin, wdbsl, rho">
29 <![CDATA[
30       {varname} = AKCALC(wtmpk, wsalin, wdbsl) * (rho**2)
31 ]]>
32          </Fortran>
33       </SolubilityProduct>
34    </CodeBits>
35
```

Solid Definition File: Calcite

```
36
37    <Alkalinity units="eq/mol">2</Alkalinity>
38
39
40    <ConservationProperties units="mol/mol">
41       <C>  1</C>
42    </ConservationProperties>
43
44 </Solid>
```

Solute Definition File: CO_3^{2-}

```
<?xml version="1.0"?>

<Solute type="normal">

   <Names>
      <Generic>CO3</Generic>
      <Long>Carbonate Ion</Long>
      <ShortID>co3</ShortID>
   </Names>


   <ChemicalComposition>
      <C> 1</C>
      <O> 3</O>
   </ChemicalComposition>

```

Solute Definition File: CO_3^{2-}

```

   <CodeBits>
      <DiffCoeff>
         <Fortran requires="wtmpdc">
<![CDATA[
      ! D_CO3 : from Boudreau (1997, Table 4.8, in cm2/s)
      {varname} =
     &    (4.33D-6 + 0.199D-6*wtmpdc)*dp_cm2_p_sec
]]>
         </Fortran>
      </DiffCoeff>
   </CodeBits>


   <Alkalinity units="eq/mol">2</Alkalinity>


   <ConservationProperties units="mol/mol">
      <C>  1</C>
   </ConservationProperties>

</Solute>
```

Solute System Definition File: Carbonate System

```
<?xml version="1.0"?>

<SoluteSystem type="normal" class="acid-base">

   <Names>
      <Generic>DIC</Generic>
      <Long>Dissolved Inorganic Carbon</Long>
      <ShortID>dic</ShortID>
   </Names>

   <Composition>
      <Solute file="xml/co2.xml"  disso="0" order="3" />
      <Solute file="xml/hco3.xml" disso="1" order="2" />
      <Solute file="xml/co3.xml"  disso="2" order="1"/>
   </Composition>


</SoluteSystem>
```

Process Definition File: Calcite Dissolution

```
<?xml version="1.0" encoding="US-ASCII"?>

<Process realms="reaclay">

   <Names>
      <Generic>CalcDissolution</Generic>
      <Long>Calcite Dissolution</Long>
      <ShortID>calcd</ShortID>
   </Names>

```

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

Process Definition File: Calcite Dissolution

```
11
12    <ChemicalReaction>
13
14       <Reactant id="r1">
15          <Name>Calcite</Name>
16          <StoechCoeff>1</StoechCoeff>
17       </Reactant>
18
19
20       <Product id="p1">
21          <Name>Ca</Name>
22          <StoechCoeff>1</StoechCoeff>
23       </Product>
24
25       <Product id="p2">
26          <Name>CO3</Name>
27          <StoechCoeff>1</StoechCoeff>
28       </Product>
29
30    </ChemicalReaction>
31
```

$$\boxed{CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}}$$

Process Definition File: Calcite Dissolution

```
32
33    <RateLaw reference_id="r1" subr="OMEGA1_POWN_C" requires="Calcite, Ca">
34
35       <RateConstant type="globalconstant"/>
36       <RateOrder    type="globalconstant"/>
37       <OmegaConc>CO3</OmegaConc>
38       <OmegaSaturationConc code="verbatim">
39          cct_ksp_calc/cct_ttcc_ca
40       </OmegaSaturationConc>
41       <Proportional>Calcite</Proportional>
42
43    </RateLaw>
44
45 </Process>
```

$$\boxed{\frac{d[CaCO_3]}{dt} = k[CaCO_3]\left(1 - \frac{[CO_3^{2-}]}{C_{sat}}\right)^n}$$

Rate Law Library (MODLIB files)

- Specially structured Fortran 95 modules that must
  1. start with a preamble to provide information required by the code generator
  2. define a derived type to encapsulate the specific parameters
  3. contain a subroutine to evaluate the rate law itself and the derivatives of the rate law w/r to the concentrations of the components involved
- Currently modules files for 15 different rate law expressions provided
- Library can be easily extended
- Fully described in the MEDUSACOCOGEN reference manual

Equilibrium Definition File: Carbonate System

```
1  <?xml version="1.0" encoding="US-ASCII"?>
2
3  <Equilibrium>
4
5     <Names>
6        <Generic>EquiDIC</Generic>
7        <Long>Carbonate Equilibrium</Long>
8        <ShortID>eqdic</ShortID>
9     </Names>
10
11
```

$$CO_2 + CO_3^{2-} + H_2O \leftrightharpoons 2HCO_3^-$$

Equilibrium Definition File: Carbonate System

```
12     <ChemicalReaction>
13
14        <Reactant id="r1">
15           <Name>CO2</Name>
16           <StoechCoeff>1</StoechCoeff>
17        </Reactant>
18        <Reactant id="r2">
19           <Name>CO3</Name>
20           <StoechCoeff>1</StoechCoeff>
21        </Reactant>
22        <Reactant id="r3">
23           <Name>H2O</Name>
24           <StoechCoeff>1</StoechCoeff>
25        </Reactant>
26
27        <Product  id="p1">
28           <Name>HCO3</Name>
29           <StoechCoeff>2</StoechCoeff>
30        </Product>
31
32     </ChemicalReaction>
33
```

$$CO_2 + CO_3^{2-} + H_2O \leftrightharpoons 2HCO_3^-$$

Equilibrium Definition File: Carbonate System

```
34
35     <LawOfMassAction subr="R1R2P1P1">
36        <Reactant1>CO2</Reactant1>
37        <Reactant2>CO3</Reactant2>
38        <Product1>HCO3</Product1>
39     </LawOfMassAction>
40
41  </Equilibrium>
```

$$[HCO_3^-]^2 - K[CO_2][CO_3^{2-}] = 0$$

Law of Mass-Action Library (MODLIB files)

- Specially structured Fortran 95 modules that must
  1. start with a preamble to provide information required by the code generator
  2. define a derived type to encapsulate the specific parameters
  3. contain a subroutine to evaluate the equilibrium equation itself and the derivatives of the equation w/r to the concentrations of the components involved
  4. contain a subroutine to derive the equilibrium constant from the boundary conditions
- Currently modules for 4 different relations provided
- Library can be easily extended
- Fully described in the MEDUSACOCOGEN reference manual

List File for a *Model Application*: MEDMBM

```
1  <?xml version="1.0"?>
2
3  <!-- List of XML files for components for the MEDMBM configuration -->
4
5  <MedusaCoCoGen>
6
7     <Composition>
8        <Solid        file="xml/clay.xml" order="1" />
9        <Solid        file="xml/calc.xml" order="2" />
10       <Solid        file="xml/arag.xml" order="3" />
11       <SoluteSystem file="xml/dic.xml"  order="4" />
12       <Solid        file="xml/orgm.xml" order="8" />
13       <Solute       file="xml/o2.xml"   order="9" />
14       <Solute       file="xml/ca.xml"   order="10" />
15    </Composition>
16
```

List File for a *Model Application*: MBM-Medusa

```
17
18      <Processes>
19         <Process      file="xml/proc_arag_diss.xml" />
20         <Process      file="xml/proc_calc_diss.xml" />
21         <Process      file="xml/proc_orgm_oxic.xml" />
22      </Processes>
23
24      <Equilibria>
25         <Equilibrium  file="xml/equi_dic.xml" />
26      </Equilibria>
27
28  </MedusaCoCoGen>
```