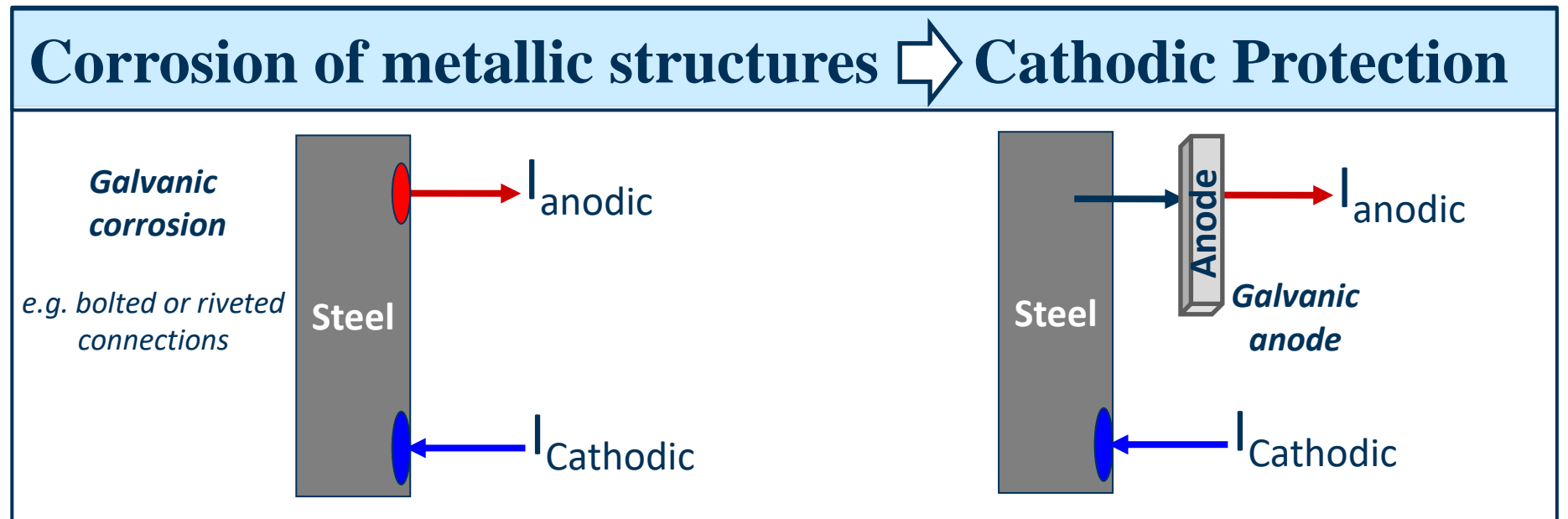
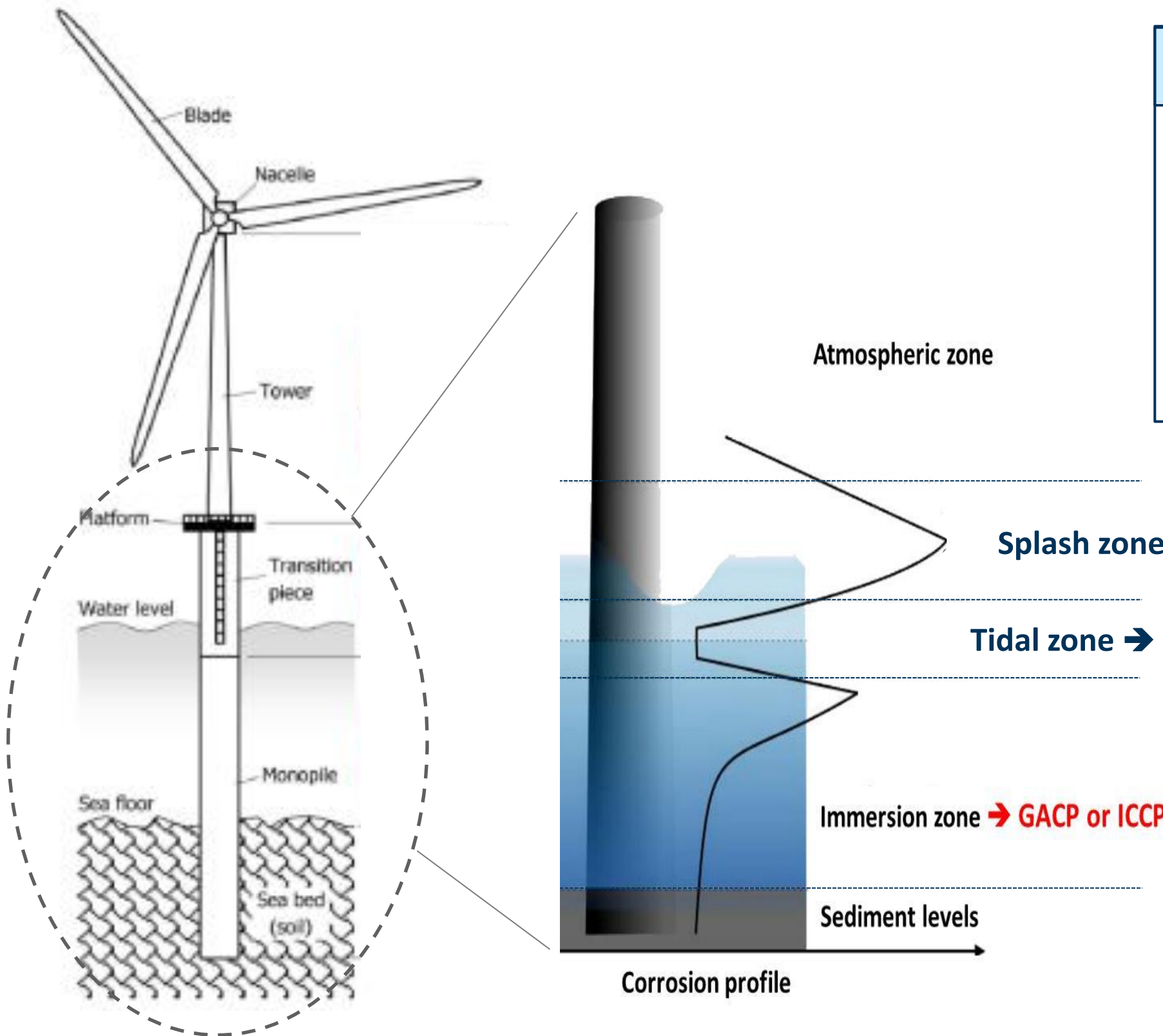


# Physicochemical characterization of galvanic anodes (GACP) released elements

---

Christelle Caplat, Université de Caen Normandie



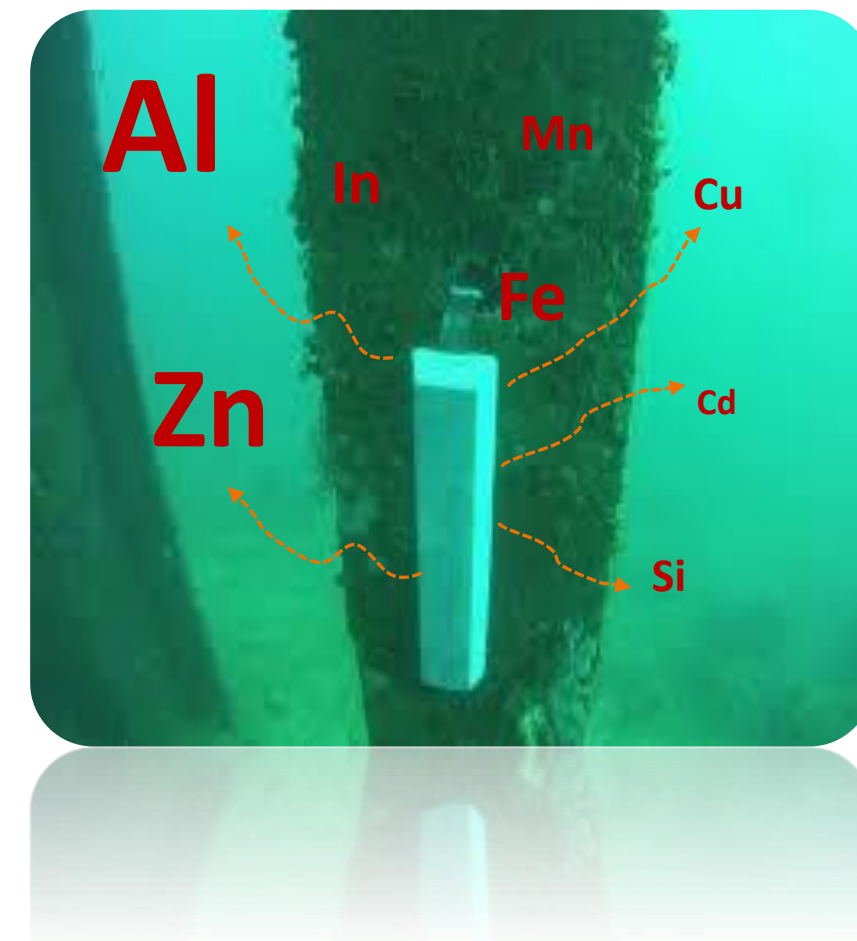
**Cathodic Protection (CP)**

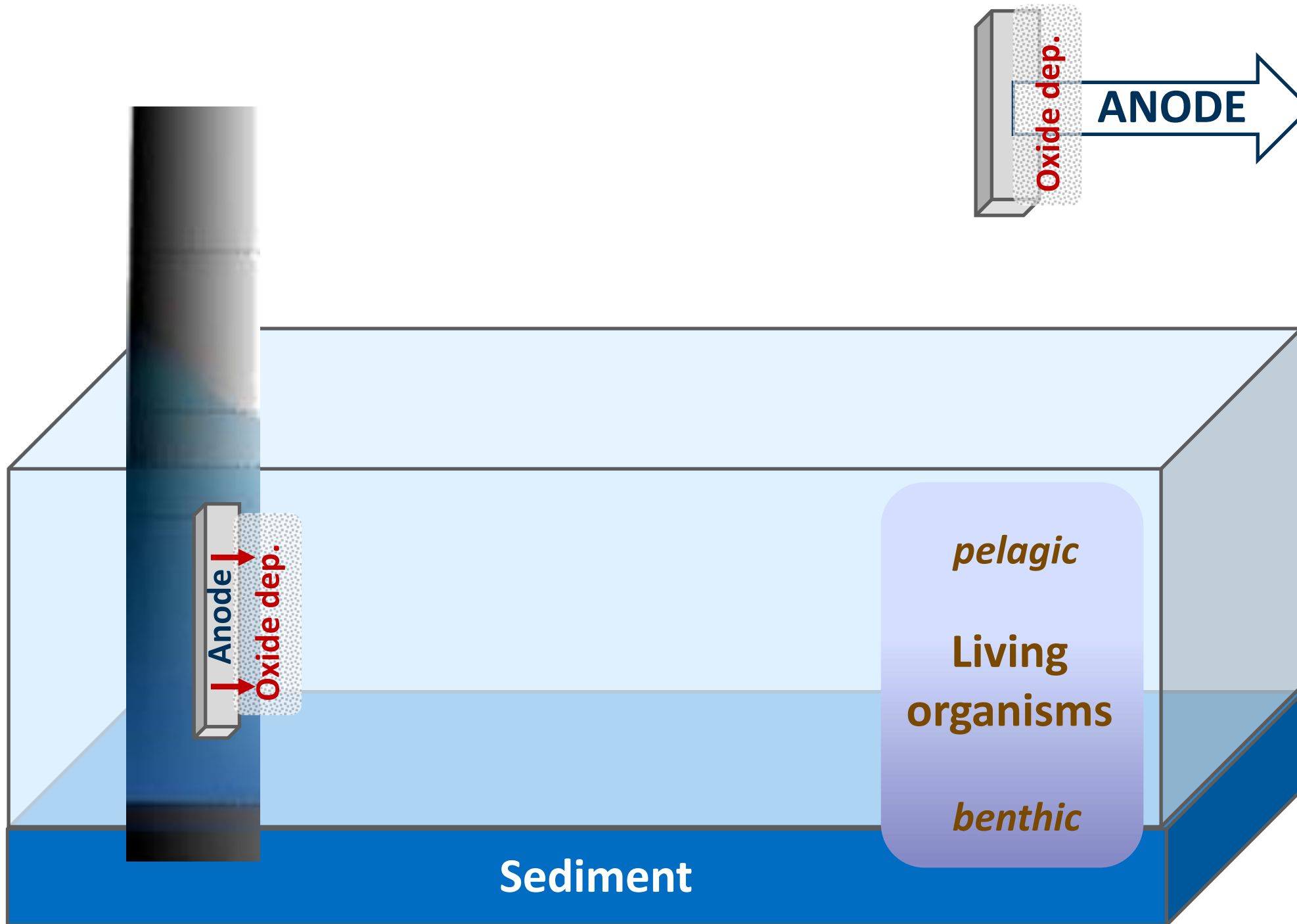


# Physicochemical characterization of galvanic anodes (GACP) released elements

Element	Aluminium anode			
	Minimum [mg kg <sup>-1</sup> ]	Maximum [mg kg <sup>-1</sup> ]	median [mg kg <sup>-1</sup> ]	average [mg kg <sup>-1</sup> ]
Aluminium	944000 ± 37000	1010000 ± 50000	1015000	1001000
Zinc (Zn)	26200 ± 300	60700 ± 300	33200	38325
Iron (Fe)	526 ± 16	1670 ± 70	720.5	909.3
Bismuth (Bi)	<0.052 (LD)	665 ± 31	665	665
Manganese (Mn)	7.6 ± 0,3	2380 ± 80	9,3	601.6
Indium (In)	143.0 ± 2,0	231 ± 13	204.5	195.8
Vanadium (V)	97.6 ± 4,5	131 ± 2	118.0	116.2
Gallium (Ga)	78.5 ± 1,0	133 ± 6	100.4	103.1
Nickel (Ni)	30.1 ± 0,9	52.4 ± 0.9	35.4	38.3
Lead (Pb)	6.7 ± 0,2	9.7 ± 0.1	8.9	8.5
Copper (Cu)	4.9 ± 0,1	17.4 ± 0.5	5.2	8.2
Magnesium (Mg)	<2 .5 (LQ)	7.2 ± 0.5	5.2	5.2
Chromium (Cr)	2.1 ± 0,1	5.6 ± 0.2	4.1	4.0
Cadmium (Cd)	0.2 ± 0,1	6.9 ± 0.1	1.4	2.5
Cobalt (Co)	1.8 ± 0,1	3.4 ± 0.1	2.1	2.4
Tin (Sn)	0.5 ± 0,4	3.4 ± 2.1	1.2	1.6
Lanthanum (La)	1.0 ± 0,1	1.3 ± 0.1	1.1	1.1
Uranium (U)	0.3 ± 0,0	1.8 ± 0.0	0.6	0.8
Cerium (Ce)	0,5 ± 0,0	1.2 ± 0.1	0.6	0.7
Silver (Ag)	<0.077 (LQ)	0.4 ± 0.0	0.4	0.4
Titanium (Ti)	<0.11 (LQ)	0.6 ± 0.0	0.2	0.3
Neodymium (Nd)	0.1 ± 0,0	0.3 ± 0.0	0.1	0.2
Gadolinium (Gd)	<0 .047 (LQ)	0.1 ± 0.0	0.1	0.1
Dysprosium (Dy)	< 0.044 (LQ)	0.1 ± 0.0	0.1	0.1
Samarium (Sm)	< 0.044 (LQ)	0.1 ± 0.0	0.1	0.1
Praseodymium (Pr)	< 0.041 (LQ)	0.1 ± 0.0	0.1	0.1

8/26 metallic elements: Al, Zn, Fe, Bi, Mn, In, V and Ga  
**Concentrations > 100 mg kg<sup>-1</sup> of anode**



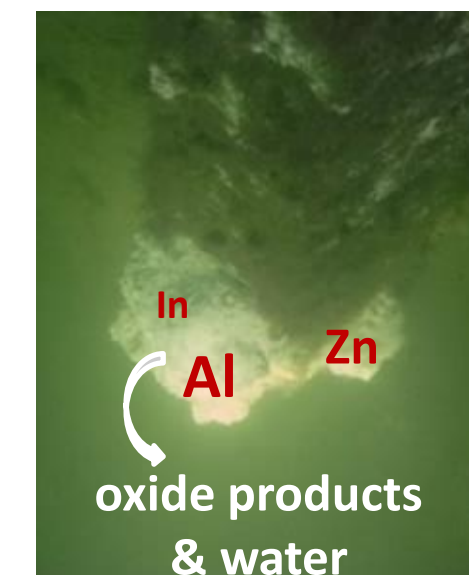


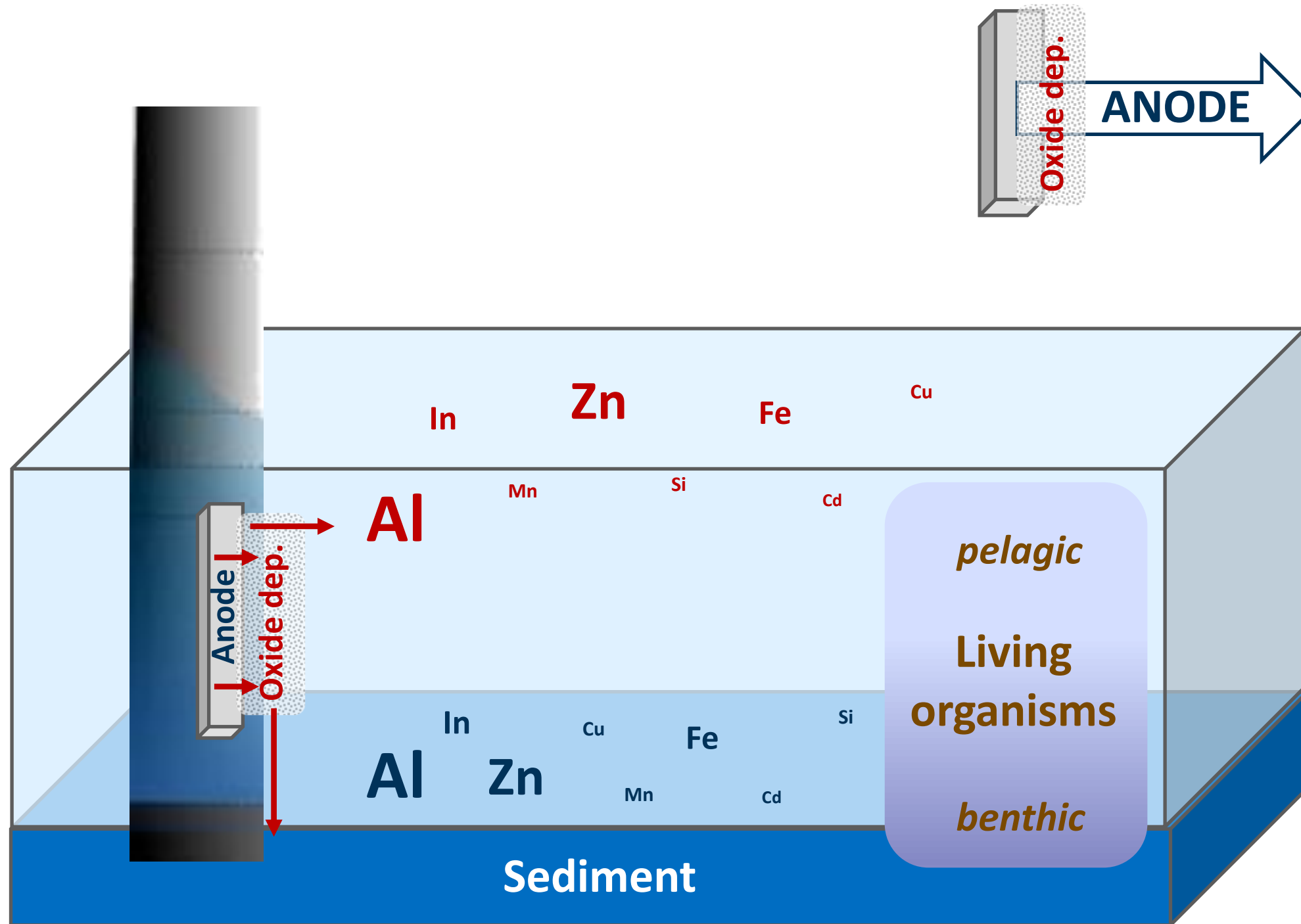
→ Diffusion of metals from GACP



1) Metallic elements change from a solid state (metallographic) to a crystallographic state (metal oxides) :

→ **oxide products** (oxide deposit)





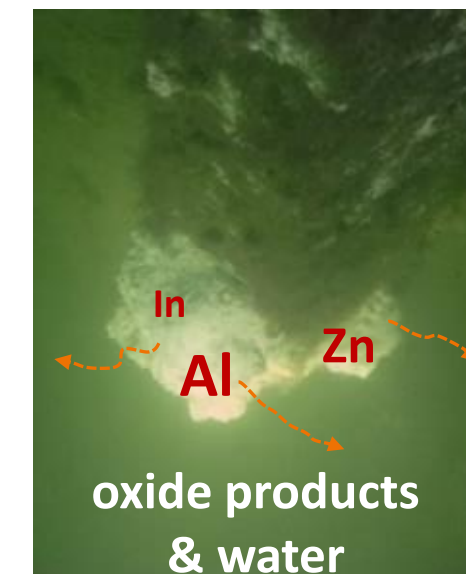
→ Diffusion of metals from GACP

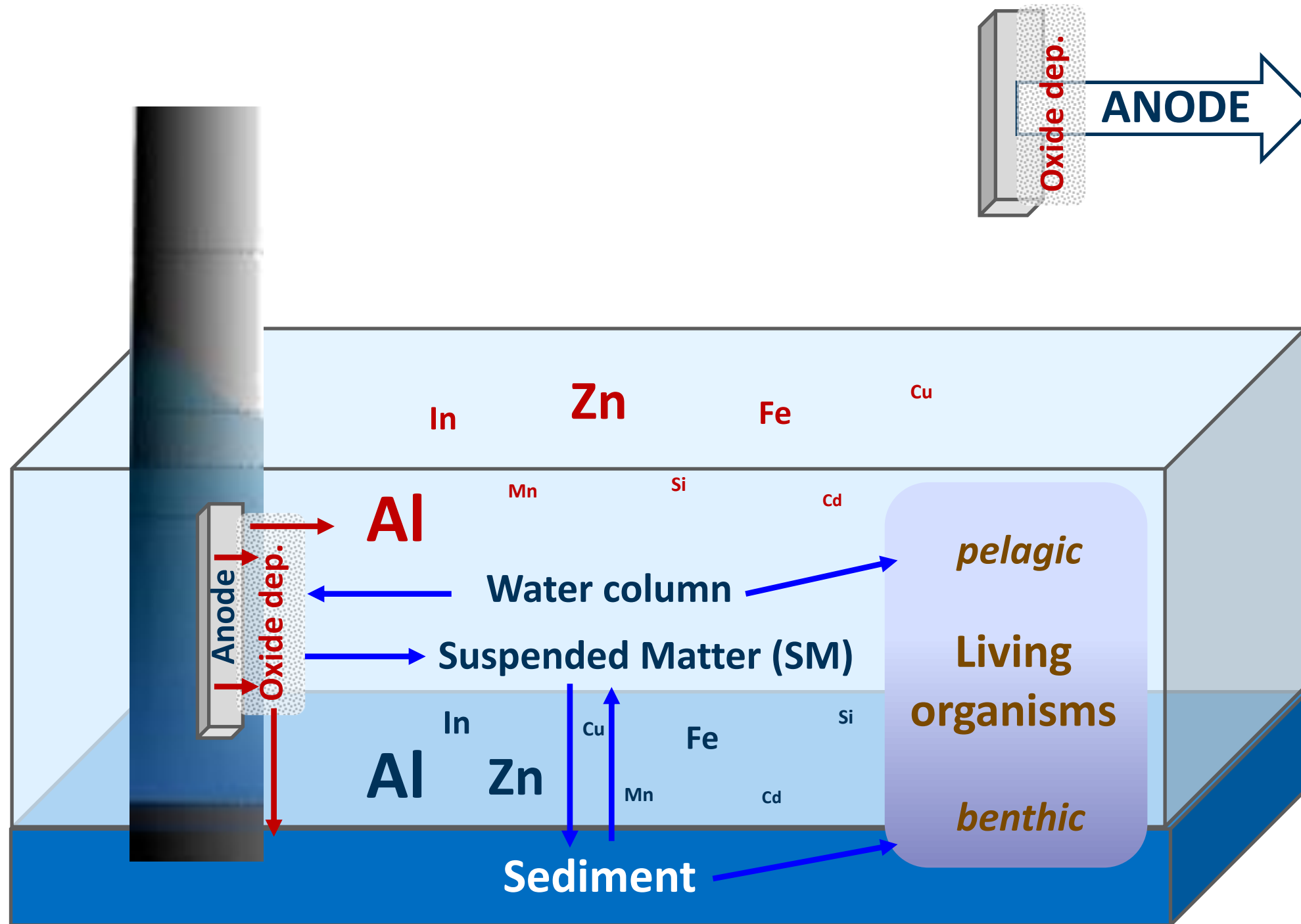


1) Metallic elements change from a solid state (metallographic) to a crystallographic state (metal oxides) :

→ **oxide products** (oxide deposit)

→ **dissolved state** in the pore water of the deposit and in the surrounding seawater

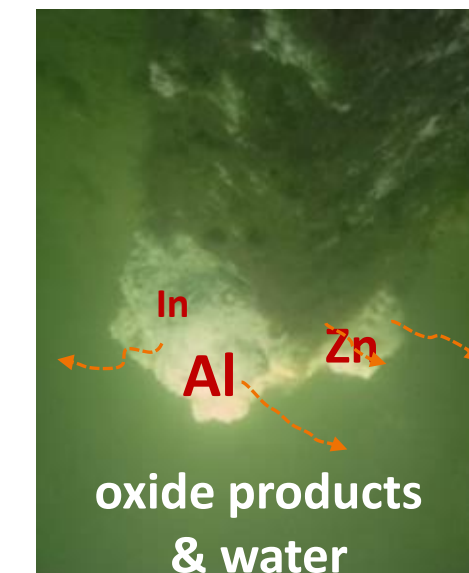




2) Released dissolved trace metals tend to interact with:

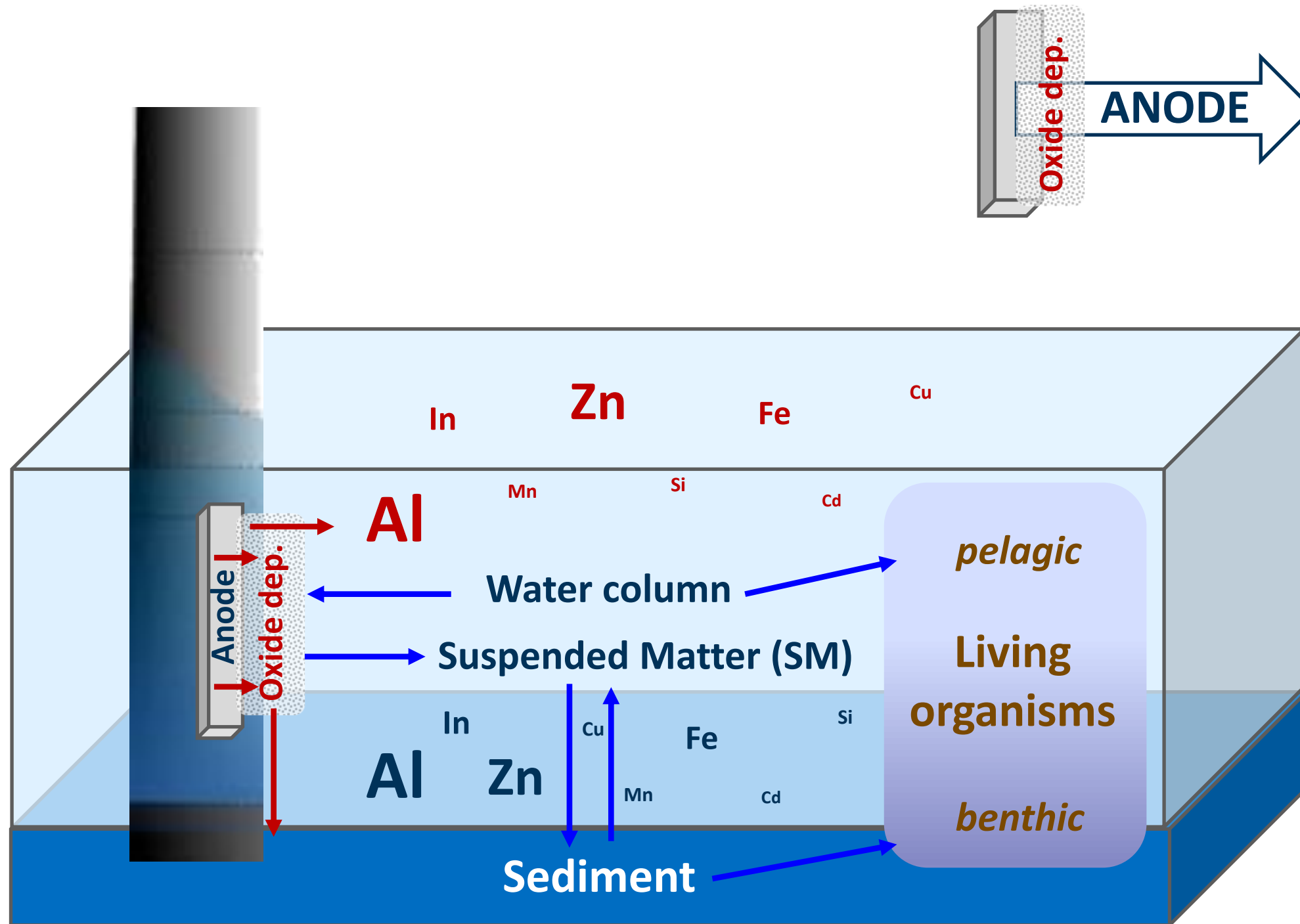
- living organisms (e.g. phytoplankton cells)
- dissolved organic matter (DOM)
- suspended Matter (SM)

↳ sediment ↔ benthos



→ Diffusion of metals from GACP

→ Transfert to different compartments



- Diffusion of metals from GACP
- Transfert to different compartments

2) Released dissolved trace metals tend to interact with:

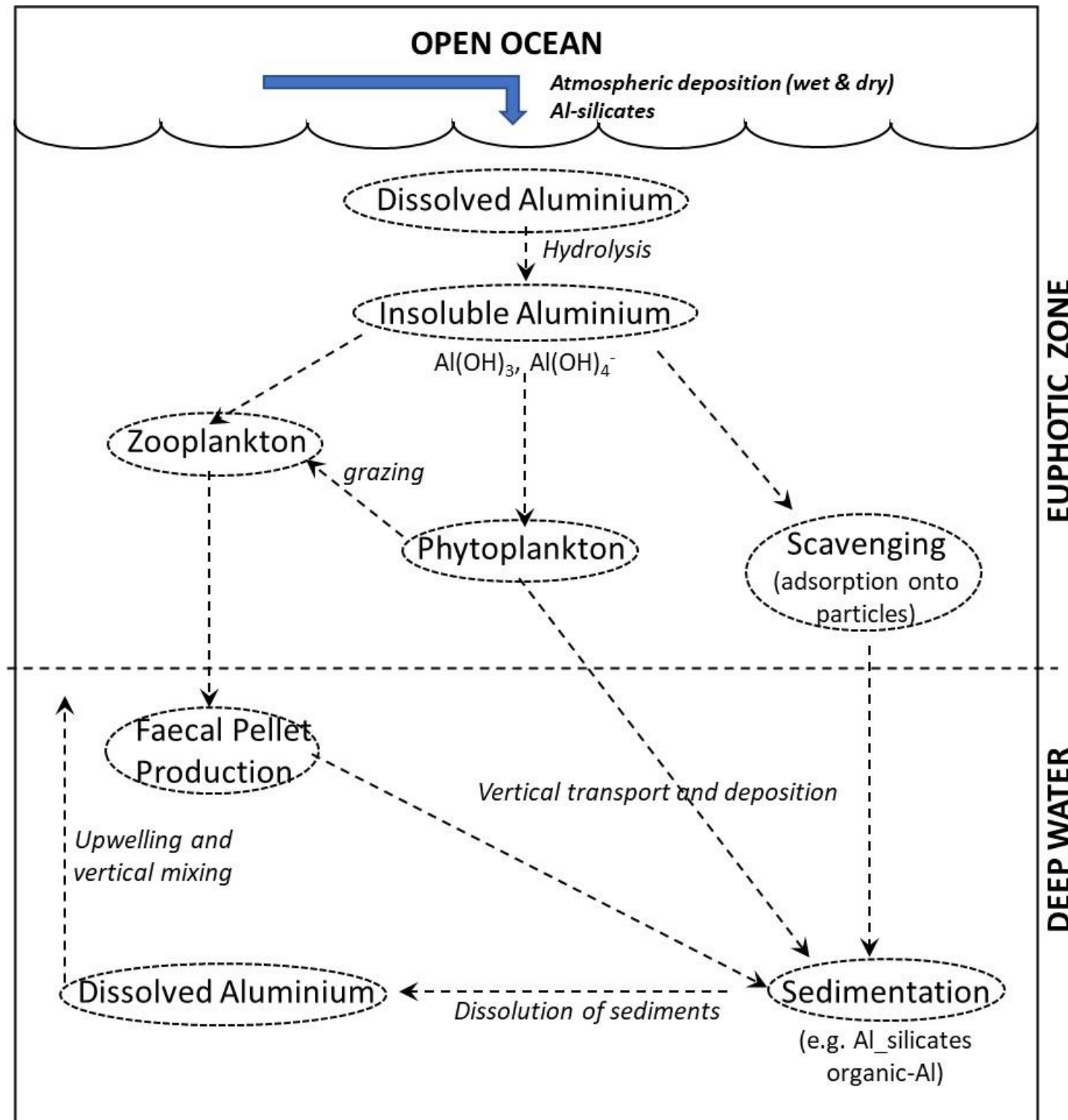
- living organisms (e.g. phytoplankton cells)
- dissolved organic matter (DOM)
- suspended Matter (SM)

↳ sediment ↔ benthos



Transfer of trace metals to different compartments :

- water column
- sediment
- living organisms



Biogeochemical cycle of aluminum according to Tria et al. (2007)

2) Released dissolved trace metals tend to interact with:

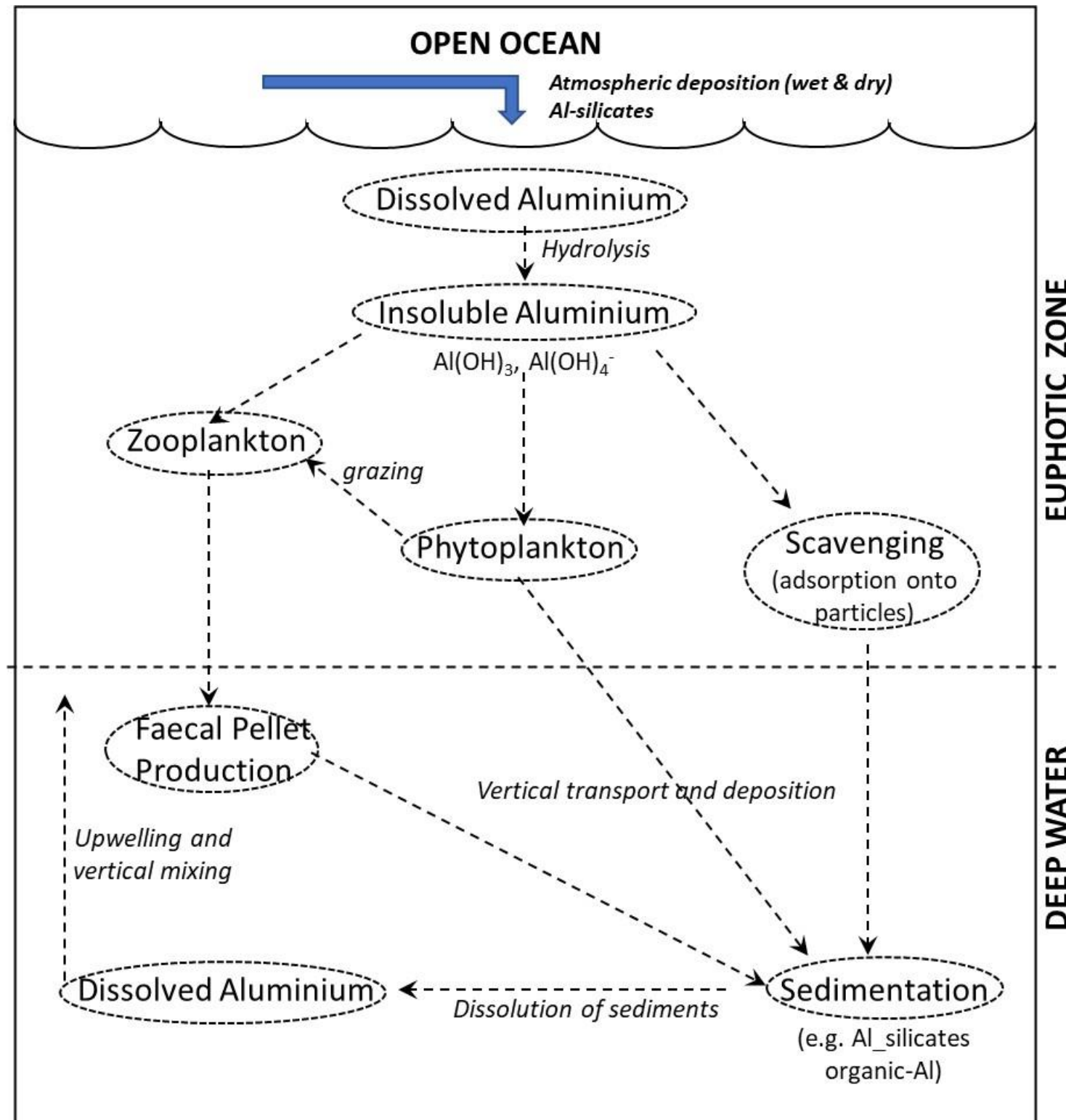
- living organisms (e.g. phytoplankton cells)
- dissolved organic matter (DOM)
- suspended Matter (SM)

↳ sediment ↔ benthos



Study the transfers of ETMs-GACP to different compartments (as described by Tria et al., 2005):

- water column
- sediment
- living organisms



Biogeochemical cycle of aluminum according to Tria et al. (2007)

2) Released dissolved trace metals tend to interact with:

- living organisms (e.g. phytoplankton cells)
- dissolved organic matter (DOM)
- suspended Matter (SM)

↳ sediment ↔ benthos

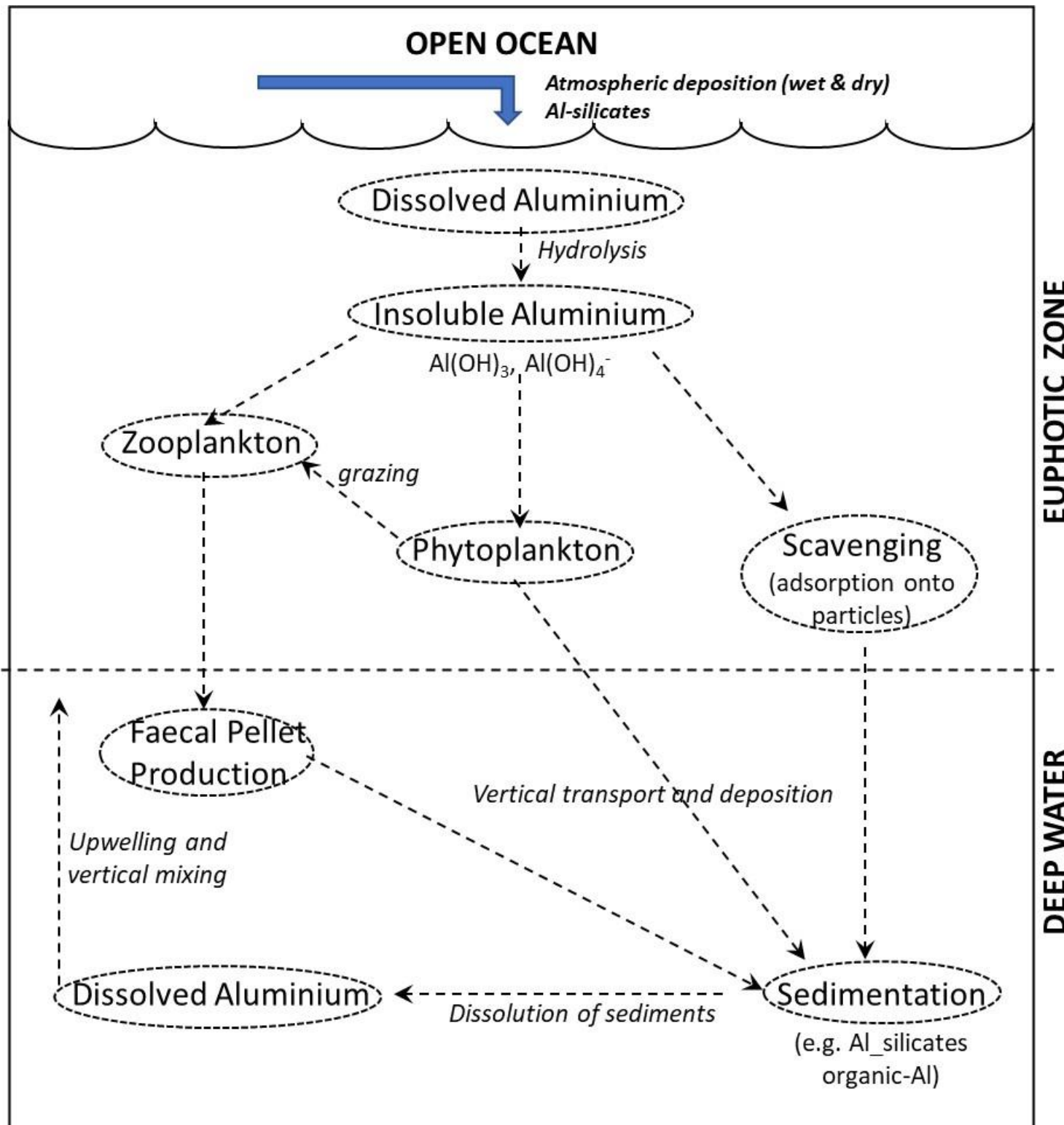


Study the transfers of ETMs-GACP to different compartments (as described by Tria et al., 2005):

- water column
- sediment
- living organisms



Only ecotoxicological results on Al-salt will be presented ...



Biogeochemical cycle of aluminum according to Tria et al. (2007)

2) Released dissolved trace metals tend to interact with:

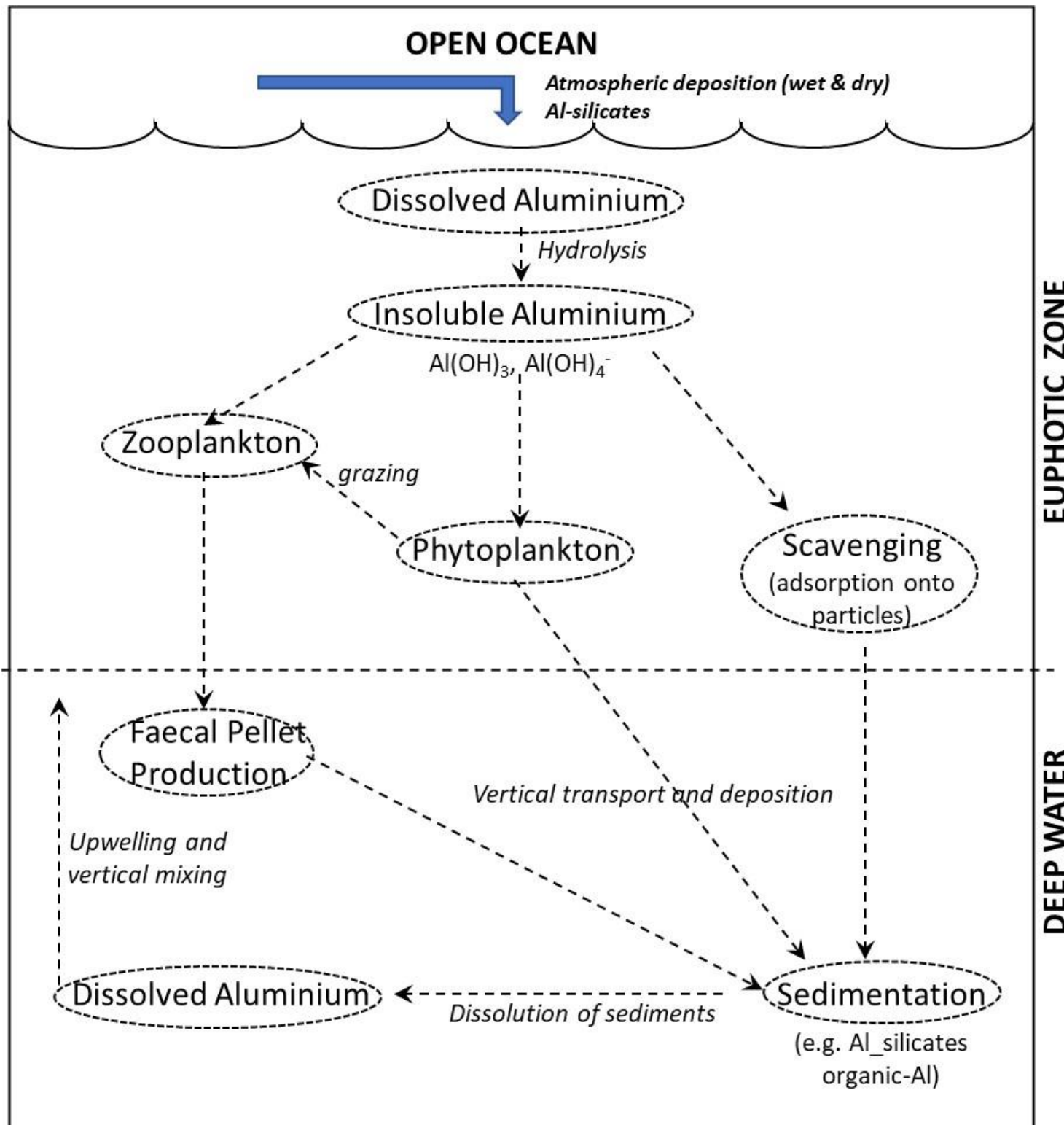
- living organisms (e.g. phytoplankton cells)
- dissolved organic matter (DOM)
- suspended Matter (SM)

↳ sediment ↔ benthos



The physicochemical parameters influence **speciation** of trace elements (e.g. Al): pH, S, [Al]<sub>m</sub>, DOM, SM, organic ligands

...



Biogeochemical cycle of aluminum according to Tria et al. (2007)

2) Released dissolved trace metals tend to interact with:

- living organisms (e.g. phytoplankton cells)
- dissolved organic matter (DOM)
- suspended Matter (SM)

↳ sediment ↔ benthos



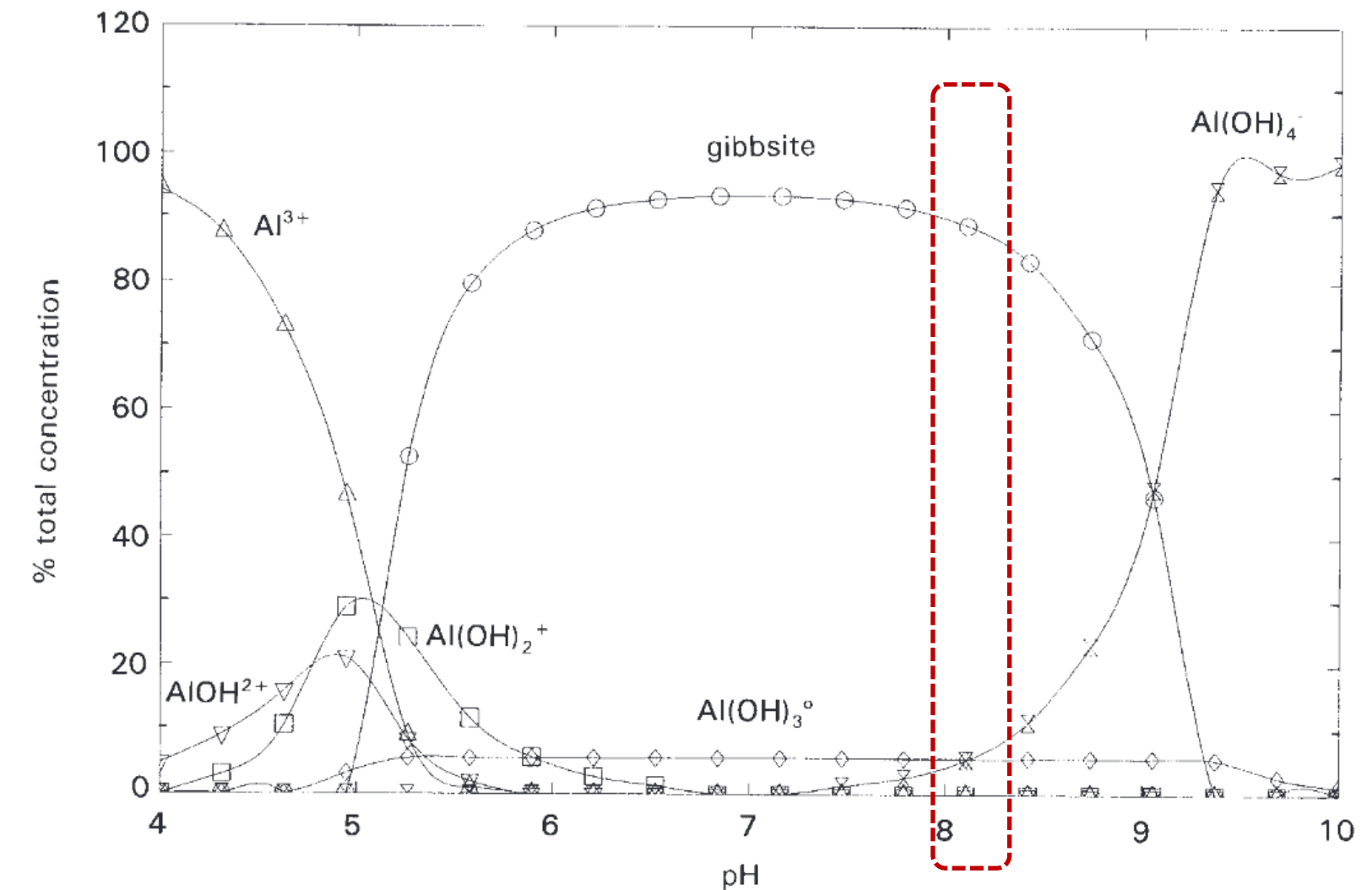
The physicochemical parameters influence **speciation** of trace elements (e.g. Al): pH, S,  $[Al]_m$ , DOM, SM, organic ligands



The speciation of aluminium released in seawater column is complex and need more understanding

## ○ Ecokinetic of Aluminium and Impact of abiotic parameters on its speciation in seawater: REVIEW

The speciation of aluminium in seawater is very different from that in freshwater

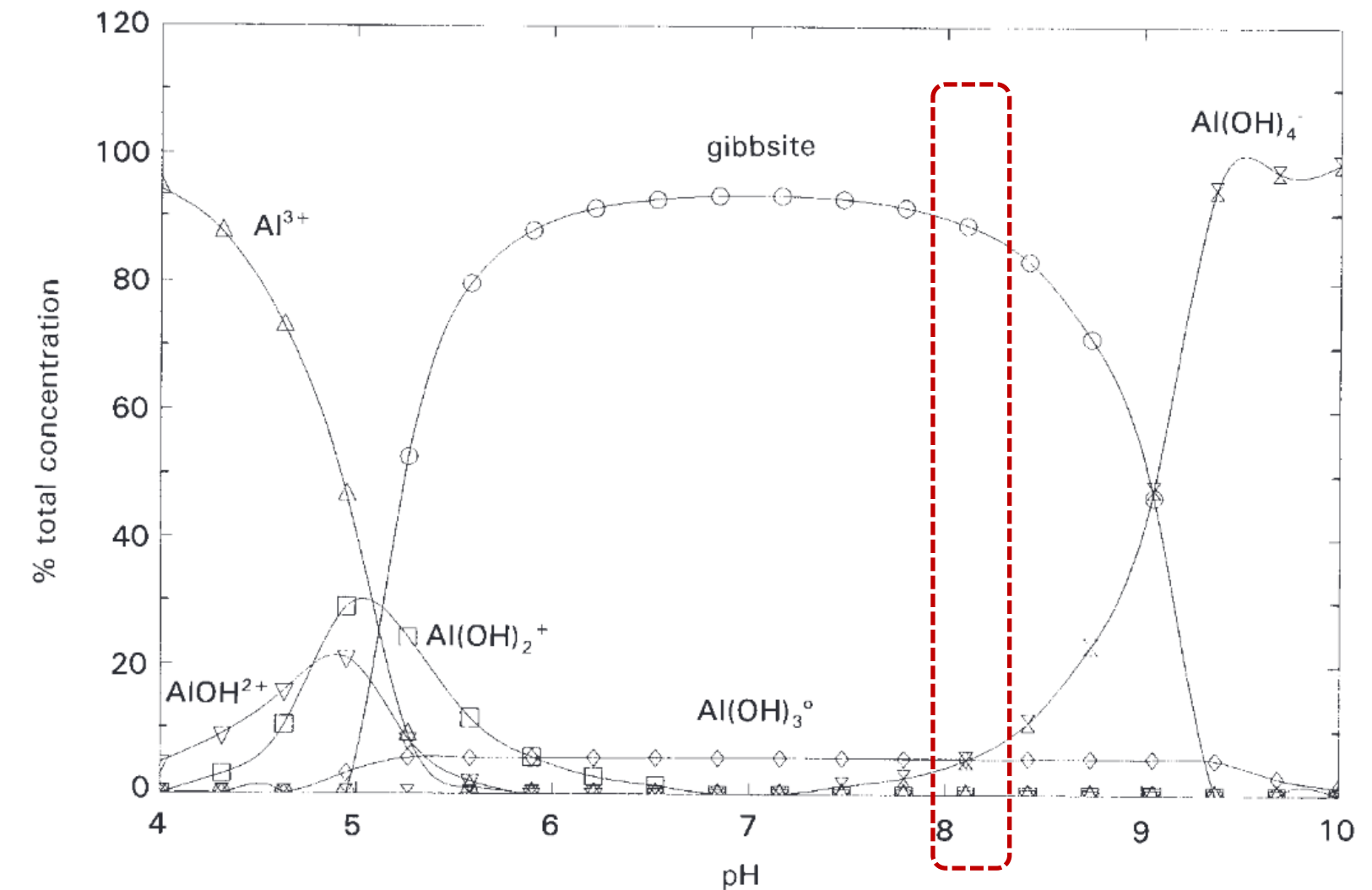


Aluminium speciation depending on pH from Gensemer and Playle (1999)

## ○ Ecokinetic of Aluminium and Impact of abiotic parameters on its speciation in seawater: REVIEW

The speciation of aluminium in seawater is very different from that in freshwater

At **pH 8.2**, the dominant inorganic ligand that complexes it is **OH<sup>-</sup>** (as well as for Fe(III) and In(III)) (Byrne *et al.*, 1988 ; Alberti *et al.*, 2005)



Aluminium speciation depending on pH from Gensemer and Playle (1999)

## ○ Eokinetic of Aluminium and Impact of abiotic parameters on its speciation in seawater: REVIEW

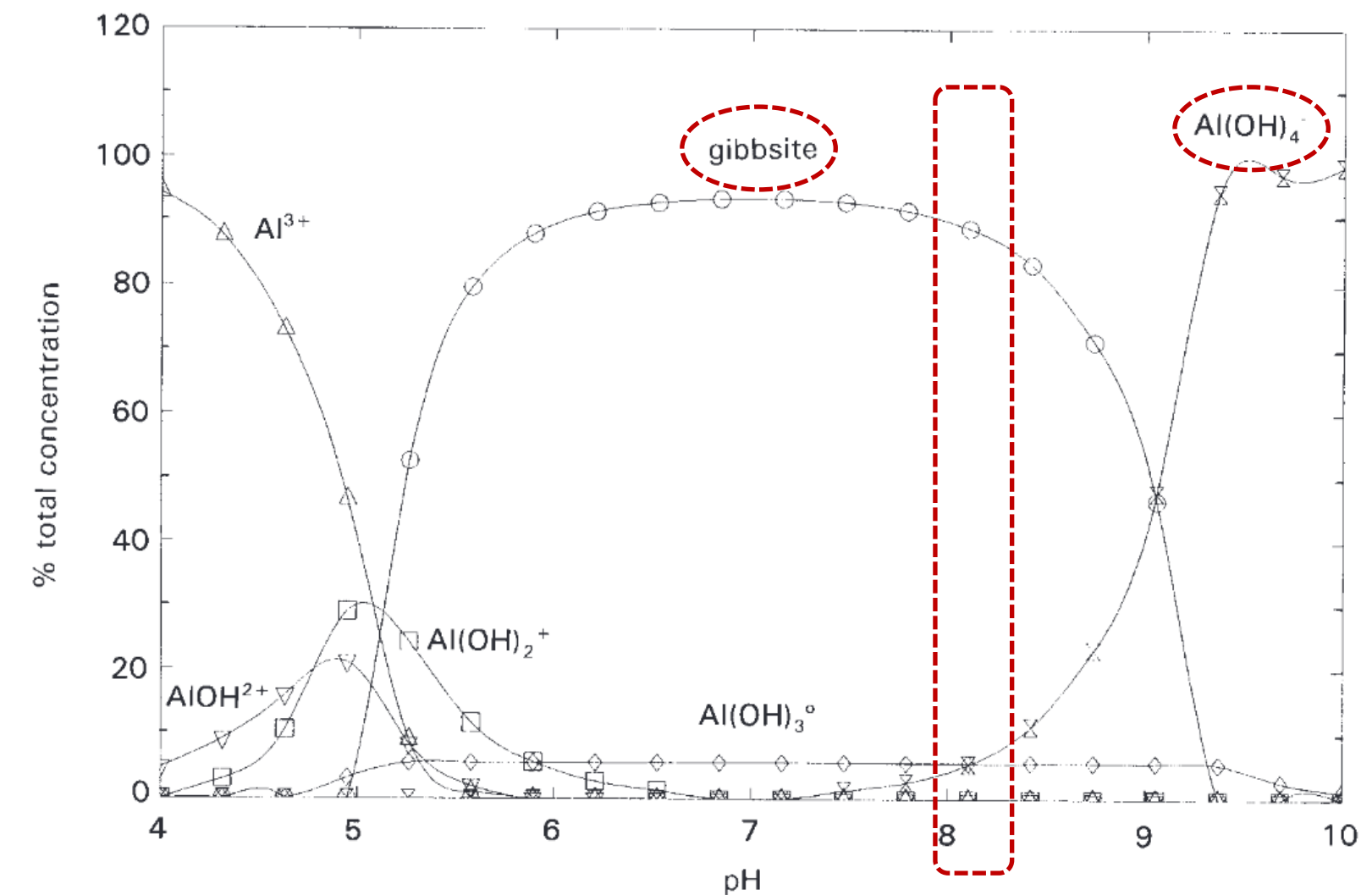
The speciation of aluminium in seawater is very different from that in freshwater

At **pH 8.2**, the dominant inorganic ligand that complexes it is **OH<sup>-</sup>** (as well as for Fe(III) and In(III)) (Byrne *et al.*, 1988 ; Alberti *et al.*, 2005)

Its principally forms of dissolved inorganic aluminium (Millero *et al.*, 2009) are :

68 % aluminate **Al(OH)<sub>4</sub><sup>-</sup>**

32 % colloidal neutral aluminium hydroxide **Al(OH)<sub>3</sub>**



Aluminium speciation depending on pH from Gensemer and Playle (1999)

## ○ Eokinetic of Aluminium and Impact of abiotic parameters on its speciation in seawater: REVIEW

The speciation of aluminium in seawater is very different from that in freshwater

At **pH 8.2**, the dominant inorganic ligand that complexes it is **OH<sup>-</sup>** (as well as for Fe(III) and In(III)) (Byrne *et al.*, 1988 ; Alberti *et al.*, 2005)

Its principally forms of dissolved inorganic aluminium (Millero *et al.*, 2009) are :

68 % aluminate **Al(OH)<sub>4</sub><sup>-</sup>**

32 % colloidal neutral aluminium hydroxide **Al(OH)<sub>3</sub>**

Importance of alkali (Na, K) and alkaline-earth (Ca, Mg) aluminate complexes (Markich, 2021):

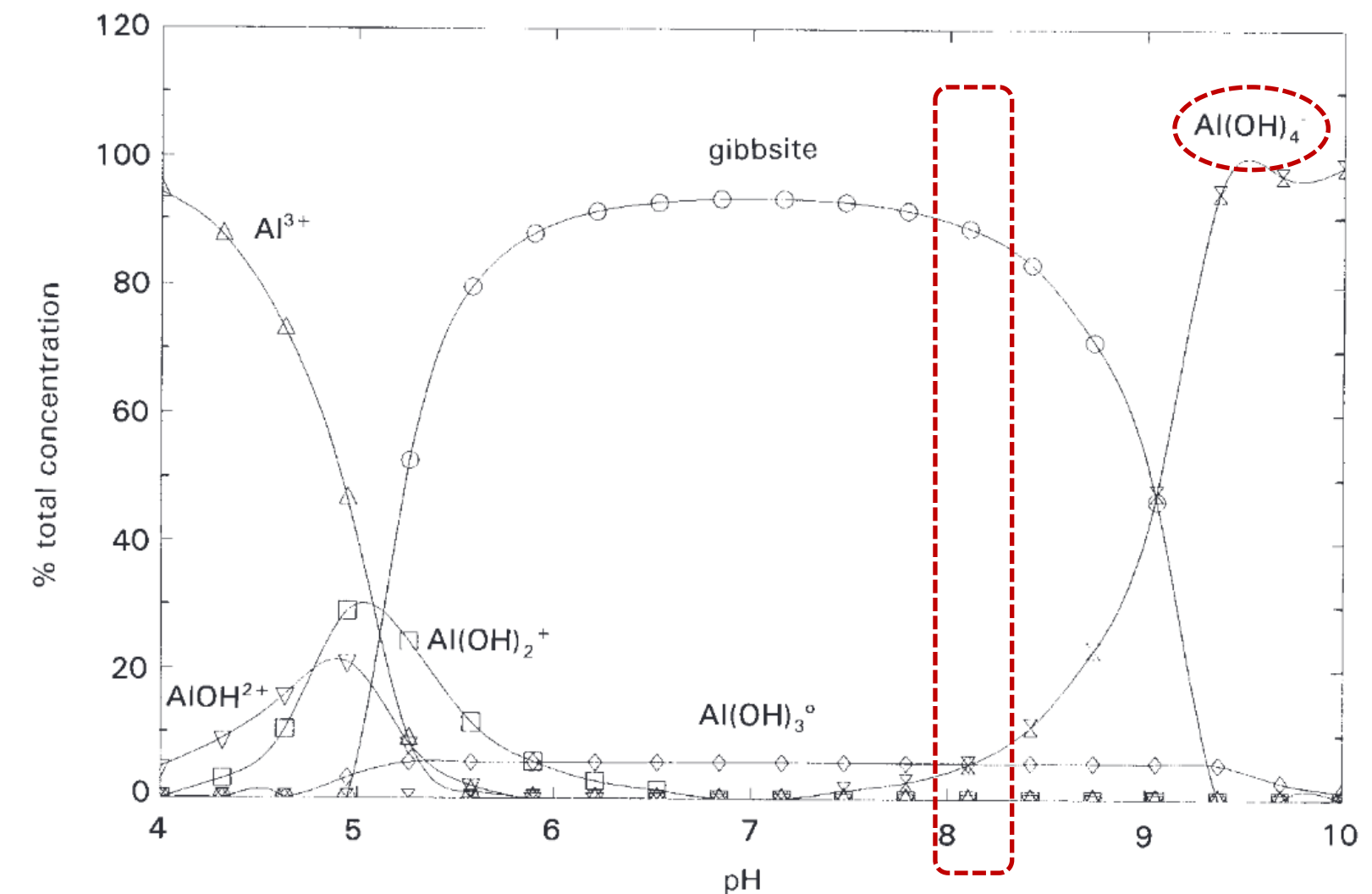
46.4 % aluminate ion **Al(OH)<sub>4</sub><sup>-</sup>**

38.2% Mg-aluminate ion **MgAl(OH)<sub>4</sub><sup>+</sup>**

11% following by Na-aluminate ion **NaAl(OH)<sub>4</sub><sup>-</sup>**

3% Ca-aluminate ion **CaAl(OH)<sub>4</sub>**

< 0.01% **Al<sup>3+</sup>**



Aluminium speciation depending on pH from Gensemer and Playle (1999)

## ○ Eokinetic of Aluminium and Impact of abiotic parameters on its speciation in seawater: REVIEW

The speciation of aluminium in seawater is very different from that in freshwater

At **pH 8.2**, the dominant inorganic ligand that complexes it is **OH<sup>-</sup>** (as well as for Fe(III) and In(III)) (Byrne *et al.*, 1988 ; Alberti *et al.*, 2005)

Its principally forms of dissolved inorganic aluminium (Millero *et al.*, 2009) are :

68 % aluminate **Al(OH)<sub>4</sub><sup>-</sup>**

32 % colloidal neutral aluminium hydroxide **Al(OH)<sub>3</sub>**

Importance of alkali (Na, K) and alkaline-earth (Ca, Mg) aluminate complexes (Markich, 2021):

46.4 % aluminate ion **Al(OH)<sub>4</sub><sup>-</sup>**

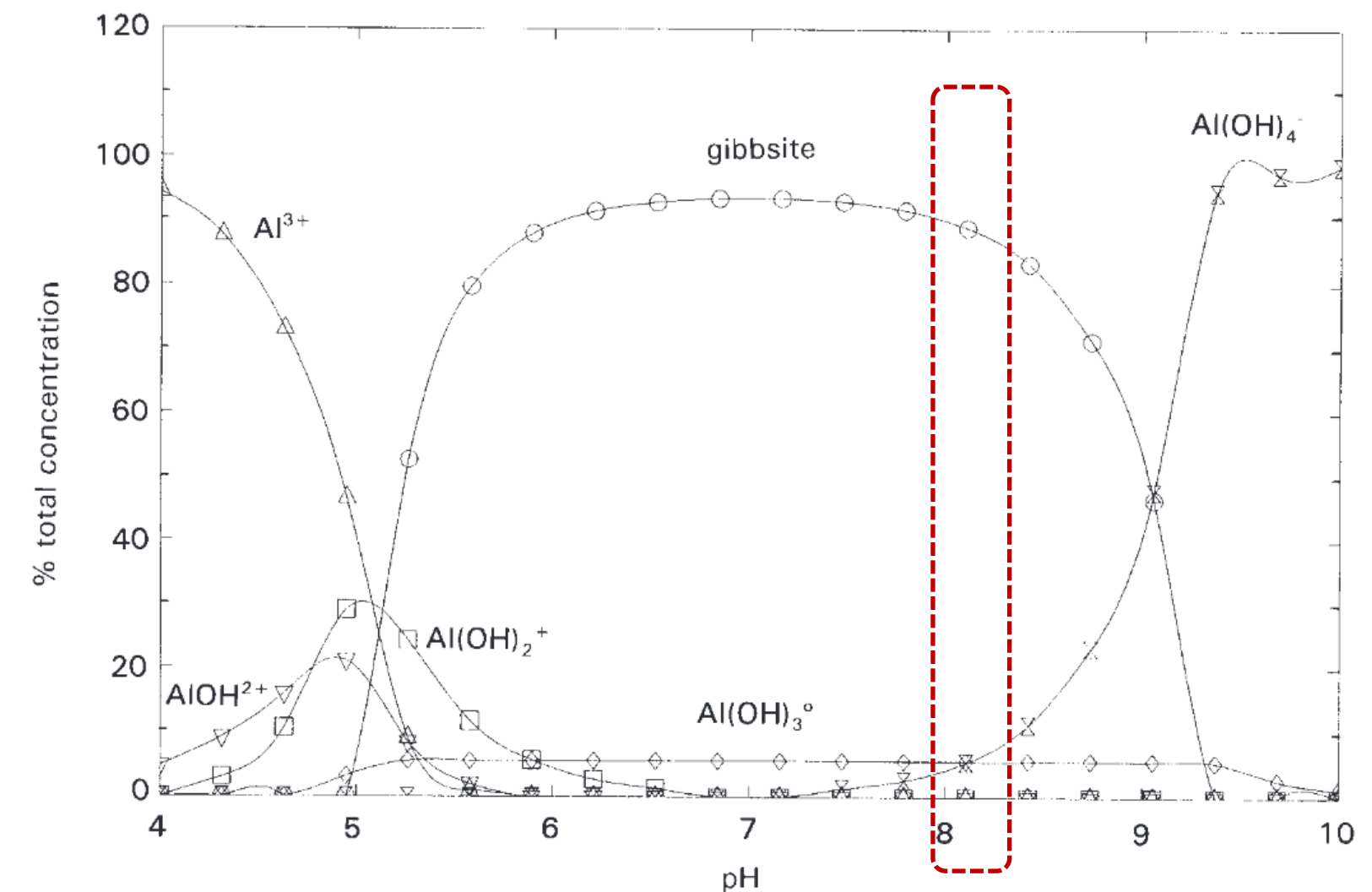
38.2% Mg-aluminate ion **MgAl(OH)<sub>4</sub><sup>+</sup>**

11% following by Na-aluminate ion **NaAl(OH)<sub>4</sub><sup>-</sup>**

3% Ca-aluminate ion **CaAl(OH)<sub>4</sub>**

< 0.01% **Al<sup>3+</sup>**

➔ need to better understand interactions between Al and the different compartments



Aluminium speciation depending on pH from Gensemer and Playle (1999)

○ **Still to be done :**

- Understand the interactions of Al-GACP elements with the suspended matters, organic matter and their bioavailability
- Necessary to develop integrative passive samplers for specific tracers of anode (e.g. In, Ga) and application in OWF
- Monitoring trace metals in SM and sediment in situ :
  - Improved knowledge of the interaction of GACP elements with the sediments
  - Define a **PNEC<sub>sediment</sub>** with adapted ecotoxicological tests (chronic)

- Because ... :

T y <sup>-1</sup> (Watson <i>et al.</i> , 2025)	Europe today (30 GW OWF)	Europe in <b>2050</b>
Al	3219	30 148 to 37 980
Zn	1148	10 756 to 13 550
In	1.2	10.9 to 13.7



Thank you for your attention

