Chemical Oceanography

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Cl^- has been Described as the Ultimate Conservative Tracer

- Highest concentration in SW
- Not biologically depleted
- Not chemically limited
- One of the longest Residence Times (1×10^8 yr)
- Generally pretty boring
- Oceanographers have used Cl^- concentration to define the concentration of ocean water masses
- Concept of Chlorinity = Cl^- ($+ Br^-$) content of SW

Chlorinity (Cl)

- Amount of Cl^-, Br^- and I^- in grams, contained in 1 kg of seawater assuming Br^- and I^- replaced by Cl^-

- The number giving chlorinity in per mille of a seawater sample is by definition identical with the number giving the mass with unit gram of atomic weight silver just necessary to precipitate the halogens in 0.3285234 kg of the seawater sample (Jacobsen & Knudsen, 1940).

Salinity (S)

- Historical Definition - Total amount of solid material, in grams, contained in 1 kg of seawater when all carbonate has been converted to oxide, the bromide and iodine replaced by chlorine, and all organic matter completely oxidized

- Practical Salinity Scale – Conductivity of seawater compared to KCl at 32.4356 g/kg (15 ^{o}C)

Practical Salinity Scale (PSS 1978)

- $R_T = C$ (sample)/C (std seawater)
- C = conductivity at specified temp. & pressure
- Formerly used units of parts per thousand ($^o/_{oo}$)
- Unitless since based on a ratio
- Often see PSU or practical salinity units
- Calibrate instrumentation with SW standard

Absolute Salinity (S_R)

■ SCOR/IAPSO

Scientific Committee on Oceanic Research

International Agency for the Physical Sciences of the Oceans

- WG 127 Thermodynamics & Equations of State of SW

- Density, Enthalpy, Entropy, Potential temp.,Freezing temp.,

- Dissolved oxygen, Alkalinity, TCO_2 , Ca, Silica

$$S_R = (35.16504 / 35) \text{ g/kg x S}$$

Precision in Salinity by Various Methods

1) **Composition Studies of major components**   ± **0.01**

2) **Evaporation to dryness**   ± **0.01**

3) **Chlorinity**   ± **0.002**

4) **Sound Speeds**   ± **0.03**

5) **Density**   ± **0.004**

6) **Conductivity**   ± **0.001**

7) **Refractive index**   ± **0.05**

8) **Inductive Salinometer**

Relationship between Salinity & Chlorinity

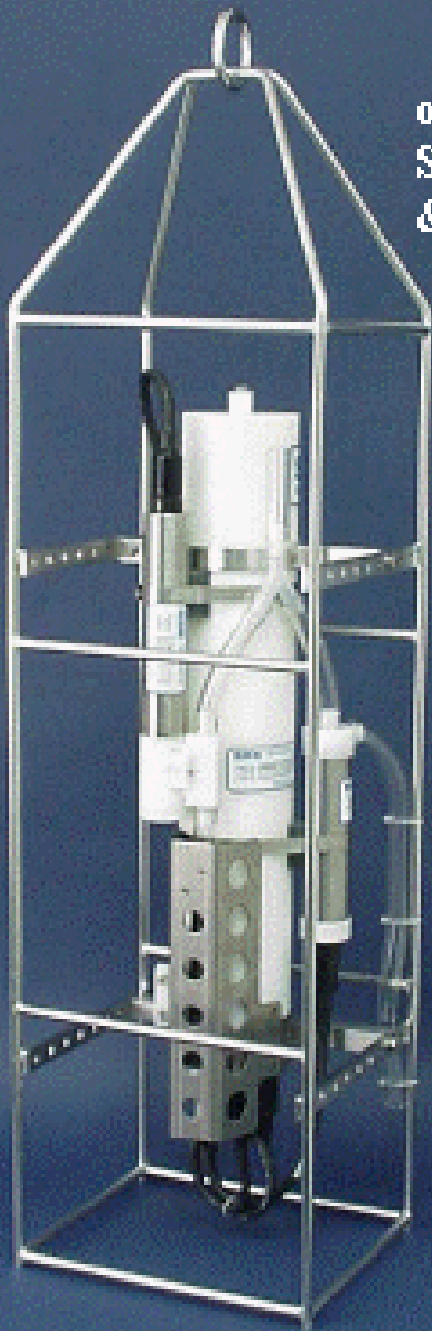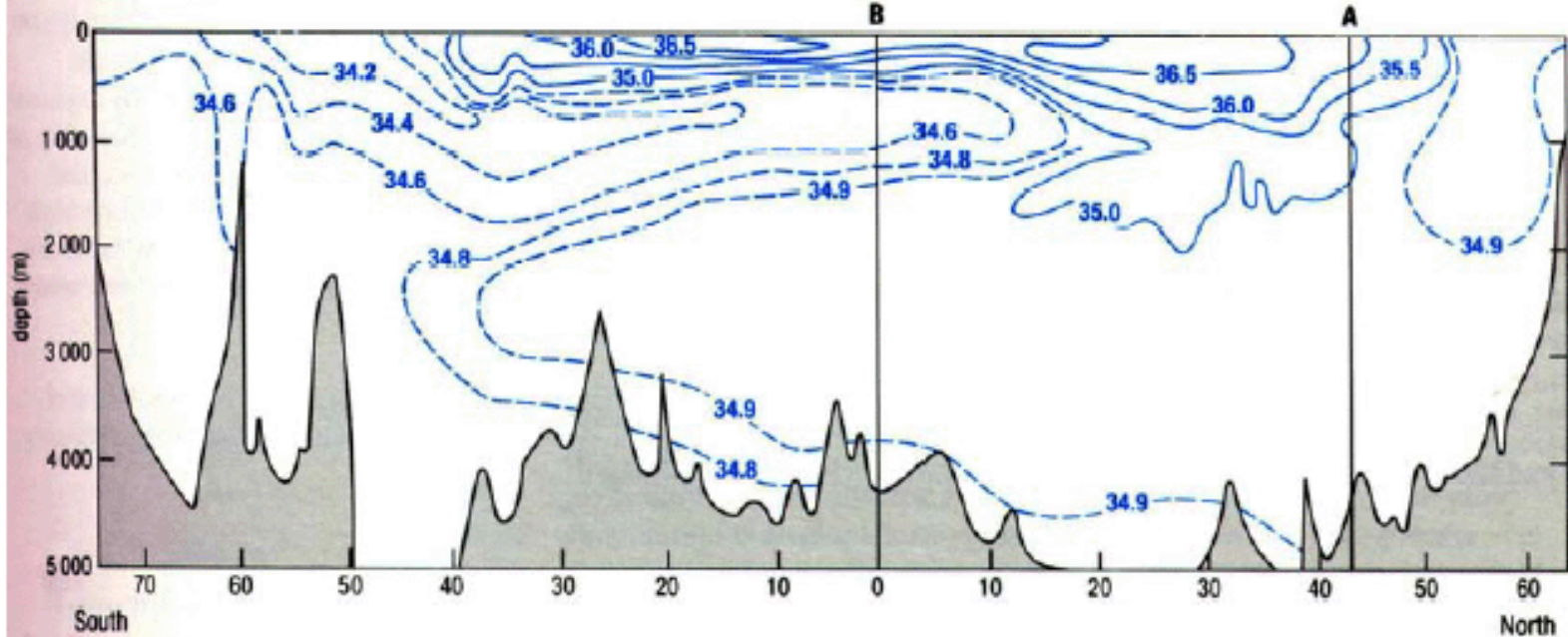**S = 1.80655 Cl**

See Website for Salinity Handouts 1 - 4

CTDs

Shown with optional cage, SBE 5T pump, & SBE 43 DO sensor
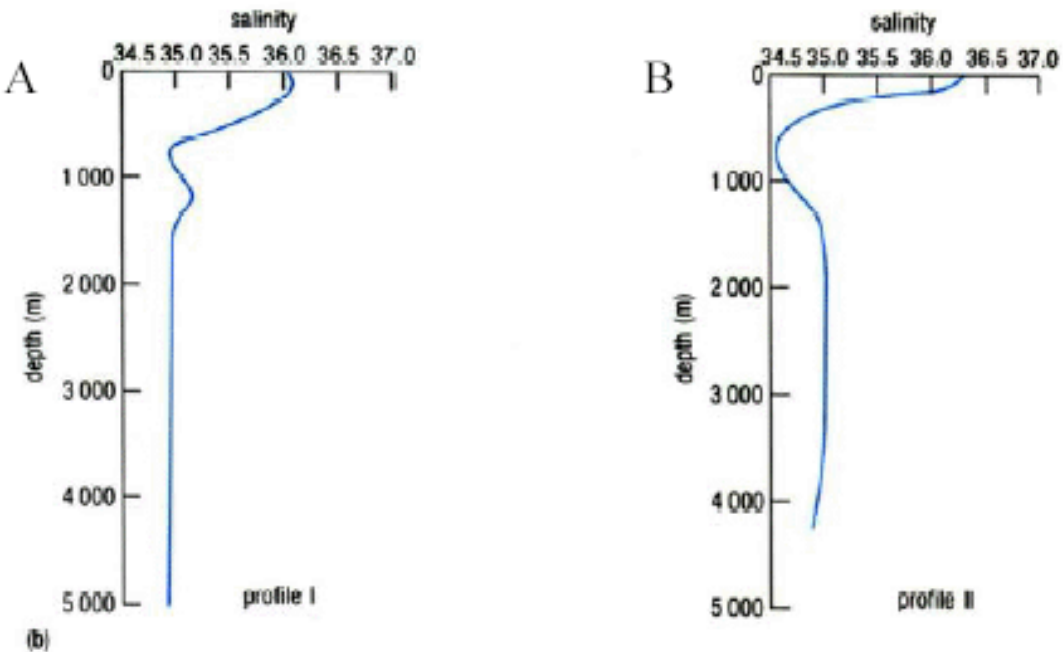
www.seabird.com
www.valeport.co.uk

(a)

A vertical section
showing the mean
distribution of salinity
in the western Atlantic
Ocean, and two
salinity depth profiles
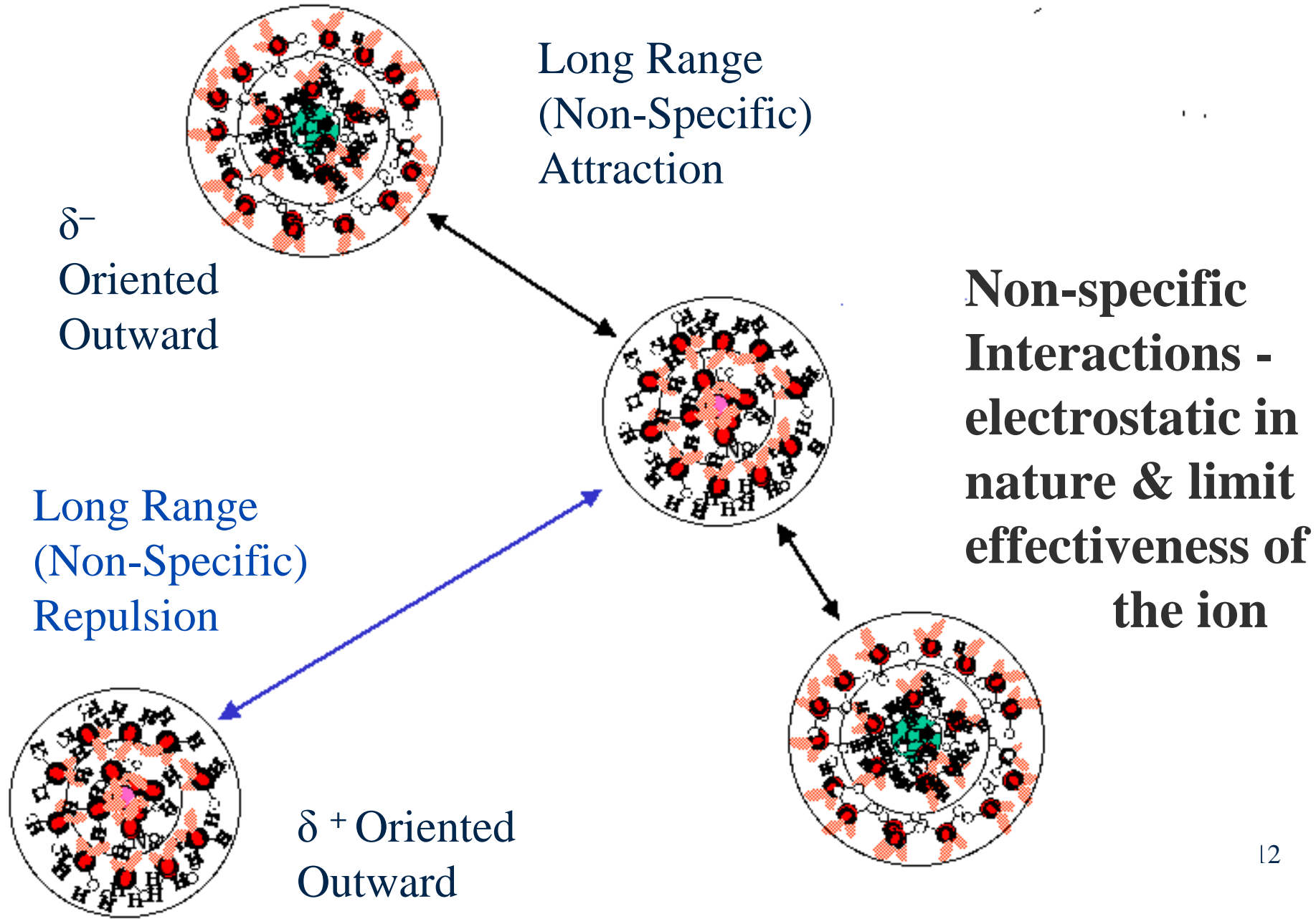corresponding to
locations A and B.

A — profile I

B — profile II

(b)

Ion-Ion Interactions

- Many types – non-specific, bonding, contact, solvent shared, solvent separated

- Non-specific i.e., long range interactions and the concepts of ionic strength, activity & activity coefficient

- Specific interactions e.g. complexation, ion pairing (strong or weak)

- Millero cartoons

http://fig.cox.miami.edu/~lfarmer/MSC215/MSC215.HTM

Long Range
(Non-Specific)
Attraction

δ^-
Oriented
Outward

Long Range
(Non-Specific)
Repulsion

δ^+ Oriented
Outward

**Non-specific
Interactions -
electrostatic in
nature & limit
effectiveness of
the ion**

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Non-specific Interaction

- Electrostatic in nature

- Limits effectiveness of ion in solution

- Use concept of **activity** to quantify effect

(accounting for non-ideal behavior in solution)

$$\mathbf{a_i = [i]_F \; \gamma_F(i)} \qquad \text{where } a_i = \text{activity of ion i}$$

$$[i]_F = \text{free ion conc. (m or M)}$$

$$\gamma_F(i) = \text{activity coefficient}$$

In short $\boxed{\mathbf{a = [i] \; \gamma}}$ $\qquad$ of ion I $\quad (\leq 1)$

Activity of Individual Ions is Influenced by Other Ions

Therefore we must know amount or concentration of all ions

■ Ionic Strength of solution

$$I = 0.5 \, \Sigma \, Z^2 \, m$$

where I = ionic strength

Z = charge on ion

m = molal conc.

$$a = [i] \, \gamma$$

Activity Coefficient (γ)

- Debye-Huckel Theory is starting point

   (Primarily for very low ionic strength)

$$\ln \gamma\pm = - A \, Z^2 \, I^{0.5} \qquad \text{original D.H.}$$

   or

$$\ln \gamma\pm = - S_f \, I^{0.5} \, /(1 + A_f \, a \, I^{0.5}) \qquad \text{extended}$$

Where $\gamma\pm$ is the mean ion activity coefficient

   S_f, A & A_f are constants related to temperature

I is ionic strength & a is the ion size parameter in Å

Z is the charge on the ion

Activity Coefficient (γ)

- Guntelberg Approximation

$$\ln \gamma\pm = - A\ Z^2\ [I^{0.5}/(1 + I^{0.5})]$$

Where $\gamma\pm$ is the mean ion activity coefficient

A is a constant

I is ionic strength

Z is the charge on the ion

Useful for
$I \geq 0.1$

Activity Coefficient (γ)

■ Davies Equation

$$\ln \gamma\pm = - A\, Z^2\, [I^{0.5}/(1 + I^{0.5}) - 0.2\, I]$$

Where γ± is the mean ion activity coefficient

A is a constant (= 1.17)

I is ionic strength

Z is the charge on the ion

Useful for
I ~ 0.5

Activity Coefficient (γ)

- Bronsted-Guggenheim

$$\ln \gamma\underline{+} = \ln \gamma_{DH} + \sum_j B_{ij}[j] + \sum_j \sum_k C_{ijk}[j][k] + \ldots$$
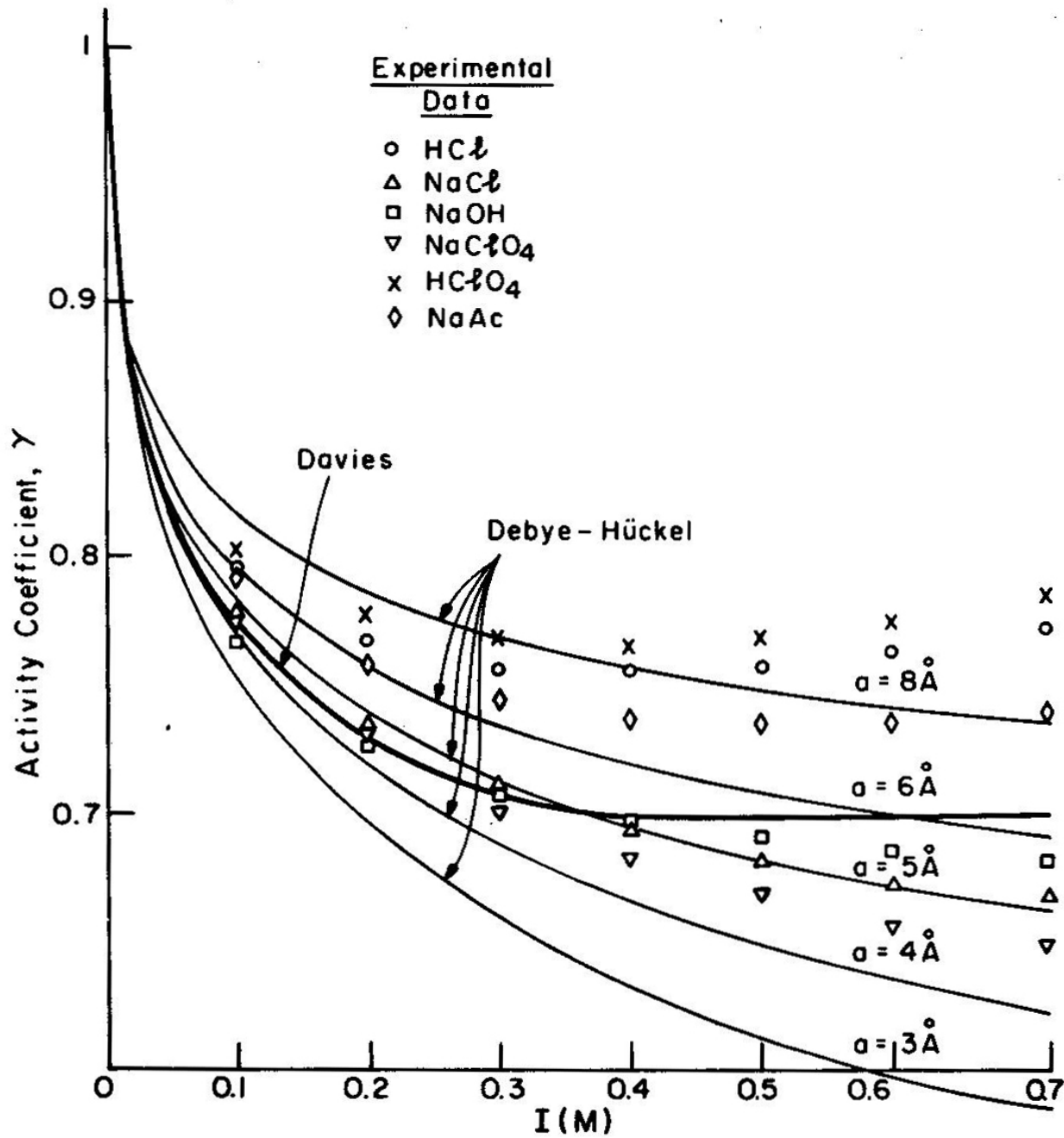
Where $\gamma\underline{+}$ is the mean ion activity coefficient

   γ_{DH} is the γ from Debye-Huckel
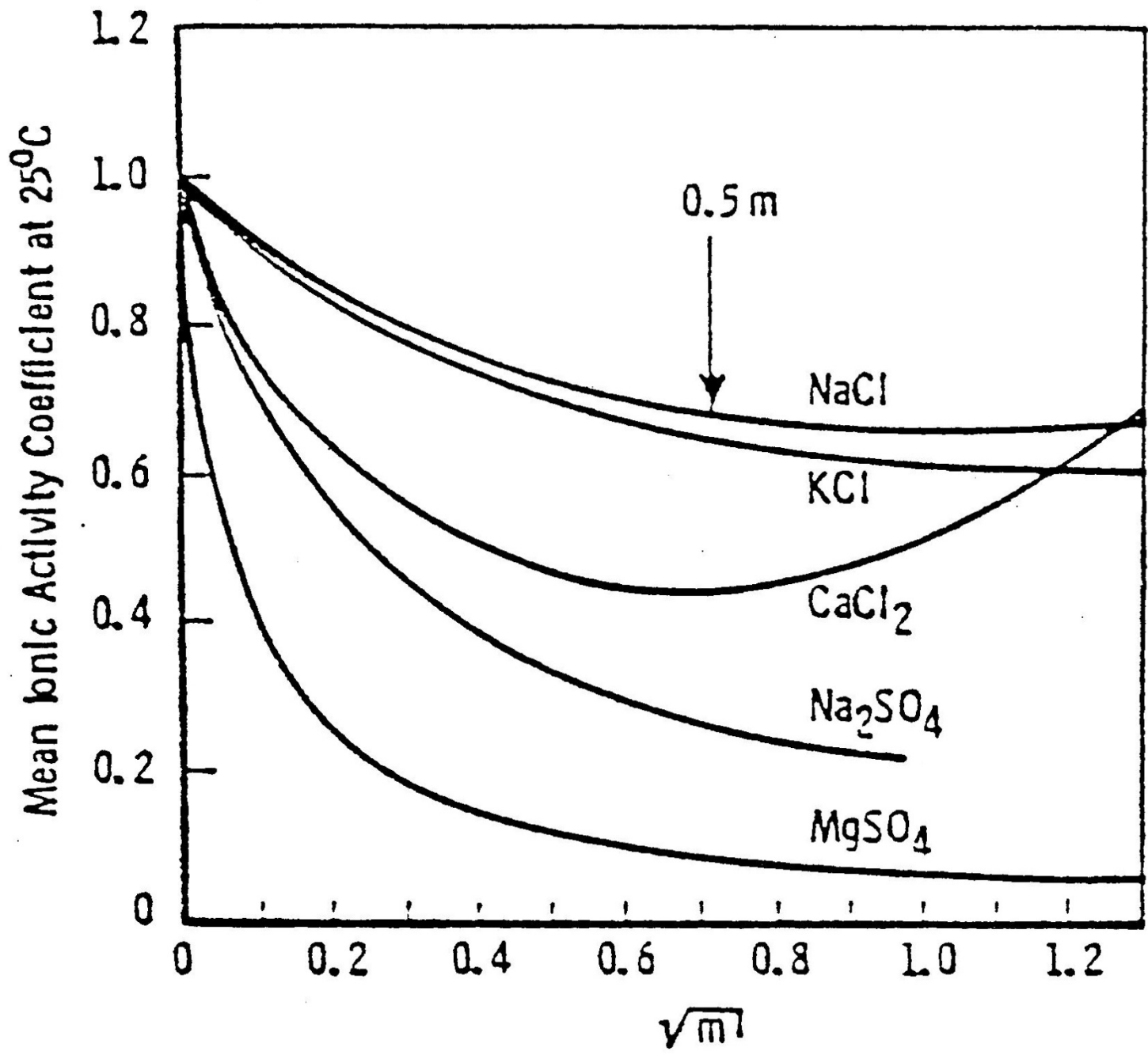
B_{ij} is a virial coefficient for ion pairs

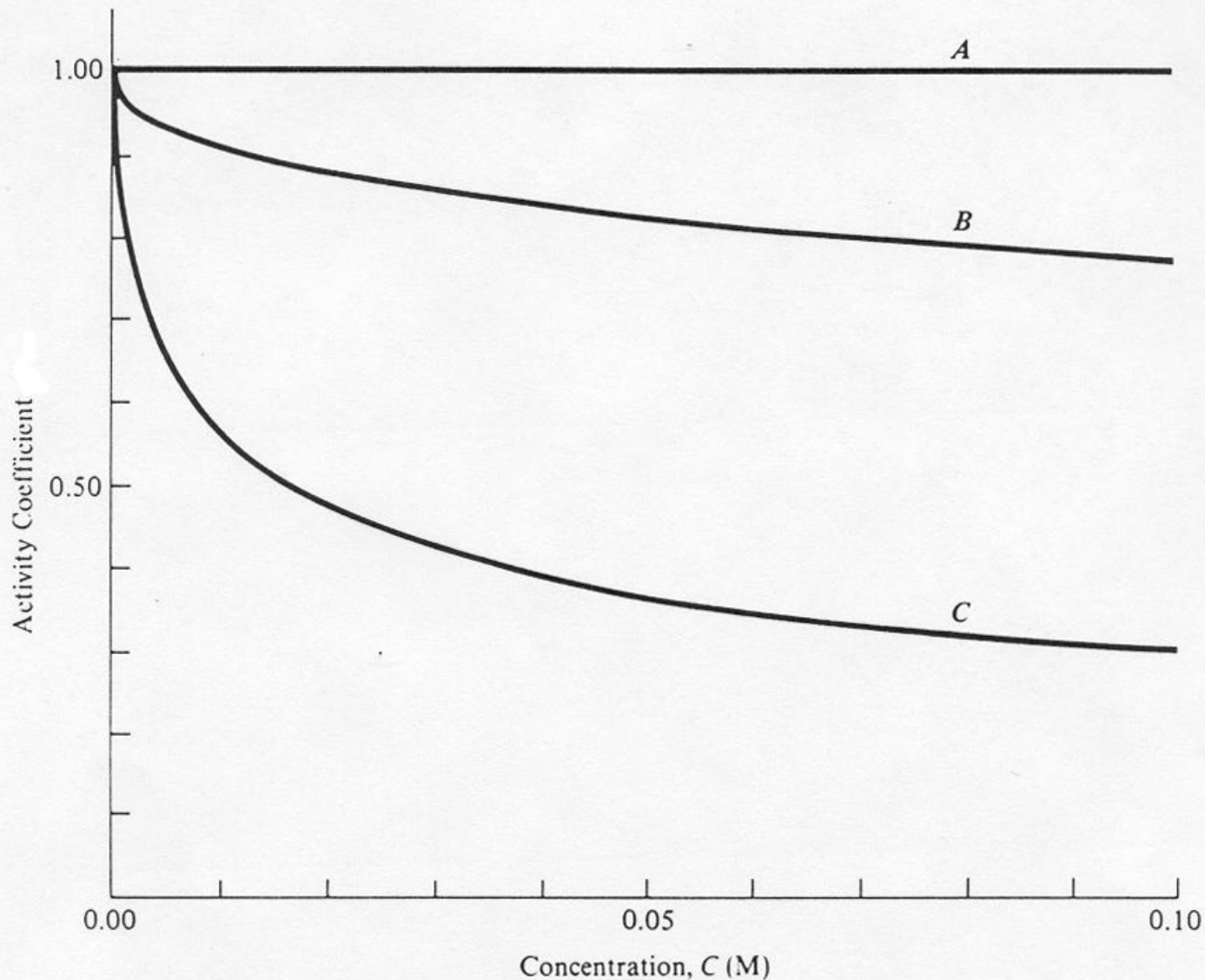C_{ijk} is a virial coefficient for three ions

Useful at any I

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Comparison of Davies Equation & Extended Debye-Huckel for monovalent Ions

Morel & Hering 1993

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Activity Coefficient vs. Conc., Monovalent & Divalent Systems

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Activity
Coefficient
vs. Conc.,
Ideal,
Monovalent
& Divalent
Systems

(Kennedy 1990)

FIGURE 4-2 Activity coefficient as a function of concentration in the solution: (A) ideal solution for which $\gamma = 1.00$ at all concentrations: (B) activity coefficient for Na^+ in NaCl solutions; (C) activity coefficient for Ca^{2+} in $CaCl_2$ solution.

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Activity
vs. Conc., Ideal,
Monovalent & Divalent
Systems

(Kennedy 1990)
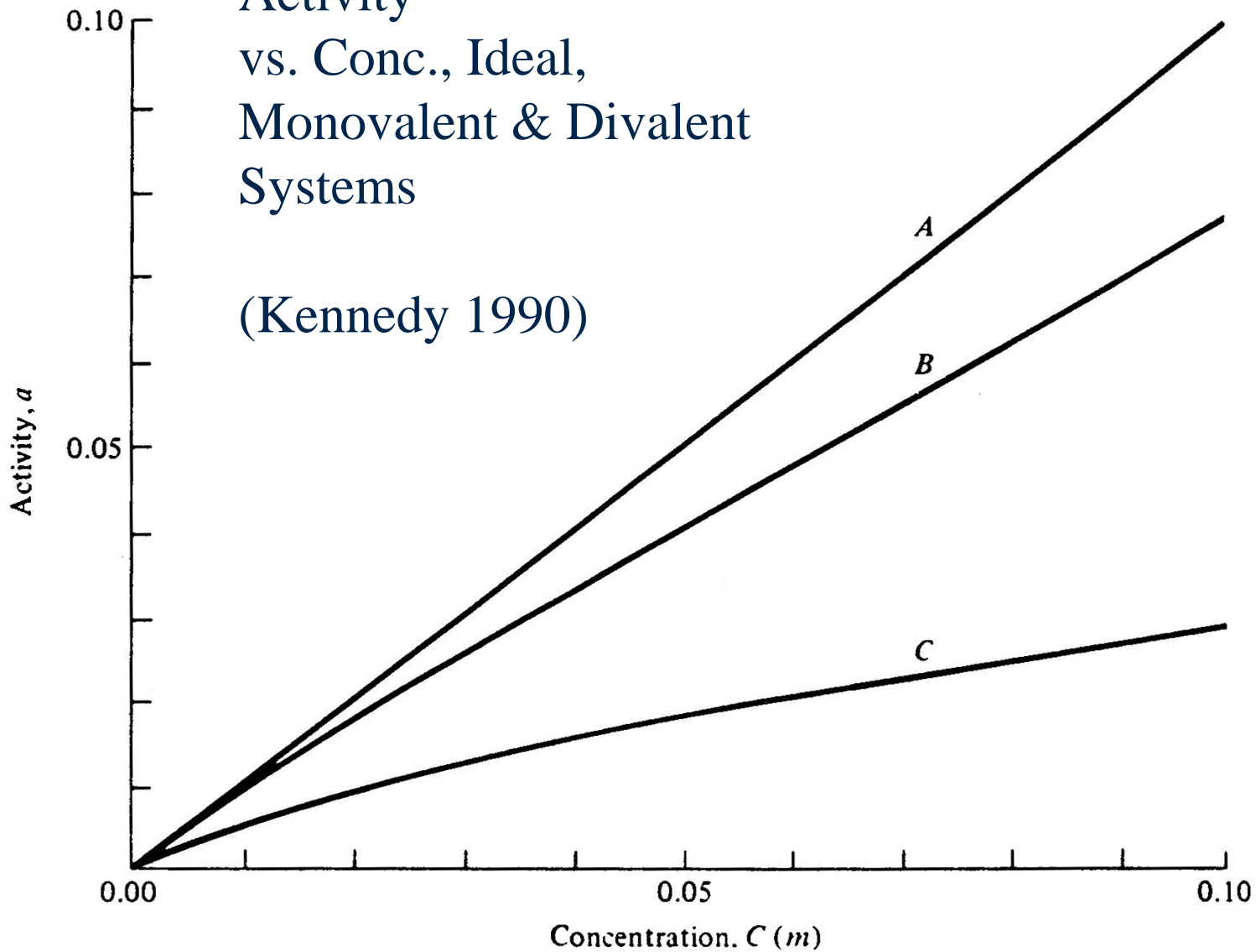
FIGURE 4-1 Activity as a function of concentration: (A) ideal solution for which $a = C$; (B) Na^+ activity in $NaCl$; (C) Ca^{2+} activity in $CaCl_2$.

Putting It All Together

- Calculate ionic strength from concentrations of all ions in solution using $I = 0.5 \, \Sigma \, Z^2 \, m$

- Use Davies Equation to calculate activity coefficients for all ions of interest (Z = 1,2,3,4)

$$\ln \gamma\pm = - A \, Z^2 \, [I^{0.5}/(1 + I^{0.5}) - 0.2 \, I]$$

- Calculate activity of the ions of interest using their concentrations and activity coefficients

$$a = [i] \, \gamma$$

Example: pH of SW

pH is defined as the negative
logarithm of the hydrogen ion activity

$$\textbf{pH = -log a}_{\textbf{H+}}$$

At a typical ionic strength of seawater **I = 0.7**

From Davies Equation H$^+$ activity coefficient

$$\textbf{ln } \gamma \textbf{ = - A Z}^2 \, \textbf{[I}^{0.5}\textbf{/(1 + I}^{0.5}\textbf{) – 0.2 I]}$$

If Z = 1 & A = 1.17 then ln γ = -0.37 & **γ = 0.69**

(using 0.3 in the Davies Equation gives γ = 0.75)

Example: pH (cont.)

If a typical seawater pH is 8.2

Then H^+ activity is $1 \times 10^{-8.2}$ or 6.31×10^{-9} M

From **a = [i]γ** or $a_{H+} = [H^+]\gamma_{H+}$ & calculated $\gamma = 0.69$

$$6.31 \times 10^{-9} \text{ M} = [H^+] \times 0.69$$

$$[H^+] = 9.14 \times 10^{-9} \text{ M}$$

Activity of H^+ is 31% lower than it's concentration

Effectiveness of H^+ is 31% lower due to crowding

This phenomenon is greater for divalent ions

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