

Activity and Concentration

- **Activity** – “effective concentration”
- **Ion-ion and ion-H₂O interactions** (hydration shell) cause number of ions available to react chemically ("free" ions) to be less than the number present
- Concentration can be related to activity using the activity coefficient γ , where $[a] = \gamma (c)$

Until now we have assumed that activity, a , is equal to concentration, c , by setting $\gamma = 1$ when dealing with dilute aqueous solutions...

But ions don't behave ideally . . .

- Concentration related to activity using the activity coefficient γ , where $[a] = \gamma (c)$
- The value of γ depends on:
 - Concentration of ions and charge in the solution
 - Charge of the ion
 - Diameter of the ion
- Ionic strength, I = concentration of ions and charge in solution

$$I = 1/2 \sum m_i z_i^2$$

- where m_i = concentration of each ion in moles per L,
 z_i = charge of ion
- Activity coefficient $\gamma_z \rightarrow 1$ as concentrations $\rightarrow 0$ and tend to be <1 except for brines

Calculation of Ionic Strength

$$I = 1/2 \sum m_i z_i^2$$

$$I = 0.5[(\text{HCO}_3^-) \cdot 1^2 + (\text{SO}_4^{2-}) \cdot 2^2 + (\text{Cl}^-) \cdot 1^2 + (\text{NO}_3^-) \cdot 1^2 + (\text{Ca}^{2+}) \cdot 2^2 + (\text{Mg}^{2+}) \cdot 2^2 + (\text{Na}^+) \cdot 1^2 + (\text{K}^-) \cdot 1^2 + (\text{Fe}^{2+}) \cdot 2^2 + (\text{SiO}_2) \cdot 0^2]$$

Substituting values for Lake Superior

$$I = 0.5(0.00082 \cdot 1^2 + 0.00005 \cdot 2^2 + 0.00004 \cdot 1^2 + 0.000008 \cdot 1^2 + 0.00035 \cdot 2^2 + 0.00015 \cdot 2^2 + 0.00013 \cdot 1^2 + 0.00001 \cdot 1^2 + 0.000006 \cdot 2^2 + 0.00007 \cdot 0^2)$$

I = 0.0016 — How does this value compare with other natural waters?

Water	Typical Ionic Strength
Rivers and lakes	0.001 - 0.005
Potable groundwater	0.001 - 0.02
Seawater	0.7
Oil field brines	>5

Sources for ions in natural waters?

TABLE 4-10 Characteristics of Subsurface Waters of Low Mineral Content Associated with Common Rock Types

Rock types	Water characteristics
Granite, rhyolite	Low total ion content; dominant ions Na^+ , HCO_3^- ; pH 6.3 to 7.9; SiO_2 content moderate to high
Gabbro, basalt	Moderate total ion content; dominant ions Ca^{2+} , Mg^{2+} , HCO_3^- ; pH 6.7 to 8.5; SiO_2 content high
Sandstone, arkose, graywacke	High total ion content; dominant ions Ca^{2+} , Mg^{2+} , Na^+ , HCO_3^- ; pH 5.6 to 9.2; SiO_2 content low to moderate
Siltstone, clay, shale	High total ion content; dominant ions Na^+ , Ca^{2+} , Mg^{2+} , HCO_3^- ; SO_4^{2-} , Cl^- ; pH 4.0 to 8.6; SiO_2 content low to moderate
Limestone, dolomite, marble	High total ion content; dominant ions Ca^{2+} , Mg^{2+} , HCO_3^- ; pH 7.0 to 8.2; SiO_2 content low
Slate, schist, gneiss	Low to moderate total ion content; dominant ions HCO_3^- ; Ca^{2+} , Na^+ ; pH 5.2 to 8.1; SiO_2 content low

Source: Data from White et al. (1963).

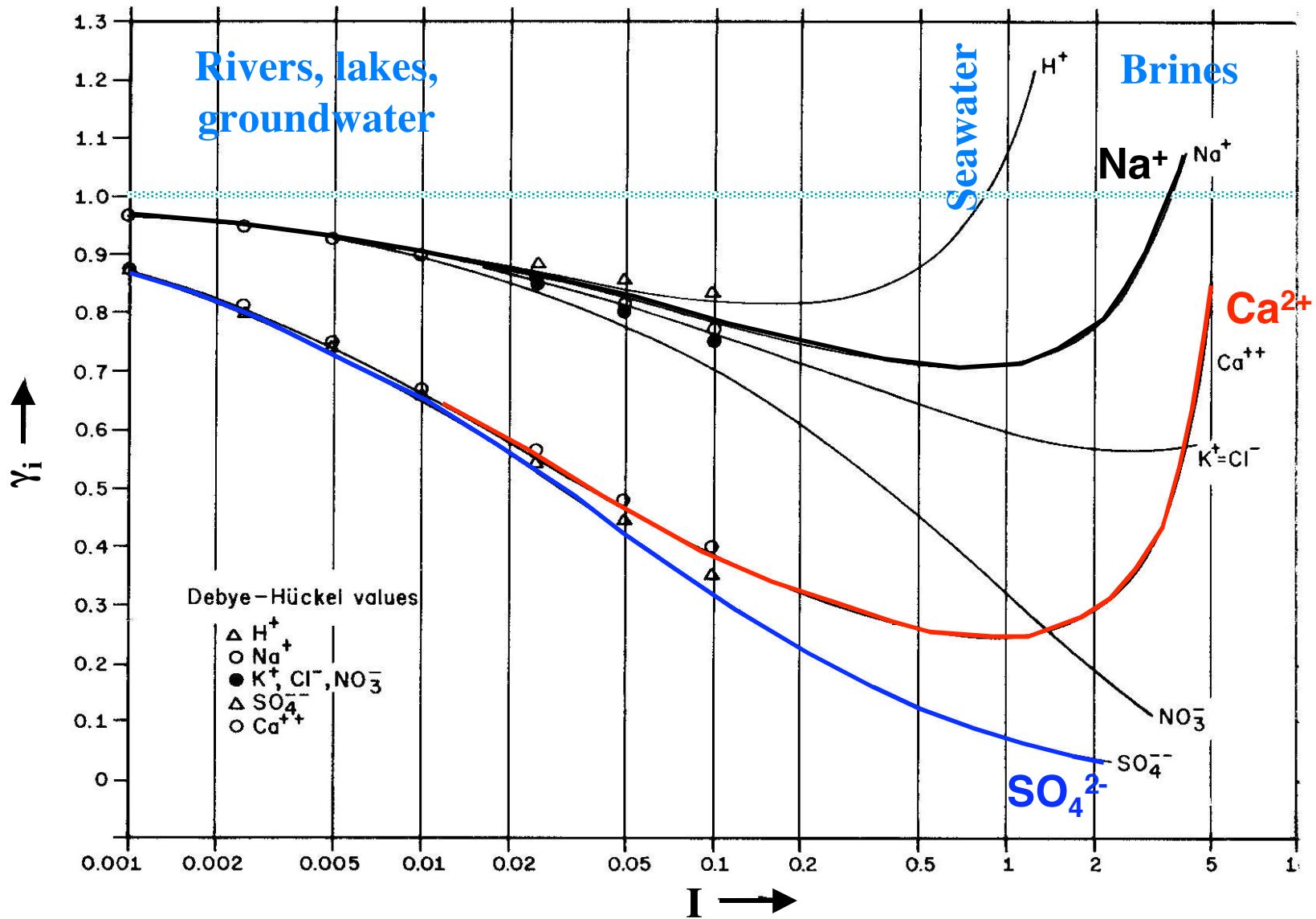


FIG. 2.15. Single ion activity coefficients vs. ionic strength for some common ions. Solid lines represent the values calculated by the mean salt method. Debye-Hückel values were calculated using equation (2.76), with $10^8/a_i^{\circ} = 9$ for H^+ ; 4 for Na^+ ; 3 for K^+ , Cl^- , NO_3^- ; 6 for Ca^{++} ; and 4 for SO_4^{2-} . The Debye-Hückel γ_i values for the monovalent ions converge, within experimental error, for $I < 0.01$.

(from Garrels and Christ, 1965)

Solution Models

- Debye-Hückel Equation

Physical model based on electrostatic interactions

$$\log \gamma_i = -Az_i^2 (I)^{1/2}$$

- At higher ionic strength, use extended Debye-Hückel equation

$$\log \gamma_i = \frac{-Az_i^2 (I)^{1/2}}{1 + Ba_o(I)^{1/2}}$$

- Davies Equation

for higher ionic strengths (<0.5)

$$\log \gamma_i = \frac{-Az_i^2 (I)^{1/2}}{1 + (I)^{1/2}} + 0.3I$$

where I is the ionic strength of the solution as defined above; z is the charge of the ion whose activity coefficient is being calculated; A and B are constants whose values depend on the dielectric constant of the solvent and the temperature; and a is the effective diameter of the ion in the solution in Å.

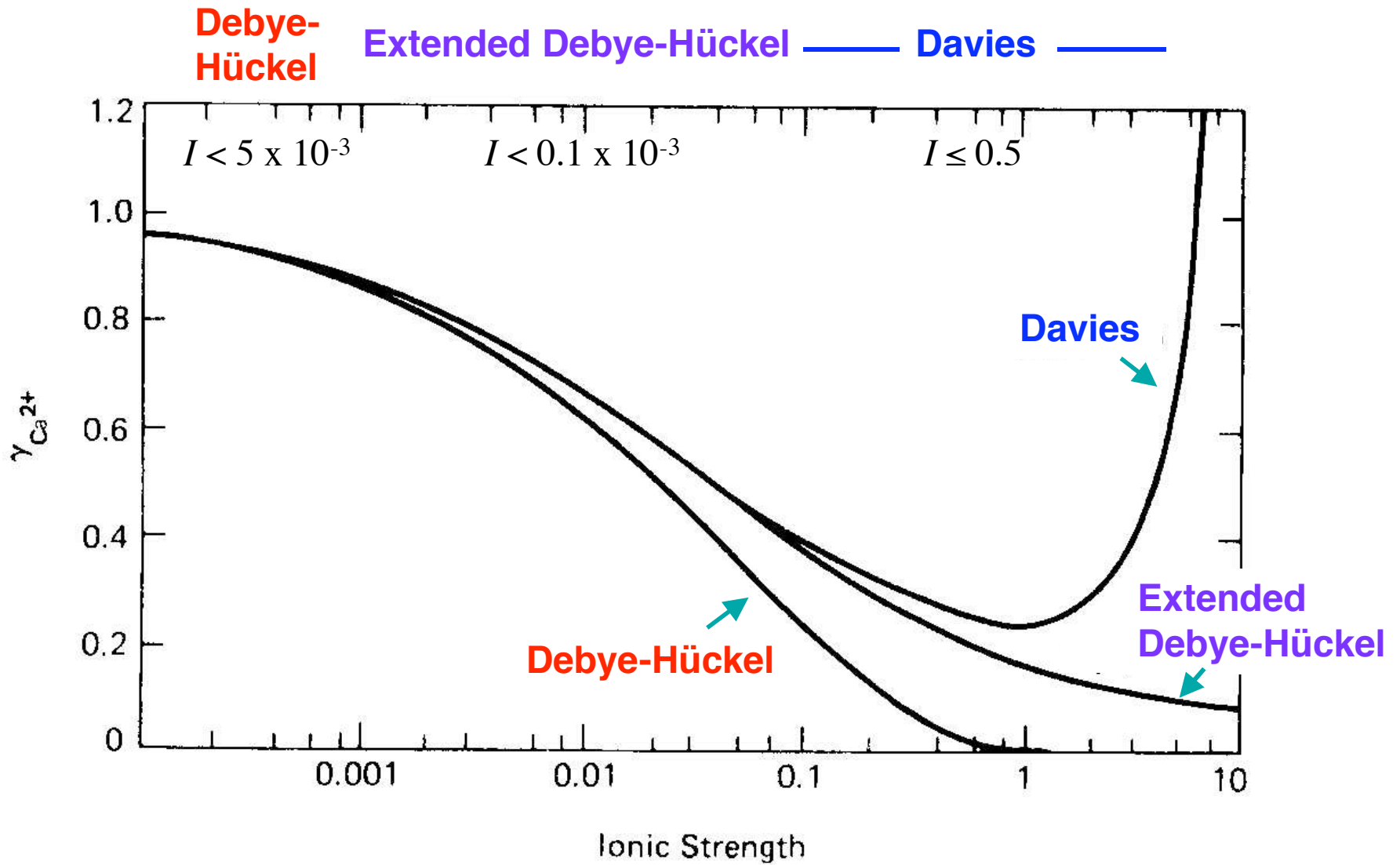


Fig. 2-2. Variation of the activity coefficient for Ca^{2+} according to the three forms of the Debye-Hückel equation (Drever, 1997)

Diagenesis and the growth of concretions

Diagenesis includes all of the chemical, physical, and biological processes that take place in sediment after it was deposited:

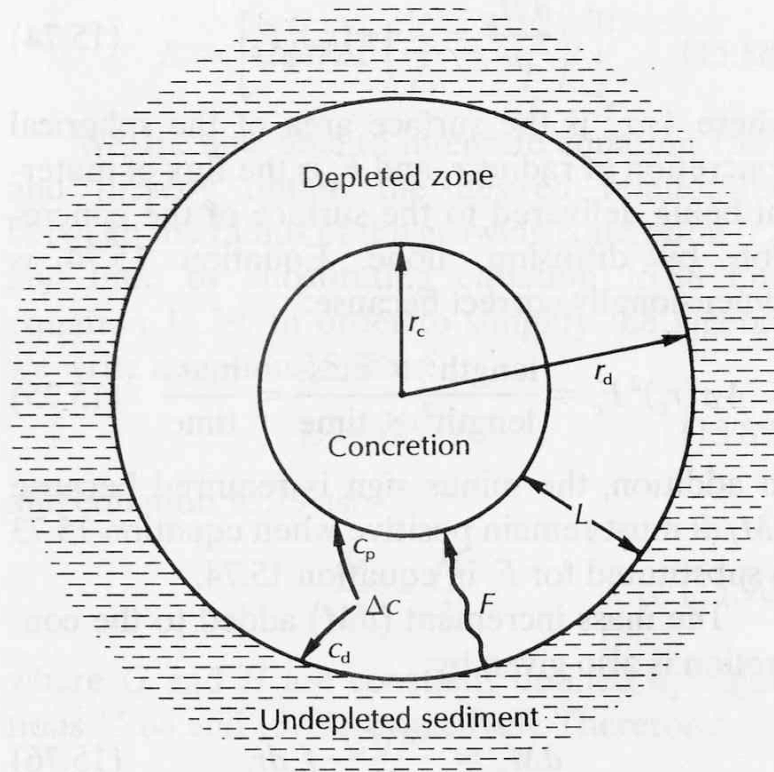
Chemical processes: dissolution of minerals in pore water, precipitation of insoluble compounds, and ion exchange reactions between aqueous species and the surfaces of solids

Biological processes: bioturbation, bacteria-driven chemical reactions (reduction of sulfate), biogenic compounds may inhibit dissolution of minerals by coating grain surfaces or enhance dissolution by adsorbing ions

Physical processes: deposition, compaction, flow of pore water...

The growth of concretions during diagenesis

Minerals may precipitate from pore water of sediment *within* pore spaces as a cement or replace pre-existing minerals that dissolve, both of which may cause the formation of concretions



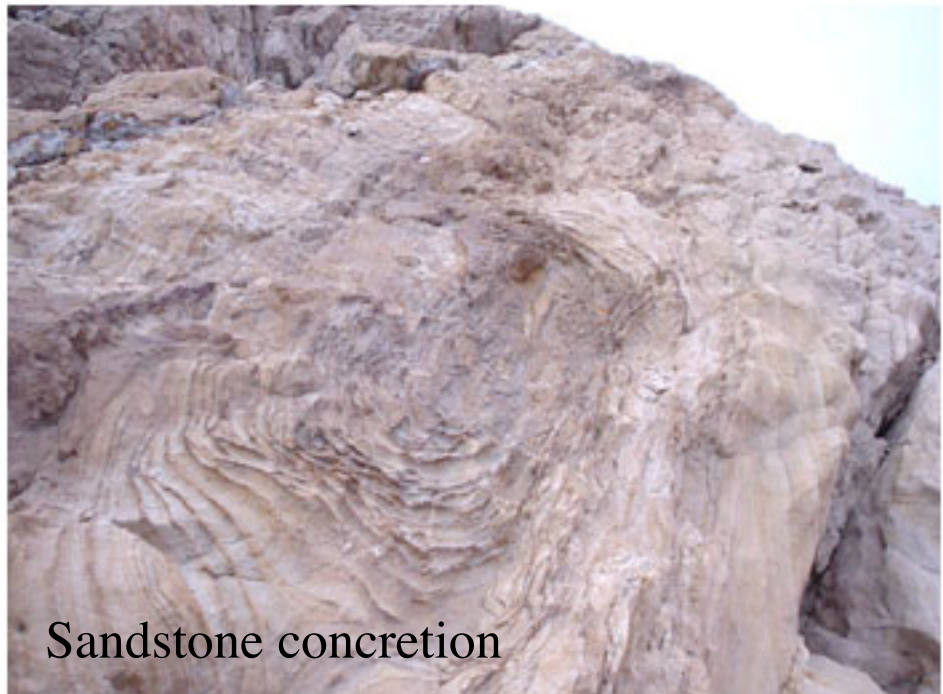
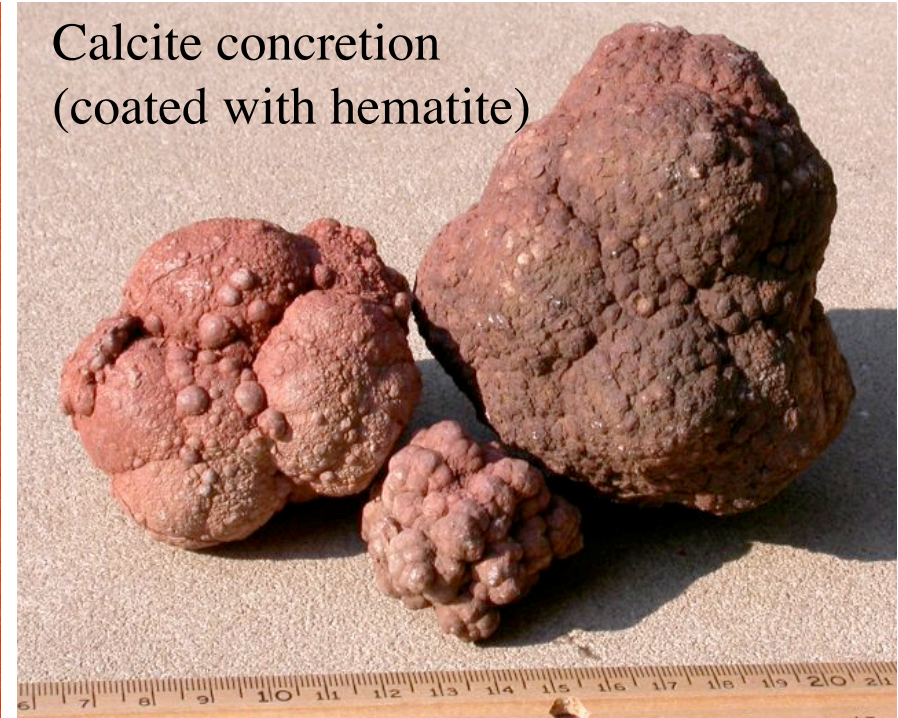
Growth of a concretion with a radius of r_c by diagenetic redistribution caused by dissolution of a mineral in the sediment, diffusion of the resulting ions to the surface of the concretion, and precipitation of a new mineral in the pore spaces of the sediment. The process is transport-dominated and causes the formation of a depleted zone with a radius r_d and a width L . Δc ($=c_d - c_p$) is the molar concentration of the material that is dissolving (c_d) and precipitating (c_p), and F is the flux of ions to the surface of the concretion and leaving the outer surface of the depleted zone.

From Faure chapter 15 — “Rates of Geochemical Processes”

Calcite concretion



Calcite concretion
(coated with hematite)



Sandstone concretion



Sandstone concretion

So what about rates?

Calculate the time required for a calcite concretion to grow by dissolution of disseminated aragonite and diffusion of the resulting Ca^{2+} ions at 10°C ?

$$t = \frac{r_c^2}{2V_p D \Delta c} \left(\frac{\phi}{f_d} - 1 \right)$$

What you are given:

r_c , radius of the concretion = 8.0 cm

D , the diffusion coefficient = 5.4×10^{-6} cm²/sec

ϕ , porosity = 0.75

f_d , volume fraction of aragonite in the sediment = 0.15

Δc , difference in equilibrium concentration of Ca^{2+} in pore water
on the surfaces of calcite and aragonite = 2.0×10^{-5} mol/kg

V_p , volume of calcite = 36.934 cm³/mol

So what about rates?

Calculate the time required for a calcite concretion to grow by dissolution of disseminated aragonite and diffusion of the resulting Ca^{2+} ions at 10°C ?

$$t = \frac{(8 \text{ cm})^2}{2(36.934 \frac{\text{cm}^3}{\text{mol}})(5.4 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}})(2 \times 10^{-5} \frac{\text{mol}}{\text{kg}})} \left(\frac{0.75}{0.15} - 1 \right)$$

$$t = 8.022 \times 10^9 \text{ sec} \cdot 1000 \div 3.154 \times 10^7 \text{ sec/year} = 254,386 \text{ years}$$

r_c , radius of the concretion = 8.0 cm

D , the diffusion coefficient = $5.4 \times 10^{-6} \text{ cm}^2/\text{sec}$ (T dependent)

ϕ , porosity = 0.75

f_d , volume fraction of aragonite in the sediment = 0.15

Δc , difference in equilibrium concentration of Ca^{2+} in pore water

on the surfaces of calcite and aragonite = $2.0 \times 10^{-5} \text{ mol/kg}$

V_p , volume of calcite = $36.934 \text{ cm}^3/\text{mol}$