Aqueous carbonate chemistry workshop, KR6, Birmingham 28th June 2011

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Programme

1. Parameters and units in aqueous geochemistry.
2. Using charge balance and electroconductivity to assess the quality of water analyses.
3. Carbonate equilibria
4. Speciation modelPHREEQC
5. MIX4 for modelling carbonate waters
    a. Structure of the program and its limitations
    b. Deriving carbonate system parameters and mixing waters
    c. Carbonate mineral dissolution: closed system
    d. Carbonate mineral dissolution: open system
    e. Simulating pyrite oxidation
    f. Simulating evaporation
    g. Degassing
    h. Degassing and calcite precipitation
    i. Adding CO_2 to find minimum original PCO_2
6. Additional constraints on back-modelling
7. A ready-reckoner for field studies.

1. Parameters and Units

See Box 5.1 and Table 5.1 of the Chapter 5 handout

We *measure* concentrations

Carbonate system characterized by measuring titration alkalinity (Ξsum of bicarbonate and carbonate) and pH

Total dissolved inorganic carbon (CTOT or DIC) can be measured, but is usually calculated.

We *calculate* activities, saturation indices, P_{CO_2} and sum of missing anions or cations.

Units of concentration

Weight (mass)

Weight units: mass of chemical per mass or volume of solute or solution.

g L^{-1} (ppt = ^{o}/oo)

→→→→→
/formula (=molecular) weight

Molecules (moles)

Molar units: number of gram-molecules per litre of solution

mol L^{-1}

→→→→→
*charge of species

Charge (equivalents)
The number of gram-units of charge per litre of solution.

eq L^{-1}

*1000↓↓ ↑↑ /1000

*1000↓↓ ↑↑ /1000

*1000↓↓ ↑↑ /1000

mg L^{-1} (=ppm)

mmol L^{-1}

meq L^{-1}

*1000↓↓ ↑↑ /1000

←←←←←
*formula (=molecular) weight

*1000↓↓ ↑↑ /1000

←←←←←
/charge of species

*1000↓↓ ↑↑ /1000

$\mu g l^{-1}$ (=ppb)

$\mu mol\ l^{-1}$

$\mu eq l^{-1}$

Molecules (moles)

Molar units:
number of gram-molecules per litre of solution

mol L^{-1}

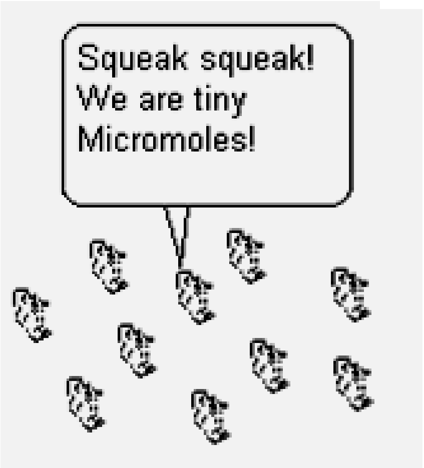
AC Fairchild

*1000↓↓ ↑↑ /1000

mmol L^{-1}

*1000↓↓ ↑↑ /1000

μmol l^{-1}



2. Charge balance.

If the positive and negative charges in the solution are not the same, then there must be deficiencies in the analysis: **Either** the analyses are imprecise or inaccurate **or** an important chemical species was not analyzed. To find out the charge balance, concentration in mass (weight) units must be converted to **molar** units and then to charge units (**equivalents**). Equivalents are a measure of the amount of charge in the solution, so the total equivalents of cations should be equal to the equivalents of anions.

The **charge balance error** can be expressed as:

(Cations-Anions)/(Cations+Anions)*100

Error values of ±5-10% are acceptable for a one-off analysis of a given solution, but should be much less if the same solution is repeatedly analyzed.

Calculation of charge balances is shown on the accompanying spreadsheet: *Figure 5.2 modelled carbonate systems diagrams.xlsx*

Select the right-hand tab: *all waters*

Electroconductivity

The units of (specific) conductivity are μSiemens per cm ($\mu S\ cm^{-1}$). A Siemen is ohm^{-1}.

TDS = i.e. ppm of total dissolved solids. The concentration of seawater is around 35000 ppm TDS, more usually referred to as 35^{o}/oo salinity which equates to around 50000 $\mu S\ cm^{-1}$.

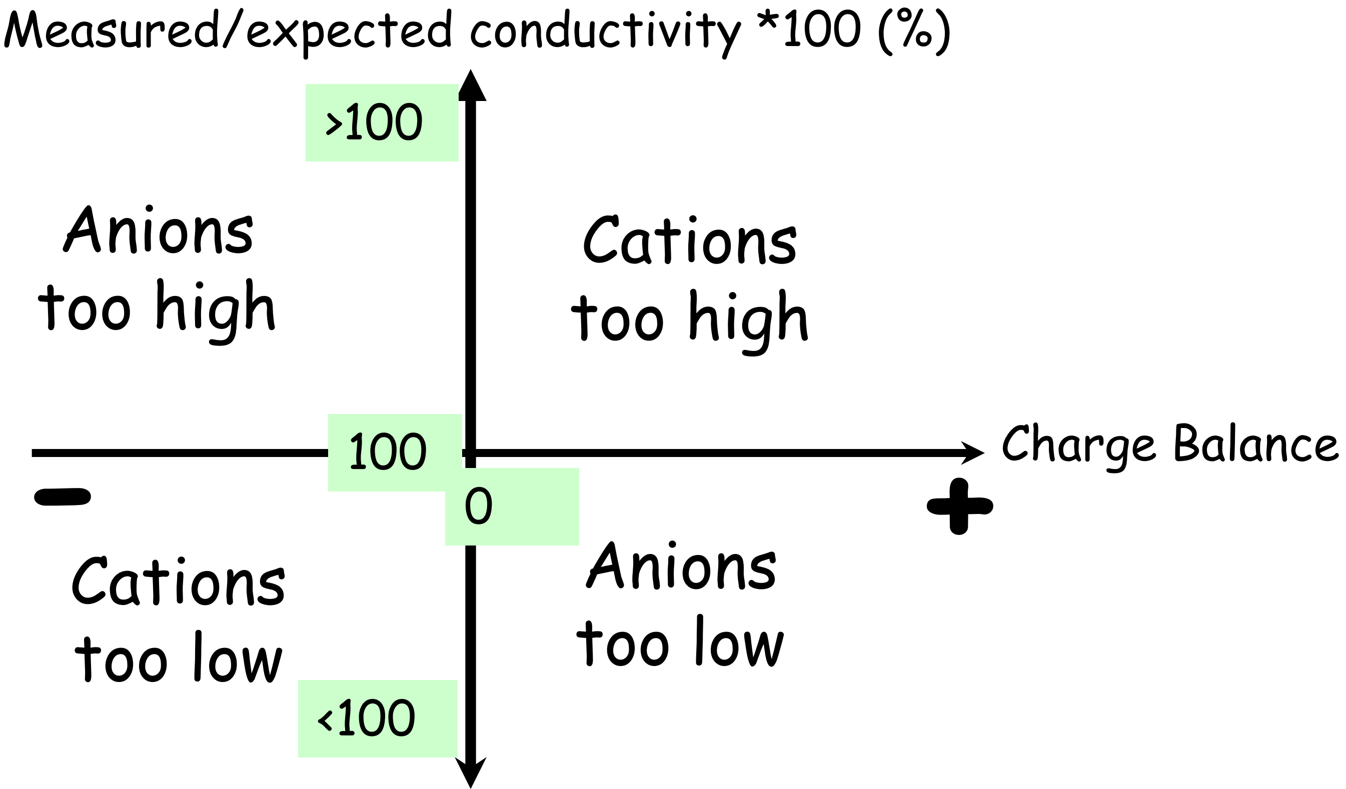
Conductivity increases with temperature, and the instrument has a facility to do a temperature correction, although this may be inaccurate at low temperatures. EC_{25} is the conductivity corrected to 25°C.

EC has a low error - around ± 1% precision and accuracy can be ensured by calibration against a standard salt solution.

Conductivity can be predicted from the composition of the solution. The contribution of ions to conductivity is roughly their concentration * the square of the charge of the ion and this is the basis of the Keily method for estimating concductivity. A more accurate method by Rossum (1984) is illustrated on the accompanying spreadsheet.

Combining the two approaches of charge balance and comparing measured and calculated electroconductivity:

- A positive charge balance implies cations are too high or anions or too low
- A negative charge balance implies cations are too low or anions are too high
- If the ratio of observed/expected (synthetic) conductivity is too low, then either or both of anions and cations are too low and the converse if this ratio is too high



Measured/expected conductivity *100 (%)

>100

Anions too high

Cations too high

100

Charge Balance

−

0

+

Cations too low

Anions too low

<100

3. Carbonate equilibria

The stability of $CaCO_3$ is governed by its solubility product (a special form of the equilibrium constant):

$$\frac{(Ca^{2+})(CO_3^{2-})}{CaCO_{3(solid)}} = K_s$$

Where terms in brackets refer to molar concentrations – or more usefully, *activities* .

K_s is the solubility product for the reaction:

$CaCO_{3(solid)} \leftarrow\rightarrow Ca^{2+} + CO_3^{2-}$

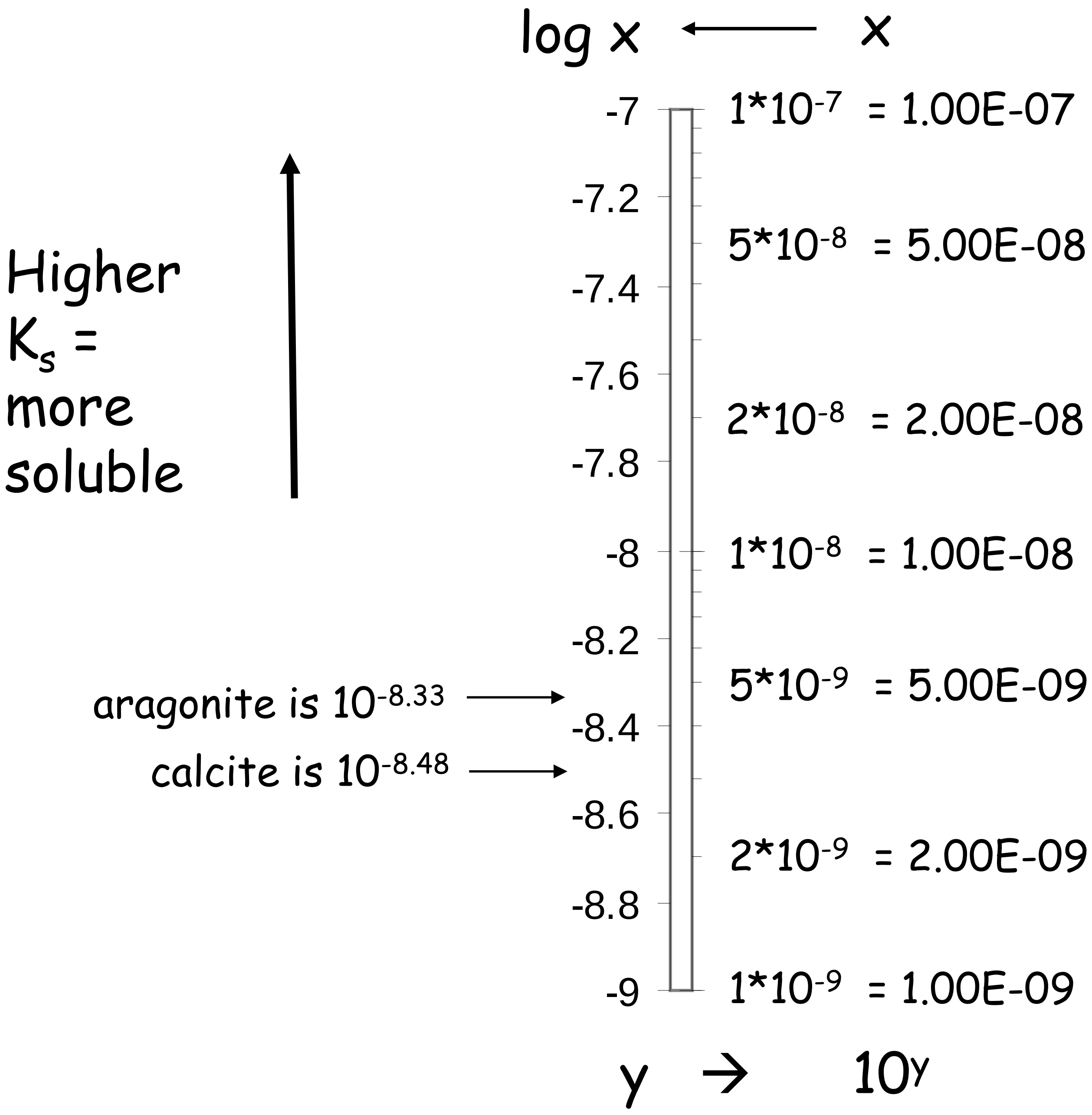
This means that we can predict the properties of a solution in equilibrium with $CaCO_3$.

At 25°C, K_s (K_{cc}) for calcite is $10^{-8.48}$ and for aragonite (K_{arag}) is $10^{-8.33}$.

Which is more soluble?

At 0°C, K_{cc} is $10^{-8.38}$ and K_{arag} is around $10^{-8.21}$

Is this sense of variation of solubility with temperature the same as for other salts?



log x ← x

Higher K_s = more soluble

aragonite is $10^{-8.33}$ →

calcite is $10^{-8.48}$ →

$1*10^{-7}$ = 1.00E-07

$5*10^{-8}$ = 5.00E-08

$2*10^{-8}$ = 2.00E-08

$1*10^{-8}$ = 1.00E-08

$5*10^{-9}$ = 5.00E-09

$2*10^{-9}$ = 2.00E-09

$1*10^{-9}$ = 1.00E-09

y → 10^y

The reason that carbonate minerals become less soluble with increasing temperature relates to the solubility of carbon dioxide in water. At higher temperatures, CO_2 escapes from the water and this promotes $CaCO_3$ precipitation by the reaction:

$Ca^{2+} + HCO_3^- \leftarrow \rightarrow CaCO_{3(solid)} + CO_2 + H_2O$

This reaction is a good approximation to what happens when $CaCO_3$ dissolves or precipitates under most natural conditions, but to see why we need to consider what is happening to the different forms of dissolved inorganic carbon.

The dissolution of carbon dioxide in water is described by Henry's Law:

$CO_{2(gas)} + H_2O \leftarrow \rightarrow H_2CO_{3\ (carbonic\ acid)}$

$$\frac{(H_2CO_3)}{P_{CO2}} = K_o = 10^{-1.47}$$

at 25 °C. If CO_2 is less soluble in water at higher temperatures, will this number get bigger or smaller at higher temperatures?

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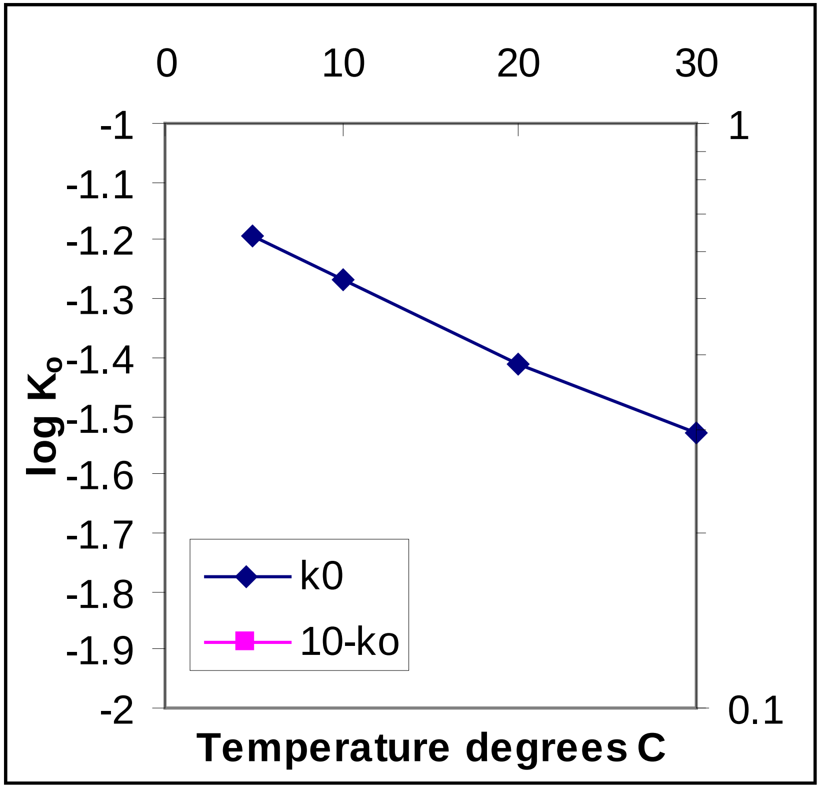


CO_2 more soluble in water at lower temperature

Carbonic acid is a *weak* acid – it dissociates strongly only at higher pH values. The first dissociation reaction involves the creation of bicarbonate ions which in turn at higher pH dissociate to yield carbonate ions.

$H_2CO_3 \leftarrow \rightarrow HCO_3^- + H^+$

Remember that pH = - log(H⁺)
e.g. pH=7.2 (H⁺) = $10^{-7.2}$

$$\frac{(H^+)*(HCO_3^-)}{(H_2CO_3)} = 10^{-6.4} = K_I$$

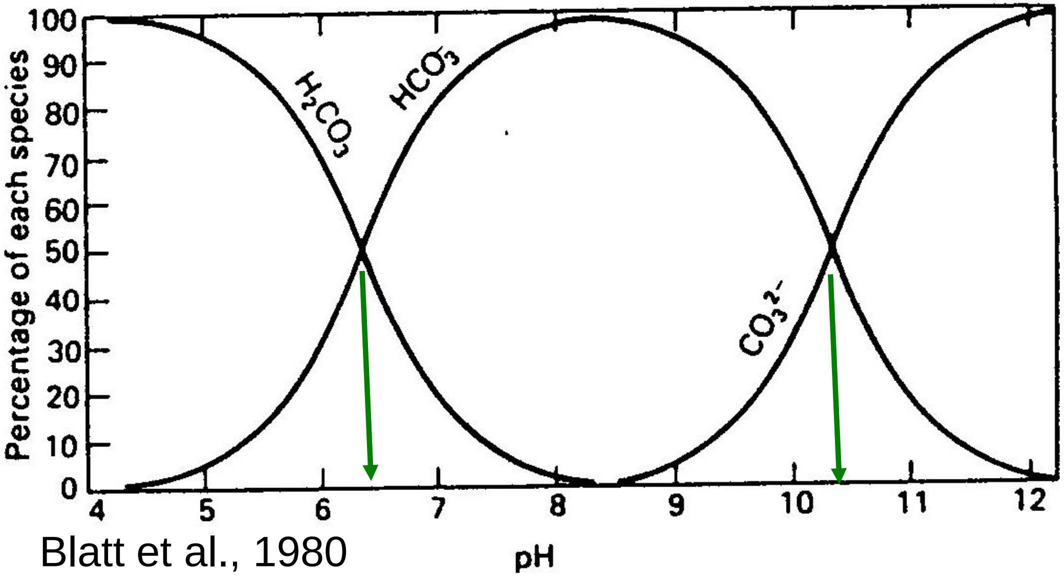
What is the situation at a pH of 6.4……..or 7.4…….or 5.4?

And for the second dissociation:

$$\frac{(H^+)*(CO_3^-)}{(HCO_3^-)} = 10^{-10.3} = K_{II}$$

$HCO_3^- \leftarrow \rightarrow CO_3^{2-} + H^+$

What is the situation at a pH of 10.3……..or 9.3…….or 11.3?



Blatt et al., 1980

Alkalinity

The major cations (Ca^{2+}, Mg^{2+}, K^+, Na^+ etc.) and anions (Cl^-, SO_4^{2-}, NO_3^-) are chemically the counterpart of strong bases and acids respectively). They can be readily analyzed by a variety of methods. pH (H^+ concentration) can also be directly determined.

Dissolved inorganic carbon species can't be directly determined because analytical methods normally interfere with the pH balance of the solution which affects the relative abundance of the species. As a result, the approach is to assume that the aqueous species are in equilibrium and to determine their total concentration. This can be done:

a) By acidifying the solution and determining the amount of CO_2 given off. This is the **total dissolved inorganic carbon:**
TDIC= $(H_2CO_3)+(HCO_3^-) +(CO_3^{2-})$
TDIC is sometimes referred to as **CTOT (**where TOT refers to total)

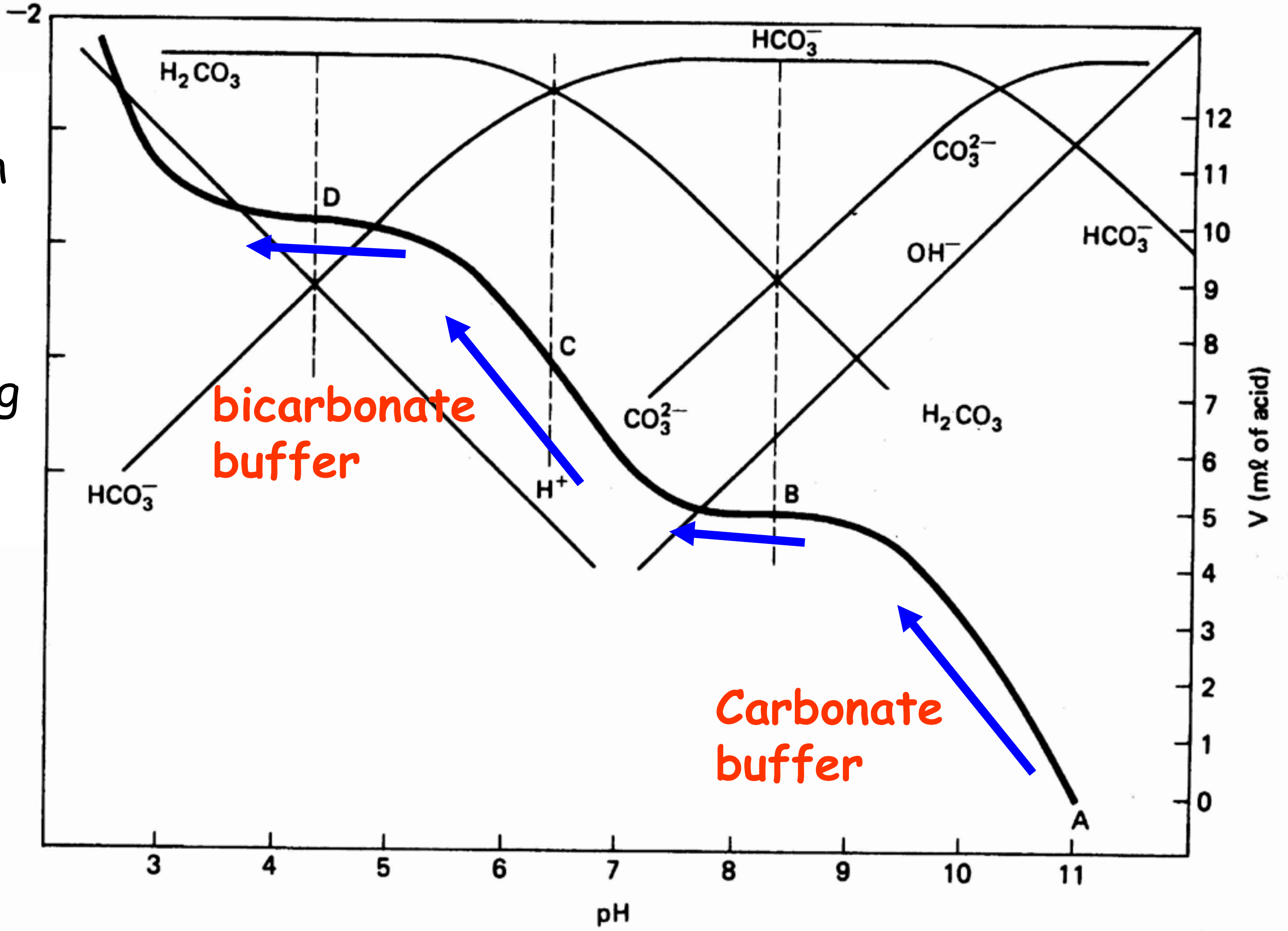
b) By carrying out a titration. The titration alkalinity is a measure of the bases present in the solution = the capacity of the solution to react with added acid. In freshwater this is normally equivalent to the carbonate alkalinity. In seawater, borates also contribute to alkalinity.

Drever, 1997, Fig. 3.2

During the first period, H^+ reacts with CO_3^{2-} ions, so its abundance doesn't increase much. The carbonate ion is acting as a buffer.

Then it runs out, and HCO_3^- becomes the buffer instead, but at a lower pH.

The end point of the titration (D) is around a pH of 4.5.



GURE 3-2 Titration curve (heavy line ABCD) for 5×10^{-3} m Na_2CO_3 with acid, and Bjerrum plot for $\Sigma CO_2 = 5 \times 10^{-3}$ m. B is the carbonate end point, C is a region of strong buffering, and D is the carbonate end point.

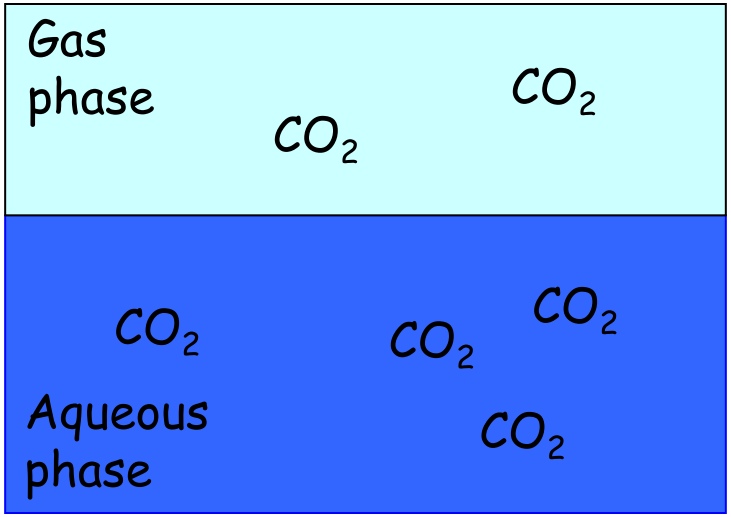
Alkalinity = $(HCO_3^-) + 2*(CO_3^{2-})$ -molar units- or $(HCO_3^-) + (CO_3^{2-})$- equivalent units.

Conversions: meq L^{-1} alkalinity *61 = mg L^{-1} HCO_3^{-1}

meq L^{-1} alkalinity *50 = mg L^{-1} alkalinity as $CaCO_3$ (i.e. 100/2 since the molecular weight of $CaCO_3$ is 100 and dissolution of $CaCO_3$ gives one CO_3^{2-} or 2 HCO_3^-)

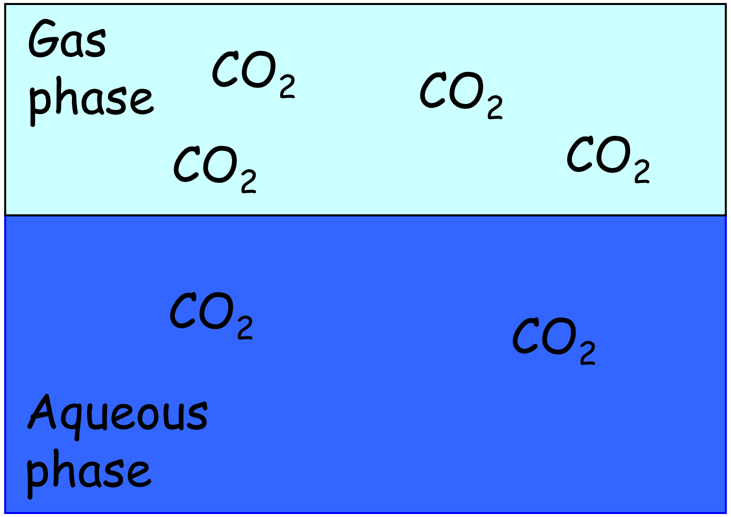
PCO_2 Whereas the K_I and K_{II} reactions can be assumed to be at equilibrium, any reaction involving gases or solids may not be so. The PCO_2 of any solution can be calculated – it represents the PCO_2 of the gas phase with which the solution would be at equilibrium. It is an important concept for predicting the evolution of a solution.

Case I: $PCO_{2(water)} > PCO_{2(gas)}$



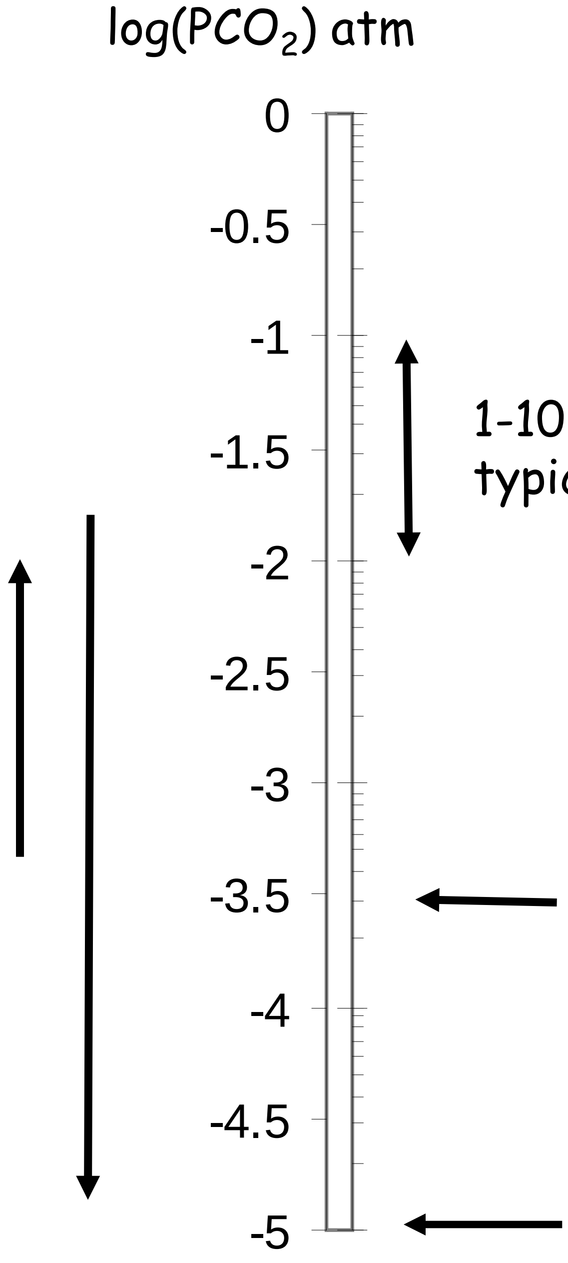
This arises when water moves from a high to a low P_{CO_2} environment or when a reaction in solution generates CO_2. An exponential decline in the difference in P_{CO_2} values over seconds to minutes will be predicted as CO_2 diffuses across the interface.

Case II: $PCO_{2(water)} < PCO_{2(gas)}$



This is likely to arise when a reaction in solution consumes CO_2, particularly by weathering reactions. Equilibration is very slow unless the interface is rough.

PCO_2



1-10% CO_2 in gas phase typical of soil gas

0.03% CO_2= atmospheric value.

minimal CO_2 e.g. removed by weathering in system closed to atmosphere, or where CO_2 removed during freezing.

Addition of a strong acid (e.g. H_2SO_4 from pyrite – FeS_2- oxidation)

Consumption of CO_2 by weathering

Calcite saturation

Similarly, solutions tend to be either supersaturated or undersaturated for calcite, but will tend towards equilibrium if left undisturbed.

Saturation index = log (IAP/K_s) = $\log\{\frac{(Ca^{2+})*(CO_3^{2-})}{K_{cc}}\}$

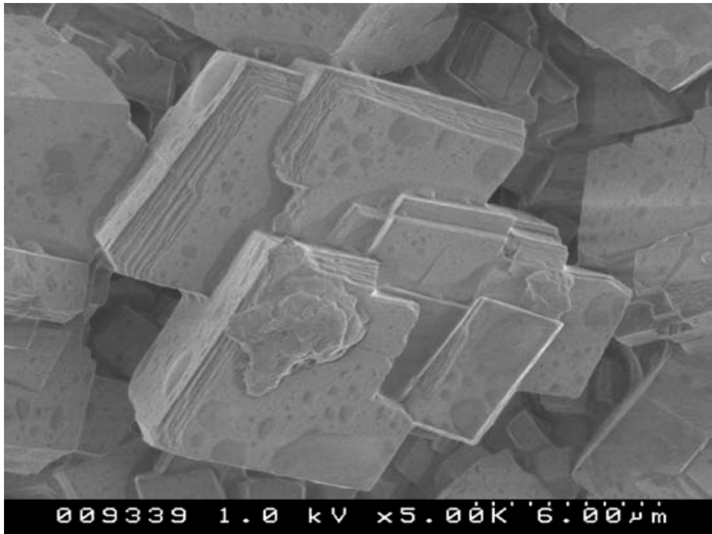
Saturation index > 0 (ratio more than 1) SUPERSATURATED SOLUTION
Precipitation of $CaCO_3$ is predicted

Saturation index = 0 (ratio of 1) SATURATED SOLUTION
Neither precipitation nor dissolution predicted

Saturation index < 0 (ration less than 1) UNDERSATURATED SOLUTION
Dissolution predicted.

The expression for aragonite is identical
but the numerical value of Ks is different

Other definitions of saturation index are often used e.g. IAP/K_s or ln(IAP/K_s)



Excel calculations
The spreadsheet *The carbonate system Q* contains field and laboratory data on three waters collected from natural environments. It has been set up as a teaching exercise with a framework to calculate the carbonate system parameters using concentrations.

(The next stage will be to compare these values with those from software taking account of the differences between activity and concentration).

Water b40tsan from the Tsanfleuron glacial meltstream

Setting of Crag Cave, Co. Kerry, Ireland

Soil profile on clayey till, with limestone fragments

Water sample 2 from soil water sampler 99SWS

Water sample 99a – dripwater from Crag Cave

You are also provided with the spreadsheet:

The carbonate system Q &A

that gives you the answers!

Grønligrotta, Norway

Activity and activity coefficients

Activity is fundamentally related to chemical potential, but in practical terms it is often convenient to think of it as the “effective concentration” of a chemical species to take part in a reaction.

Activity (dimensionless) = activity coefficient (litres/mole)*concentration (moles/litre)
$a = \gamma * C$

The activity of any pure substance is 1.

The activity coeficient of a gas is 1,so the activity = pressure in atmospheres, assuming that ideal behaviour occurs. At relatively low partial pressures this is a reasonable assumption.

The activity of a dissolved substance = the molarity when it behaves ideally. For ions, they only behave ideally at infinitely low concentrations.

At higher concentrations, interactions occur. We use **ionic strength (I)** as a measure of concentration.

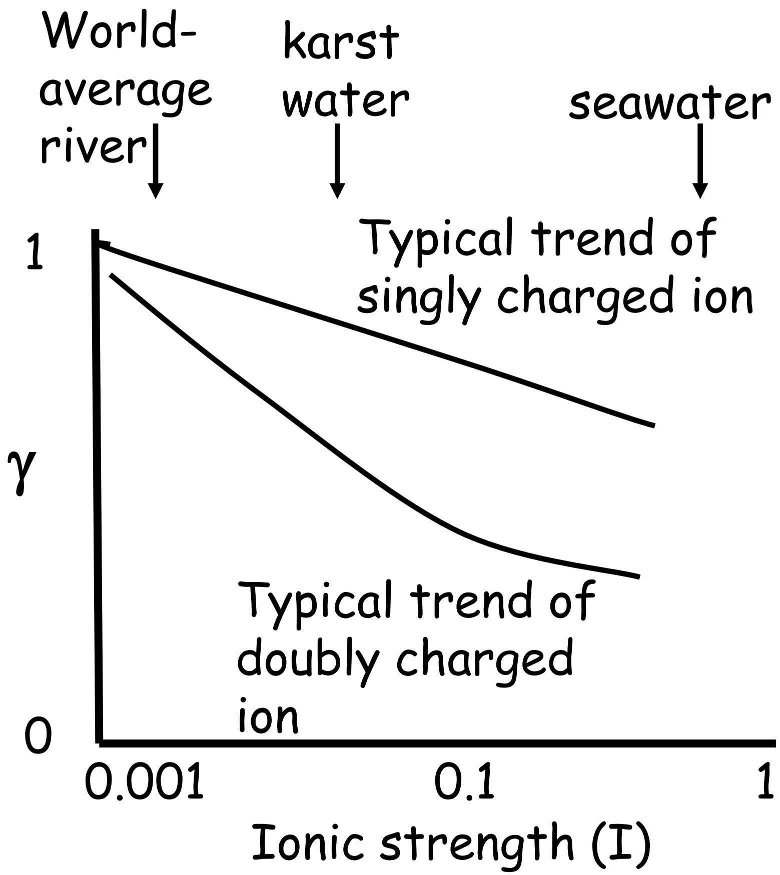
$$I = 0.5 \sum m_i z_i^2$$

Where m_i is the molar concentration of ion I and z_i is its charge. Seawater has an ionic strength of 0.7.

Activity and activity coefficients

At higher concentrations, two types of interaction occur:

a) Electrostatic attractions. At moderate concentrations these are described by the Debye-Huckel theory. The activity coefficients drop with increasing I, particularly for more highly-charged ions. (At very high concentrations, the ions dehydrate and γ can be more than 1; Pitzer theory is used to predict behaviour).



b) Formation of ion pairs/triplets.

e.g. $CaCO_3^0$ (a $CaCO_3$ molecule dissolved in the solution), $CaCl^+$ $NaSO_4^-$

Each particular pairing has its own equilibrium constant, so the extent to which these reactions occur depends on the particular solution composition. Because these effects are complex, software has been developed to calculate solution properties.

4. PHREEQC

Because these effects are complex, software has been developed to calculate solution properties. The United States Geologic Survey were the leaders in this. The program PHREEQ is comprehensive, although fiddly to use. A simpler program (MIX) was originally developed for carbonate systems and we will use a modified version of it in the next section.

The most user-friendly versions of PHREEQ are:

WEB-PHREEQ, a WWW implementation of the aqueous geochemical modeling program PHREEQC by David Parkhurst of the U.S.G.S.

http://www.ndsu.edu/webphreeq/

PHREEQC for Windows is a 32 bit Windows version of the geochemical model PHREEQC-2 , the popular aqueous geochemical modelling code by David Parkhurst and Tony Appelo. It was developed to add an easy-to-learn, intuitive graphical user interface (GUI) to PHREEQC.
http://pfw.antipodes.nl/

Now open the spreadsheet: *Carbonate dissolution Q*
and turn to tab *PHREEQE output b40tsan*

Double precision number format is used:

1.01D+02 = 101
1.01D+01 = 10.1
1.01D+00 = 1.01
1.01D-01 = 0.101
1.01D-02 = 0.0101

MOLALITY	log molality
4.765895D-04 =0.000476589 =$10^{-3.3219}$	-3.3219

The most important ion pair is $CaSO_4$. Why?

Values for γ_{CO3} are 0.83, but most others are above 0.9………

The saturation index is lower (-1.34) than by our calculation using molar concentrations instead of activities. Is this expected?

Now we take a short cut by looking at answers as well as question in the spreadsheet:
Carbonate dissolution Q &A

5. Modelling using MIX4

5a. Structure of the program and its limitations

Go into the subdirectory “MIX4 GGM221”. Here you will find the file “MIX4 instructions.doc”. MIX4 is a Fortran program that calculates carbonate system parameters and which can be used for mixing solutions and carrying out chemical reactions to solutions, including bringing a solution to equilibrium with a solid phase with a user-defined stability (K_s value).

The strengths of MIX4 are its versatility and relative ease of use.

The weaknesses of MIX4 are:

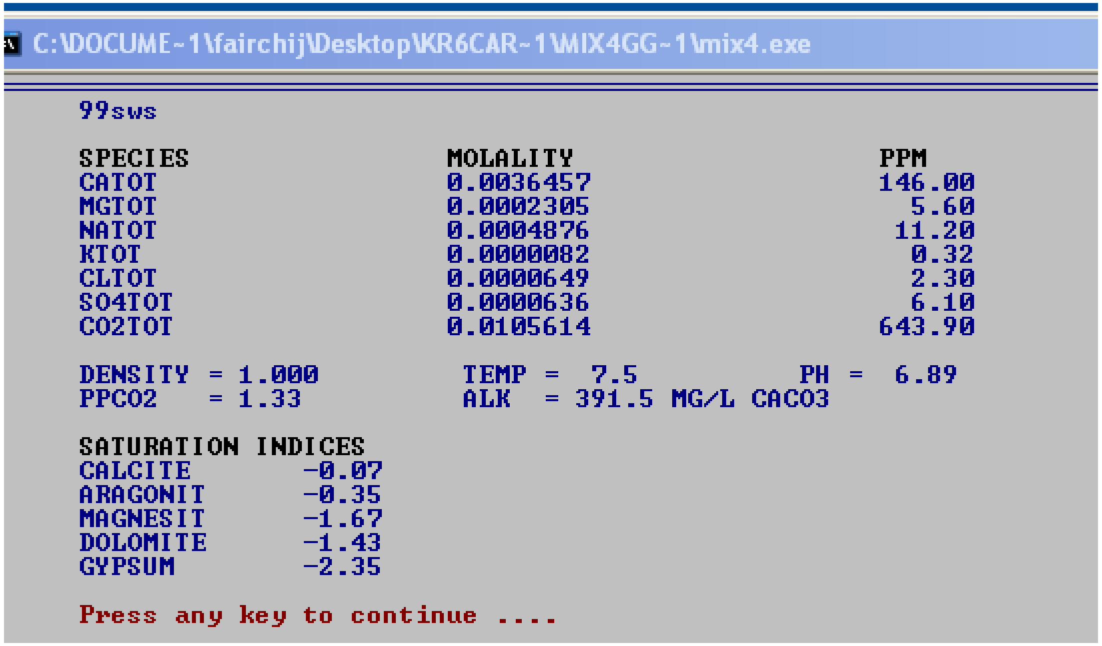
1) It only uses a limited range of major ionic species. The main absence is nitrate, but by default the program will balance the solution charge by chloride (or sodium), and nitrate does not form strong ion pairs, so this is not a big problem.
2) The thermodynamic database contains an old equation for calculating K_{cc} – depending on temperature, you have to add a small value (typically around 0.05) to obtain values consistent with the latest thermodynamic data. (Details are given in the spreadsheet *Carbonate dissolution Q &A* in the sheet called: “*correcting MIX4 output*”

5b. Carbonate system parameters and mixing waters

Now we will carry out the exercises in the set in the spreadsheet:
Carbonate dissolution Q &A

- *Find the carbonate parameters for the soil water sws.*

We use the "MIX" option in the software



```
99sws

SPECIES                 MOLALITY                   PPM
CATOT                   0.0036457                  146.00
MGTOT                   0.0002305                    5.60
NATOT                   0.0004876                   11.20
KTOT                    0.0000082                    0.32
CLTOT                   0.0000649                    2.30
SO4TOT                  0.0000636                    6.10
CO2TOT                  0.0105614                  643.90

DENSITY  = 1.000         TEMP  =  7.5         PH  =  6.89
PPCO2    = 1.33          ALK   = 391.5 MG/L CACO3

SATURATION INDICES
CALCITE         -0.07
ARAGONIT        -0.35
MAGNESIT        -1.67
DOLOMITE        -1.43
GYPSUM          -2.35

Press any key to continue ....
```

Molality (moles/kg water) coincides with molarity (mole/litre solution) at low ionic strengths

ppm = mg/litre solution

Note that the "p convention" is used. E.g. pH = -log(H^+) Therefore pPCO2 or PPCO2 = -log(PCO_2).

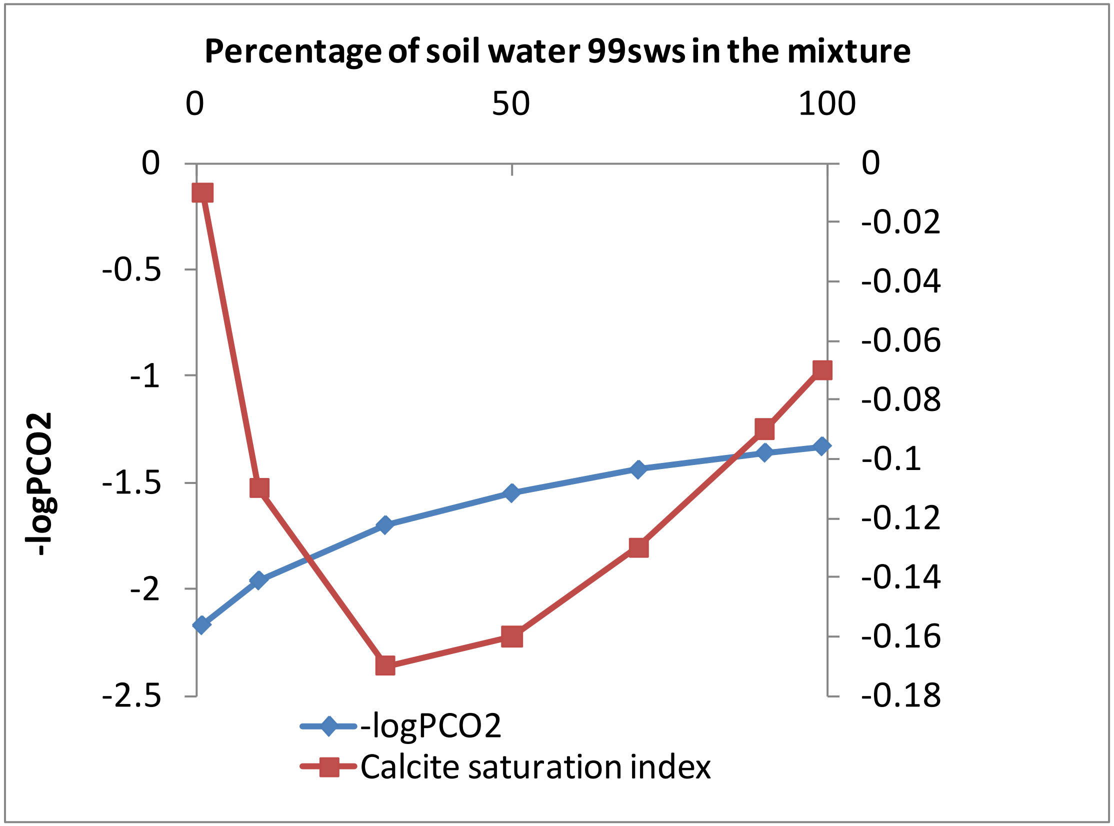
Alk is short for alkalinity

Saturation indices: Magnesit is short for magnesite (MgCO3), not Mg-calcite!

Mixing waters

- *Effects of mixing soil water 99sws and 99a-sat in different proportions*

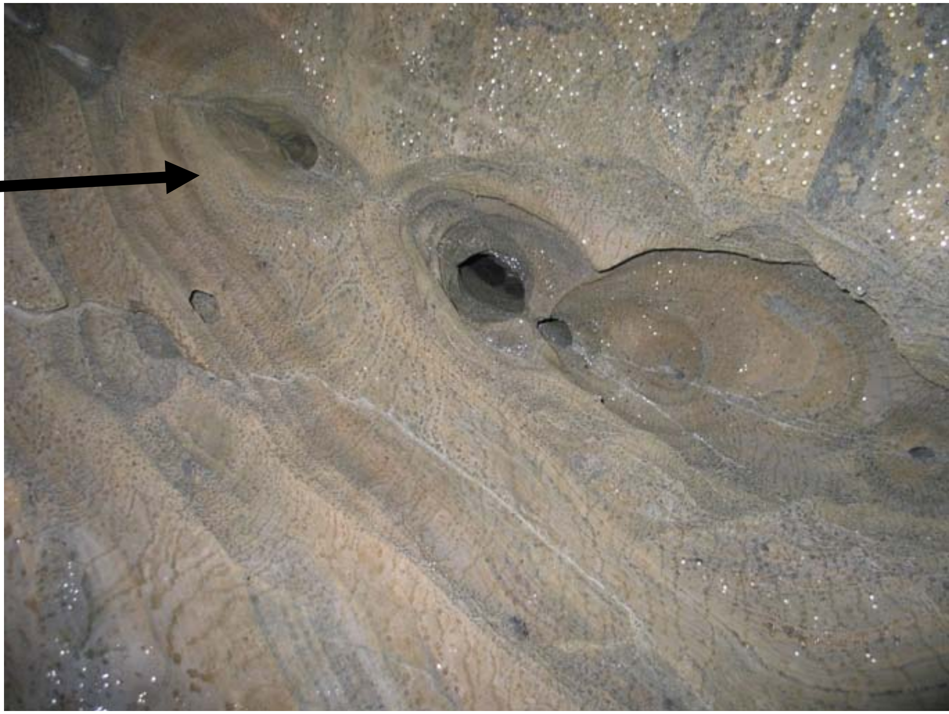
If you want to record the results of this run on a datafile for viewing, printing or graphing then press F4. (see MIX4 instructions.doc for details)



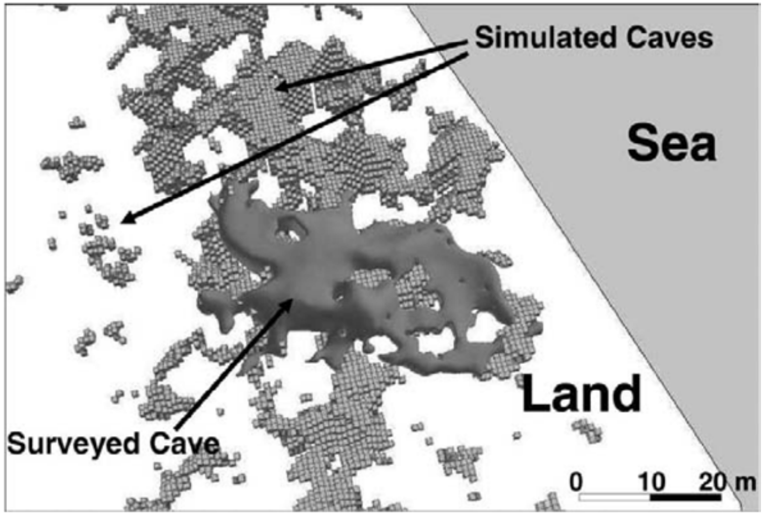
If you mix two waters (e.g. one flowing laterally and one percolating sub-vertically) with different amounts of dissolved CO_2 the mixed waters is more undersaturated (corrosive) to $CaCO_3$ than either of the parent waters.

Mixing corrosion

Corrosion pits in a phreatic tube cave roof, Norway. Bögli, among others, interpreted such relationships in terms of mixing corrosion where the tube waters are joined by waters from above.

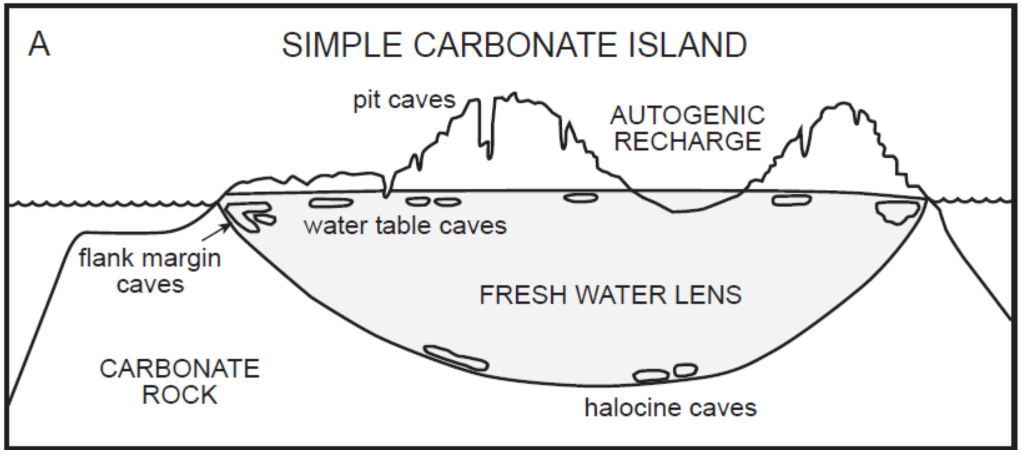


This is still controversial, but a more widely accepted role for mixing corrosion is in seawater-freshwater mixing zones where flank margin caves form.



Labourdette et al. (2007)

Jenson et al. (2006)



5c. Closed system dissolution

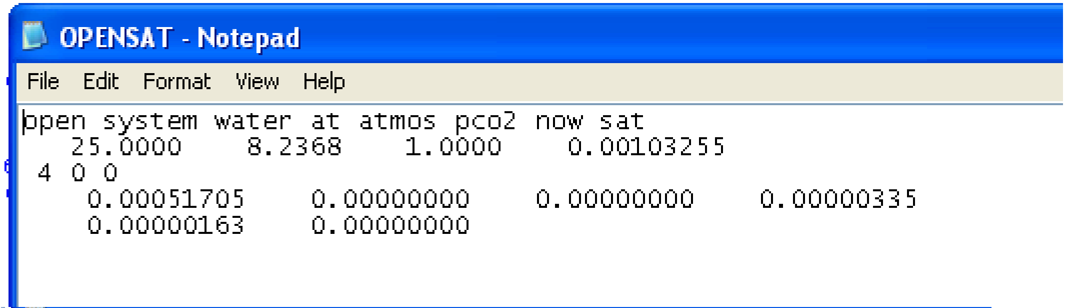
- *Now we use the "Reaction" option in the software*
- *First we define the nature of the reaction*
- *Then we specify the water to be used: purewat2.dat*
- *Then we experiment with different amounts of reaction – each time the software goes back to the original solution.*
- *We finish by getting a water that just reaches saturation. Our target is a saturation index of -0.06 because of the old* K_s *value used by MIX4.*

5d. Open system dissolution

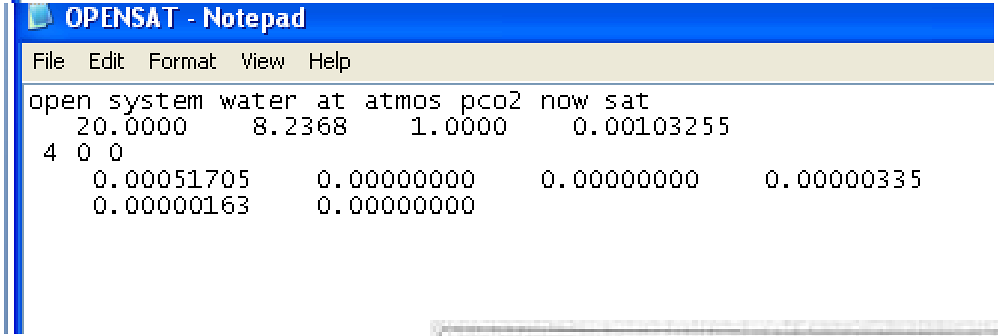
- Our target is to reach calcite saturation at atmospheric PCO2 of $10^{-3.4}$.
- Here there is an additional step because we now want to equilibrate with the phase $CaCO_3$ and our target is to reach equilibrium at a specified PCO2. We have to specify the log solubility product of $CaCO_3$. For calcite at 25 degrees, this is $\log(10^{-8.48})$ and so we type -8.48.
- You can save the new water you have made by pressing F3 and you then need to name it. Names are limited to 8 characters and should be given the suffix .dat In this case save it as **opensat.dat**

Sensitivity analysis exercise

The simplest way to do this is by adjusting the file that you already have. If you open the file **opensat.dat** (that you just made) in Notepad, it looks like this:



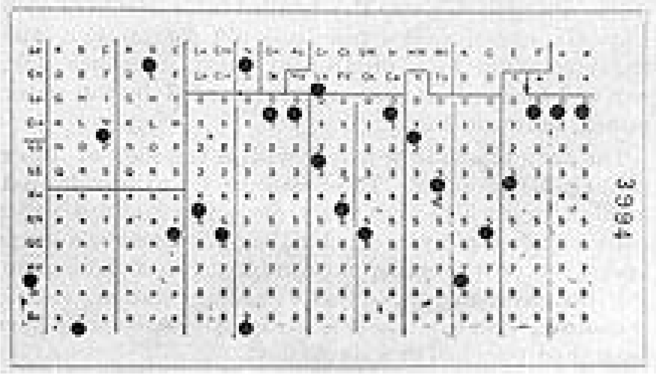
```
open system water at atmos pco2 now sat
    25.0000     8.2368     1.0000     0.00103255
 4  0  0
     0.00051705     0.00000000     0.00000000     0.00000335
     0.00000163     0.00000000
```



```
open system water at atmos pco2 now sat
    20.0000     8.2368     1.0000     0.00103255
 4  0  0
     0.00051705     0.00000000     0.00000000     0.00000335
     0.00000163     0.00000000
```

You can for example change the temperature to 20 degrees. Be careful to keep each character in exactly the same position – this software was written originally using punched cards!

You can use this technique to enter a suite of water analyses saving each with a new name.



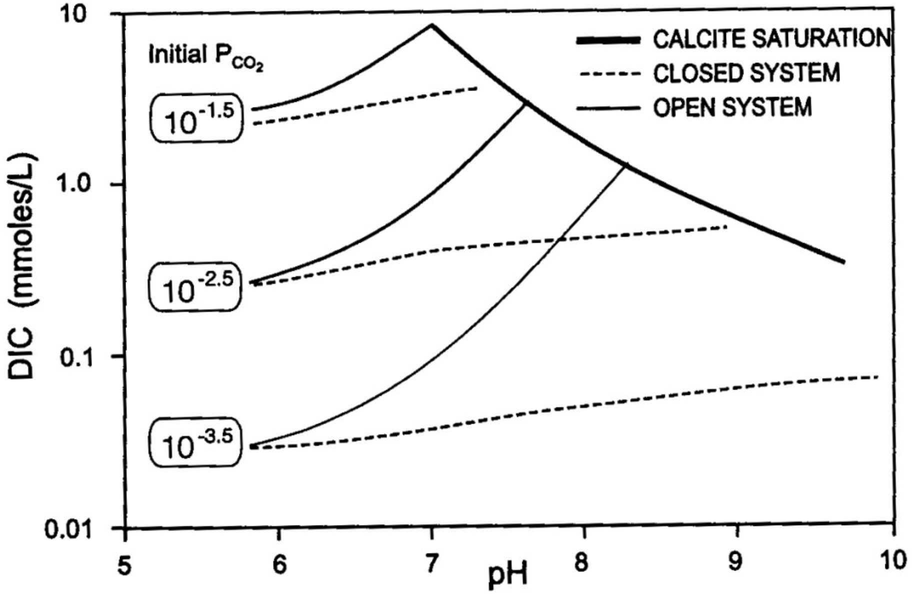
The alternative is to enter the water from scratch as follows:

CREATE INPUT FILE PROMPTED INPUT:
-Type in the water chemistry when the ENTER DETAILS screen appears, keying the "enter" key
after each step (remember F1 to go back up the screen if you make a mistake):

Enter:	
opsat20	title = (a name or a sentence to identify the water sample)
25	temperature = (temperature in °C)
8.237	PH = (pH)
1	density = (specific gravity; e.g. 1 for dilute solutions; 1.023 for sea water)
0.00103	carbon = (=ctot or DIC, dissolved inorganic carbon, i.e. the sum of the concentrations of dissolved CO_2 , H_2CO_3, $HC03^-$ and $C0_3^{2-}$)
4	flag = (= 2 if concentrations are entered as mgl^{-1}or =4 if concentrations are entered as moles l^{-1}
0	ihold = (=0 normally. See Plummer et al, 1975 for details)
0	iopt7 = (=0 normally, but =1 if you want to use H^+ rather than K^+ or Cl^- to balance the charges; see Plummer et al, 1975 for details)
0.000517 and zero for the others	catot, mgtot, natot, ktot, citot, so4tot = (concentrations of Ca, Mg, Na and K, Cl and SO_4.)

Summary: Open and closed system dissolution

Clark & Fritz



Closed system dissolution arises where a system is closed to input of CO_2 when dissolution occurs. Dissolution occurs by water hydrolysis and by reaction with the CO_2 dissolved in the solution. The amount of dissolution is limited

Open system dissolution arises where there is a supply of CO_2 throughout dissolution and environmental conditions such that the system can be maintained at the original PCO_2 condition.
The most substantial dissolution occurs when open system dissolution occurs in soils (high-PCO_2 environment) containing $CaCO_3$.

Additional dissolution by strong acids

Addition of a strong acid (e.g. H_2SO_4) leads to further $CaCO_3$ dissolution. It can be simulated in MIX4*

*under an option (2-0-1 rather than 2-0-0) where the program balances the charge of the solution by H+ in order to determine pH (it is necessary to start with a perfectly charge-balanced solution).

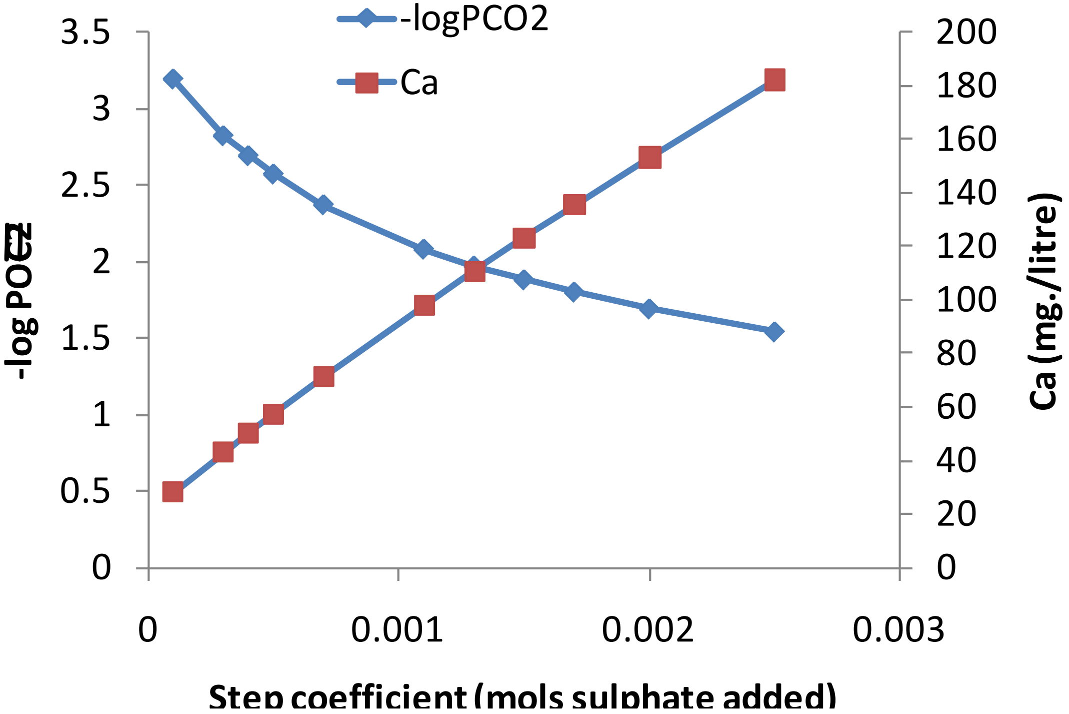
5e. Additional dissolution by strong acids

Addition of a strong acid (e.g. H_2SO_4) leads to further $CaCO_3$ dissolution.

It can be simulated in MIX4. It is necessary to start with a perfectly charge-balanced solution, i.e. one created by a MIX4 calculation and saved in MIX4 in the first place, e.g. opensat.dat

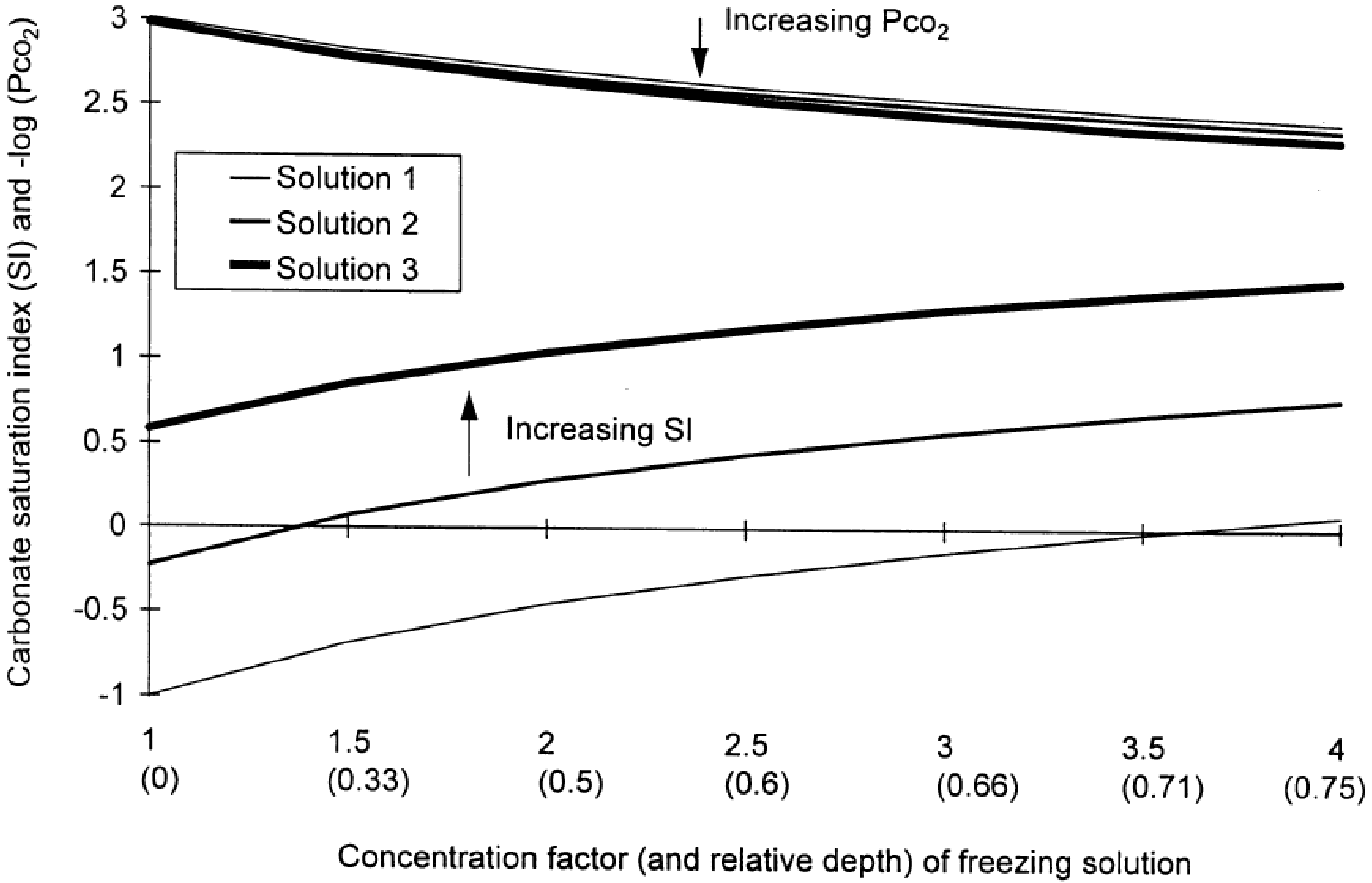
Open opensat.dat in notepad and change 4 0 0 to 4 0 1 . Now the program balances the charge of the solution by H+ in order to determine pH.

Carry out a reaction by addition of sulphate. MIX4 will balance the charges with acid which gives the right stoichiometry for addition of sulphuric acid. You can also equilibrate with $CaCO_3$.



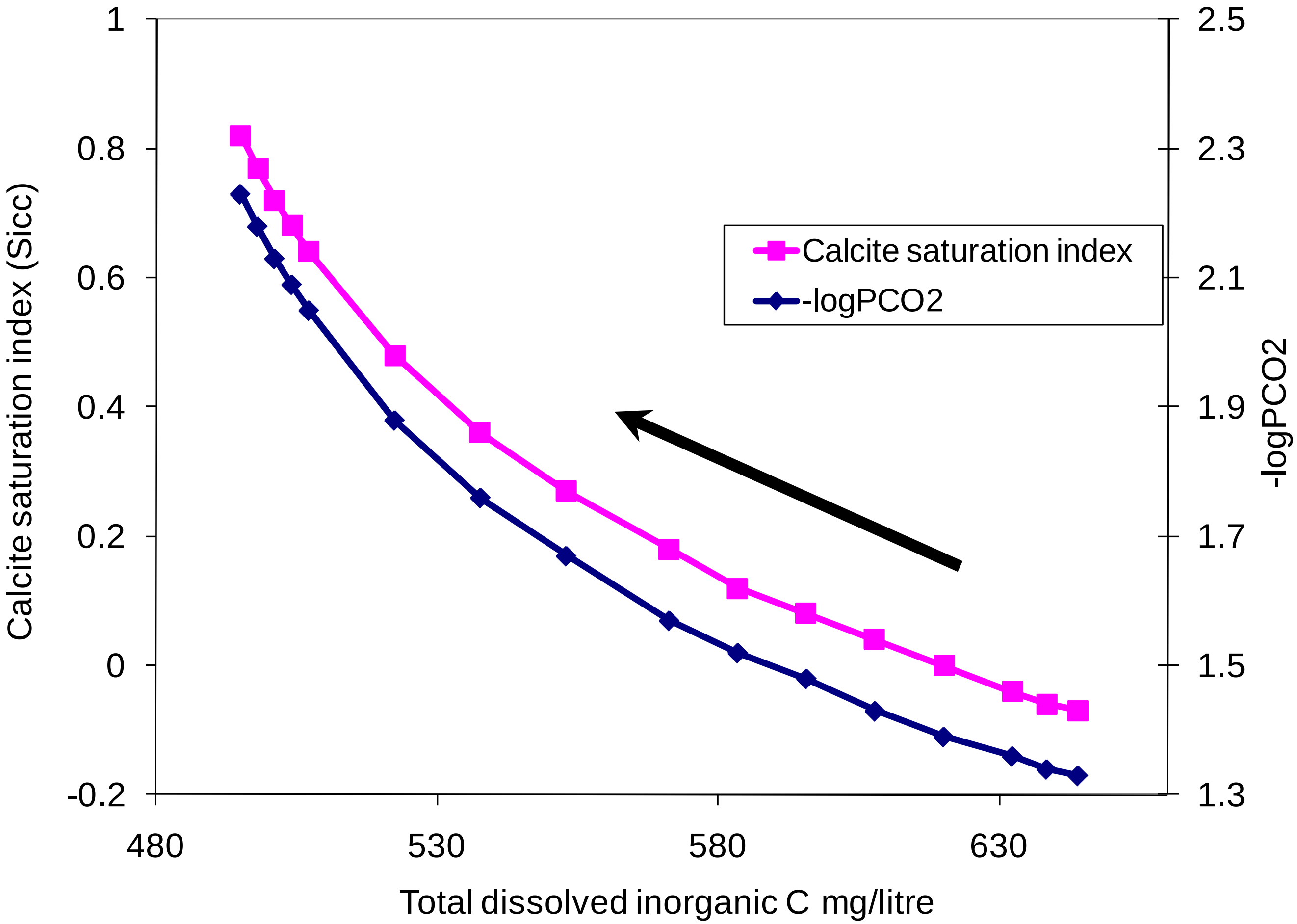
5f. Simulating evaporation or freezing

Killawee et al. (*GCA*, 1998) used MIX4 to simulate progressive solution concentration – using system parameters and multiplying them up. The effects of progressive $CaCO_3$ precipitation could also have been added.



5g. Simulating degassing

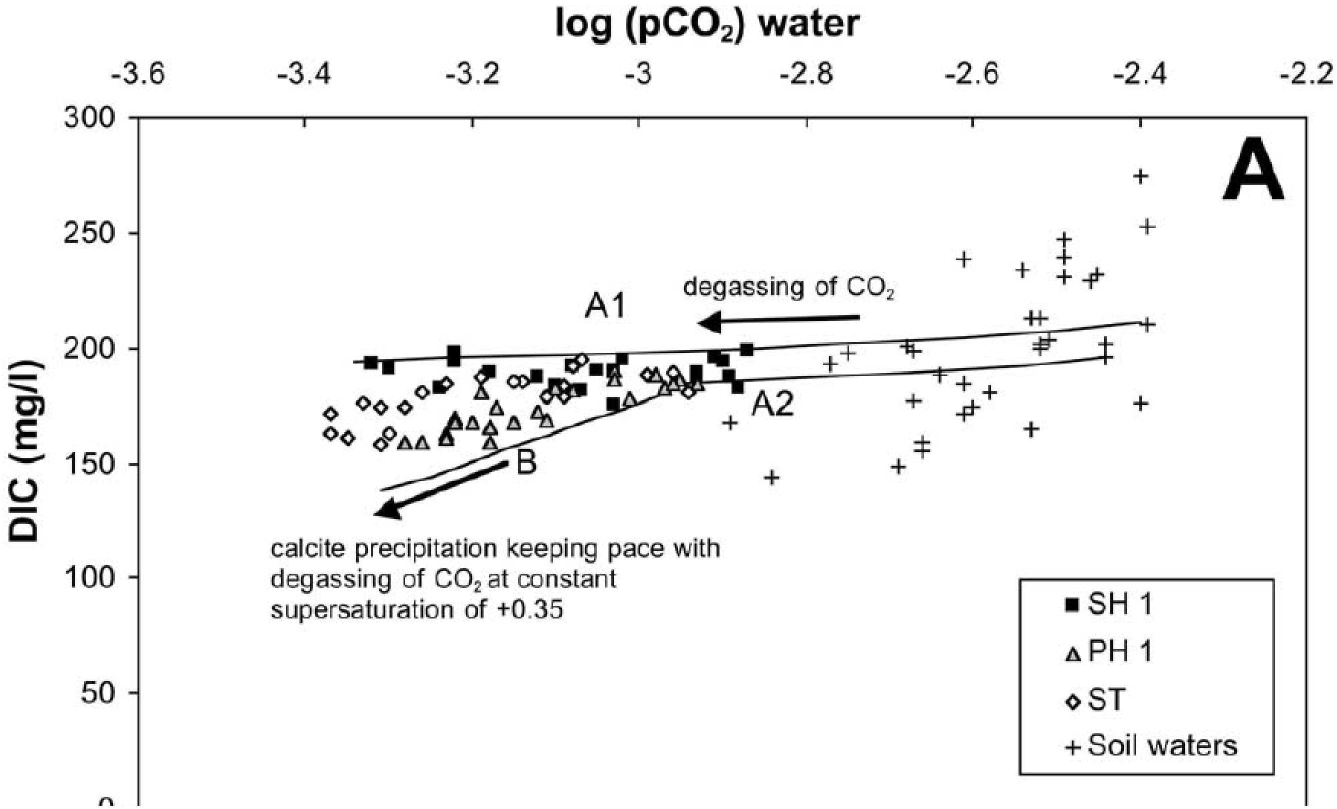
Open spreadsheet “Carbonate precipitation Q&A.xls” on the “Problems” sheet. We will degas the soilwater 99sws until its PCO_2 reaches $10^{-2.3}$, as in the cave. Save the final file as deg99sws.dat



5h. Simulating degassing and calcite precipitation

Experiment to precipitate $CaCO_3$ from new file deg99sws.dat and see how close the resulting solution is to cave water 99a. Use the same reaction, but this time equilibrate with $CaCO_3$ of logK = -7.65 to yield a solution saturated at +0.6. Compare results with spreadsheet.

Something similar was done by Spotl et al (*GCA*, 2005) using data from Obir: 3



5i. Adding CO_2 to find minimum original PCO_2

Reverse the degassing process for water 99-a to determine the minimum PCO_2 it once experienced. Use reaction option, do not follow phase boundary and +1 for CO_3 to simulate adding CO2 (i.e. reversing the degassing process). We deduce that the minimum soil PCO_2 is $10^{-1.56}$ (see spreadsheet)

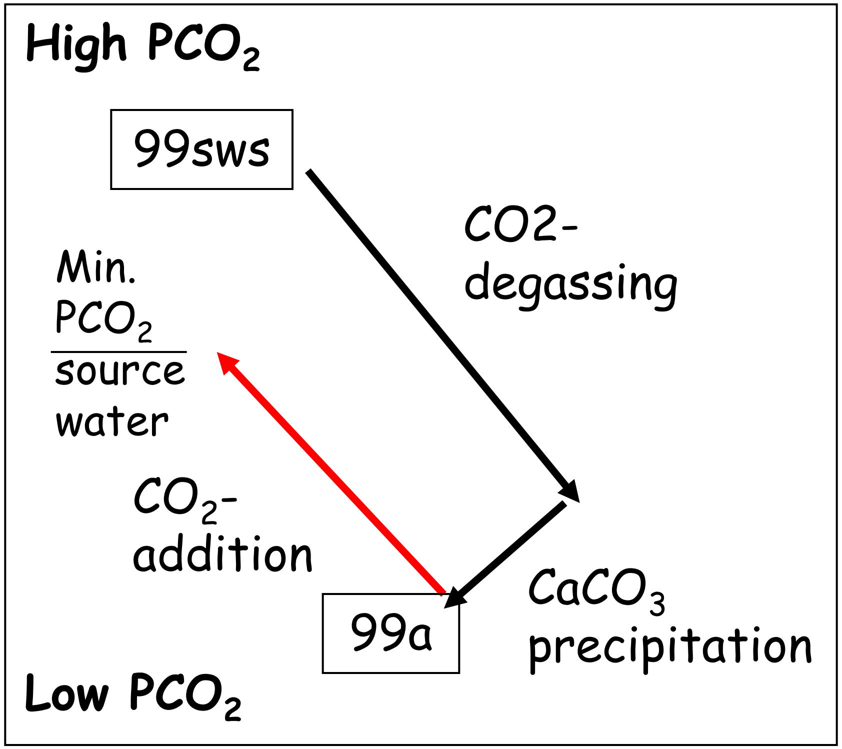
Conclusions:

1. degassing the soil water solution leads to steady changes in $\log PCO_2$ and SI_{cc} – they both change at exactly the same rate.

2. When we do an experiment to precipitate some $CaCO_3$ in addition to degassing, we find we can reach a close approximation to the observed water at 99a.

3. We can also determine the minimum PCO_2 of the parent water that degassed to form 99a.

Mattey et al. (Geol Soc Spec Publ, 2010) used PHREEQC to simulate degassing and calcite precipitation, exploring various different ratios of the two processes.



High PCO_2

99sws

CO2-degassing

Min. PCO_2 source water

CO_2-addition

$CaCO_3$ precipitation

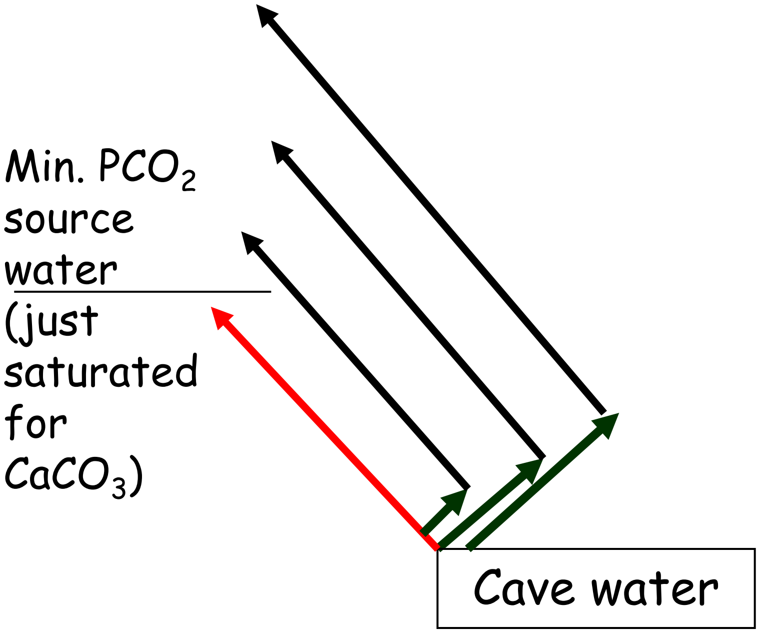
99a

Low PCO_2

Summary of the last three completed experiments

General case, working from the cave water various solutions to the problem are possible because the amount of $CaCO_3$ removed from the solution is undefined.

So we need an independent estimate of the amount of Ca removal.



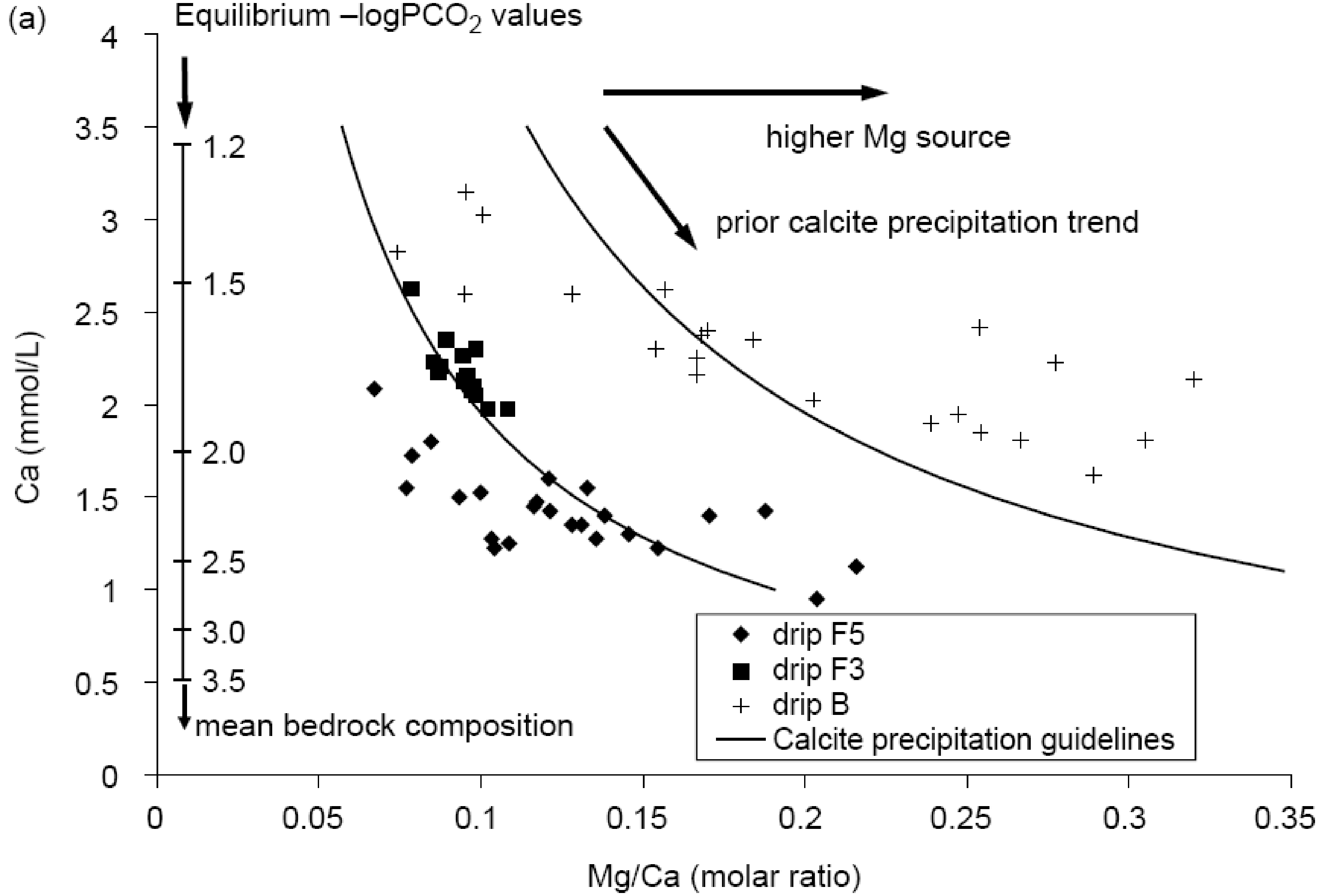
Min. PCO_2 source water

(just saturated for $CaCO_3$)

Cave water

6. Additional constraints on back-modelling

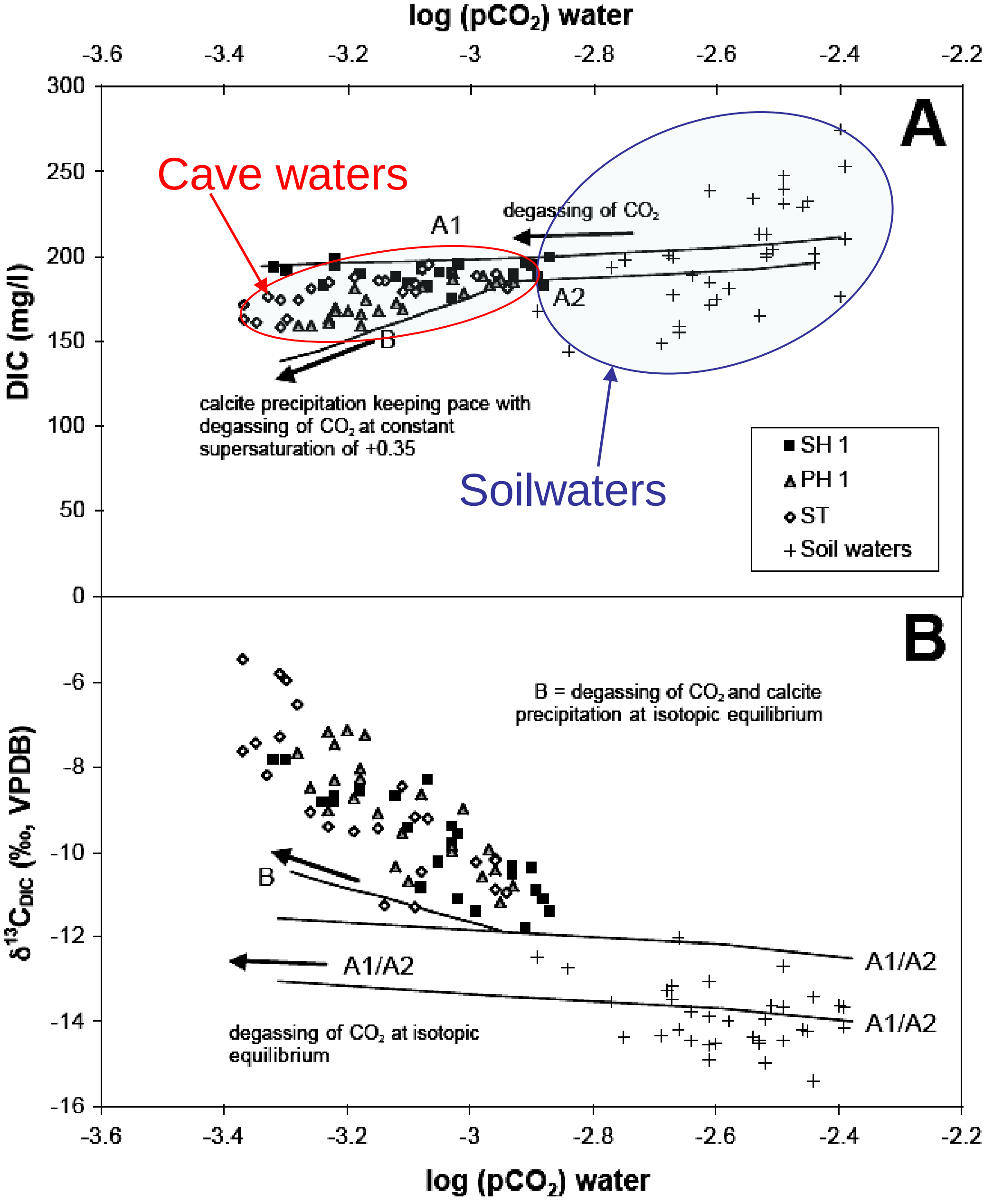
If a characteristic primary weathering trace element to Ca ratio is known, then the amount of Ca removal by prior precipitation can be estimated.



Modelled degassing and $CaCO_3$ precipitation at equilibrium leads to increases in $\delta^{13}C$ of the remaining water.

The observed increases are bigger – this is due to kinetic enhancement of the fractionation – CO_2 escaping can sometimes be 20 or 30 per mil lighter than the water rather than around 10. This is strongly developed here because of the ventilation. Frisia et al. (GCA< 2011) show that such kinetic effects are more widespread than previously thought.

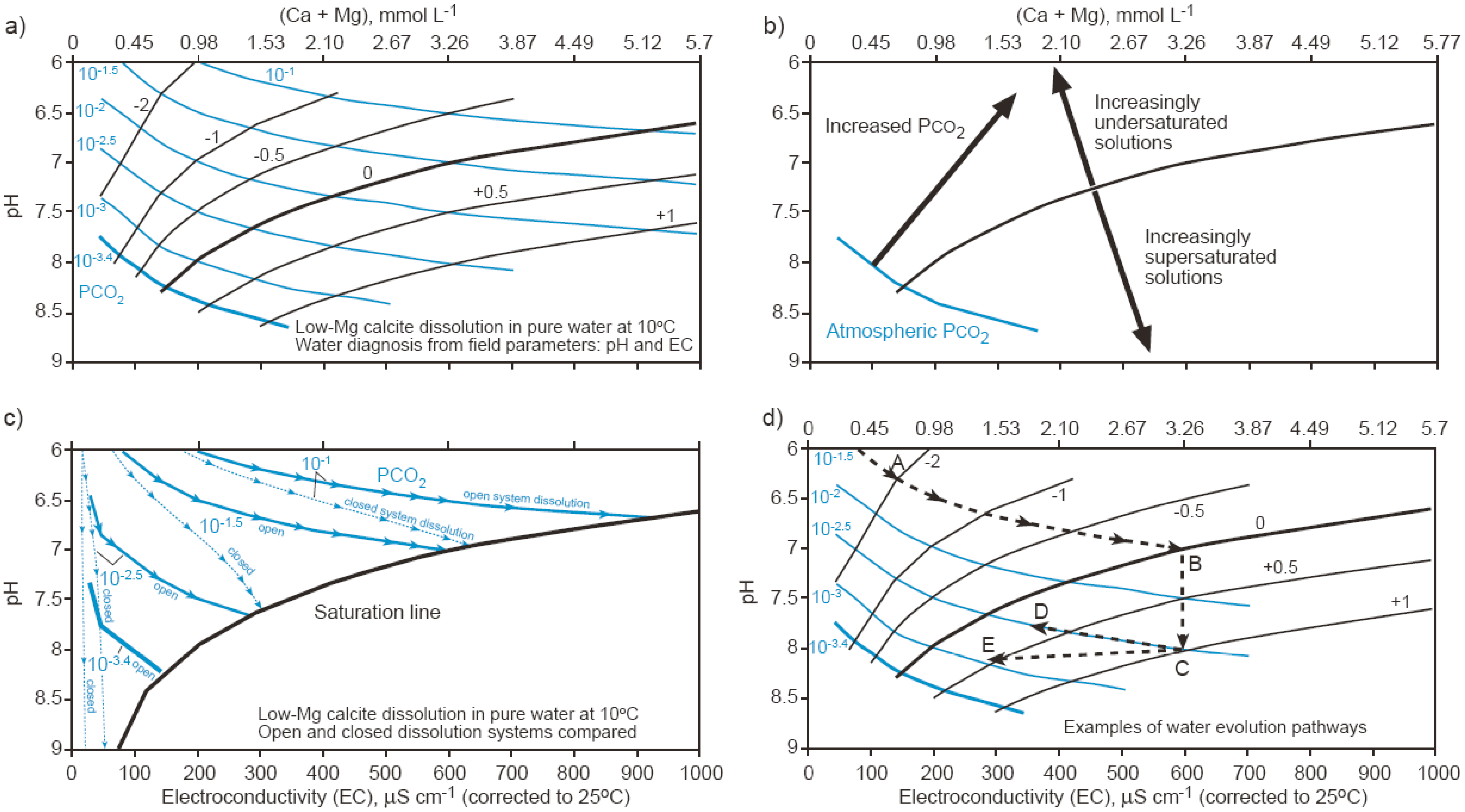
By comparison, CO_2 degassing from seawater into the atmosphere is only slightly lighter (about 1 per mil) than expected at equilibrium. In some other caves (e.g. in Soreq cave, Israel), degassing occurs at equilibrium.



After Spötl et al. (GCA, 2005)

6. A ready-reckoner for field studies

See spreadsheet "Figure 5.2 modelled carbonate system diagrams"



Fairchild & Baker (2012)

This ready-reckoner uses a specific low ratio of Mg/Ca in limestones being weathered and a fixed low proportion of non-carbonate ions. It can also be modified for higher-Mg conditions and would need a higher correction to EC if non-carbonate ions were more abundant.