Water-rock-CO_2 interactions for CO_2 geological storage

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Outline

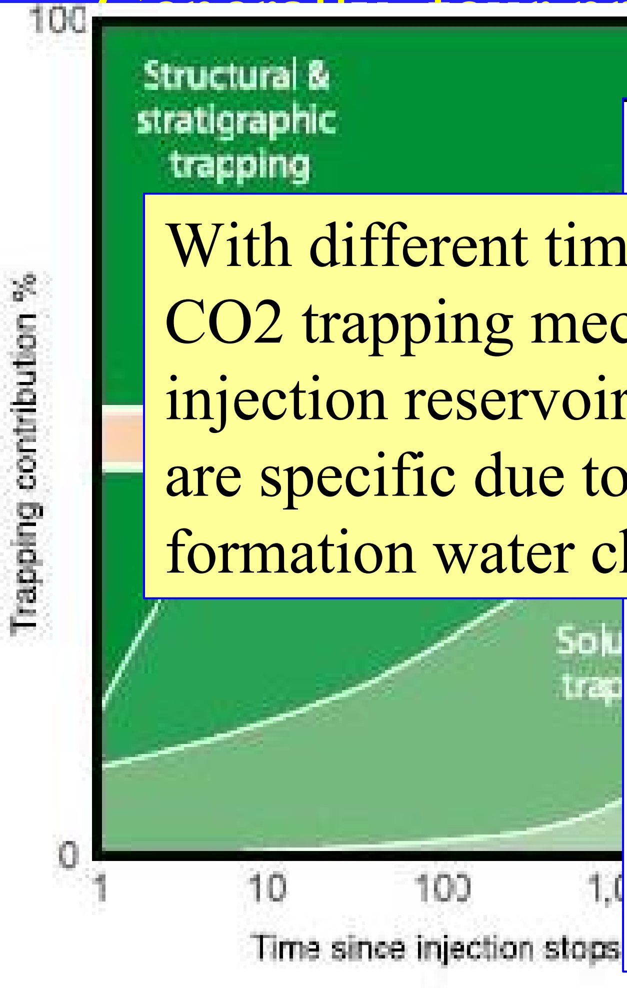
- Purposes for water-rock-CO_2 interaction study
- Typical water-rock-CO_2 interactions for CO_2 geological storage
- Methods for water-rock-CO_2 interaction study
- Future focuses

Purposes for water-rock-CO2 interactions study

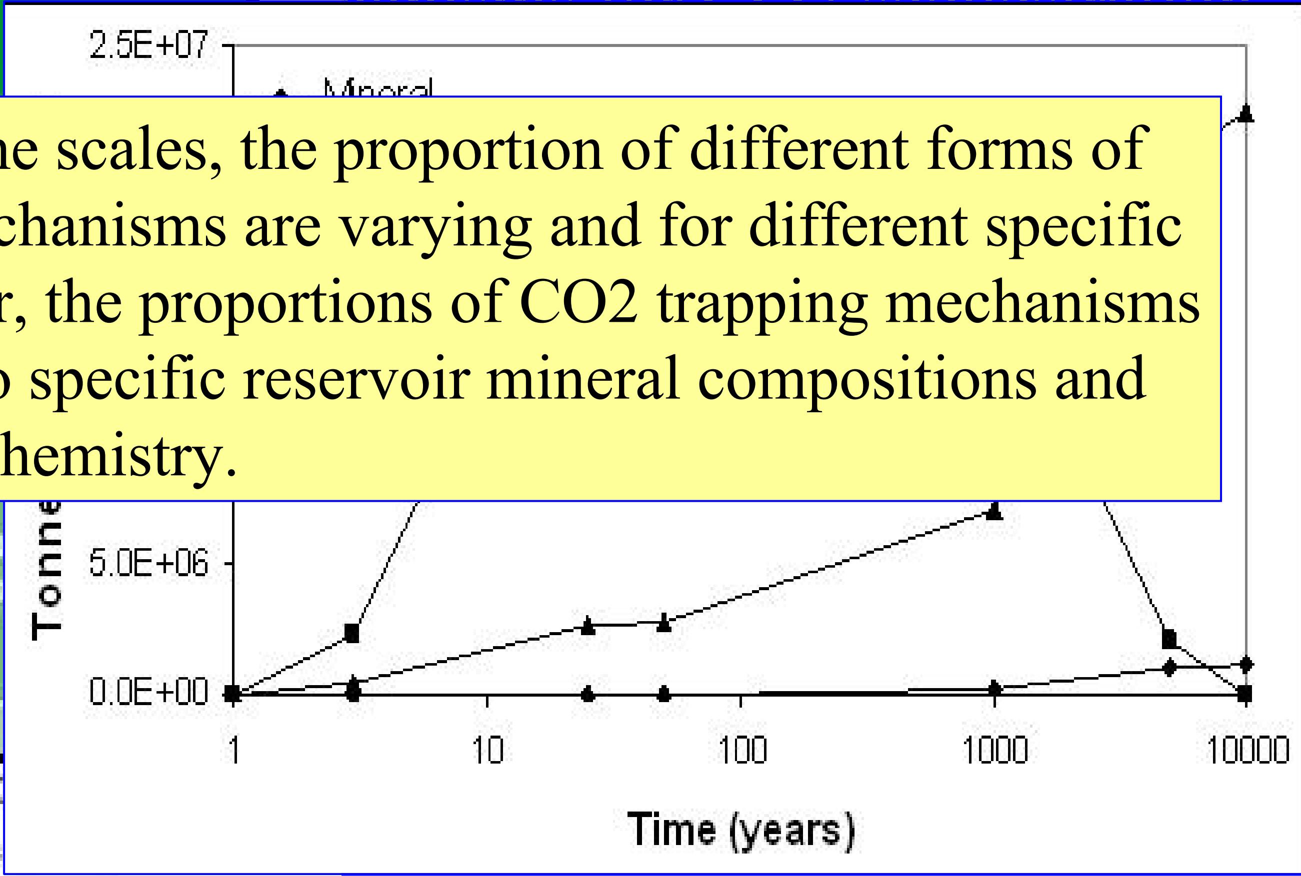
- determining CO_2 trapping mechanisms in saline formations
- understanding reservoir geochemical responses
- providing geochemical monitoring indicators
- assessing impact of CO2 storage on groundwater systems
- ……………

CO_2 trapping mechanisms in saline formations

Generally, four processes have been identified as the most
hanisms for CO2 sequestration



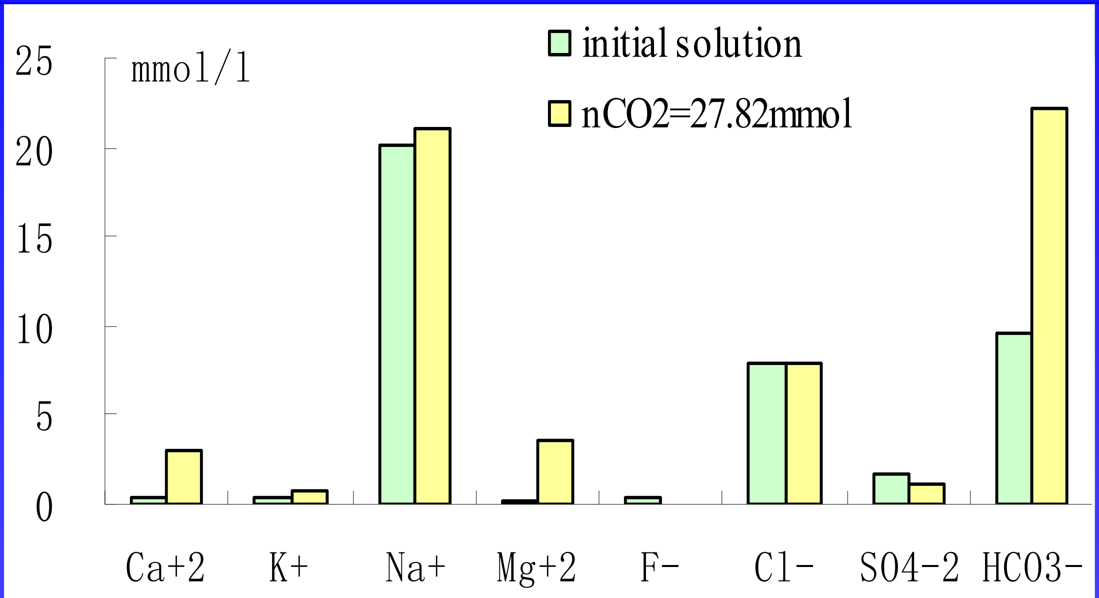
(IPCC,2005)

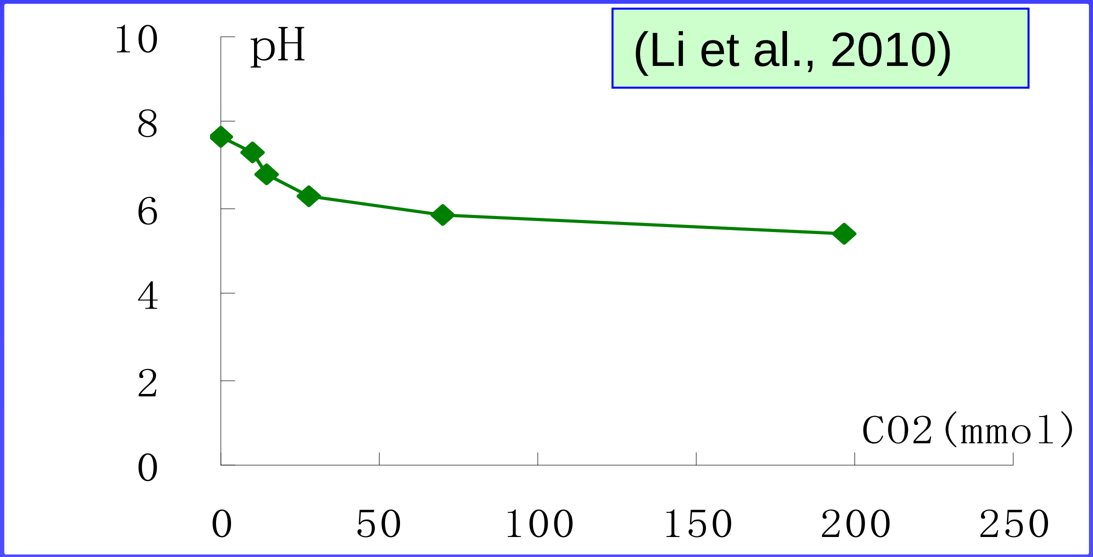


(Audigane P. et al., 2007)

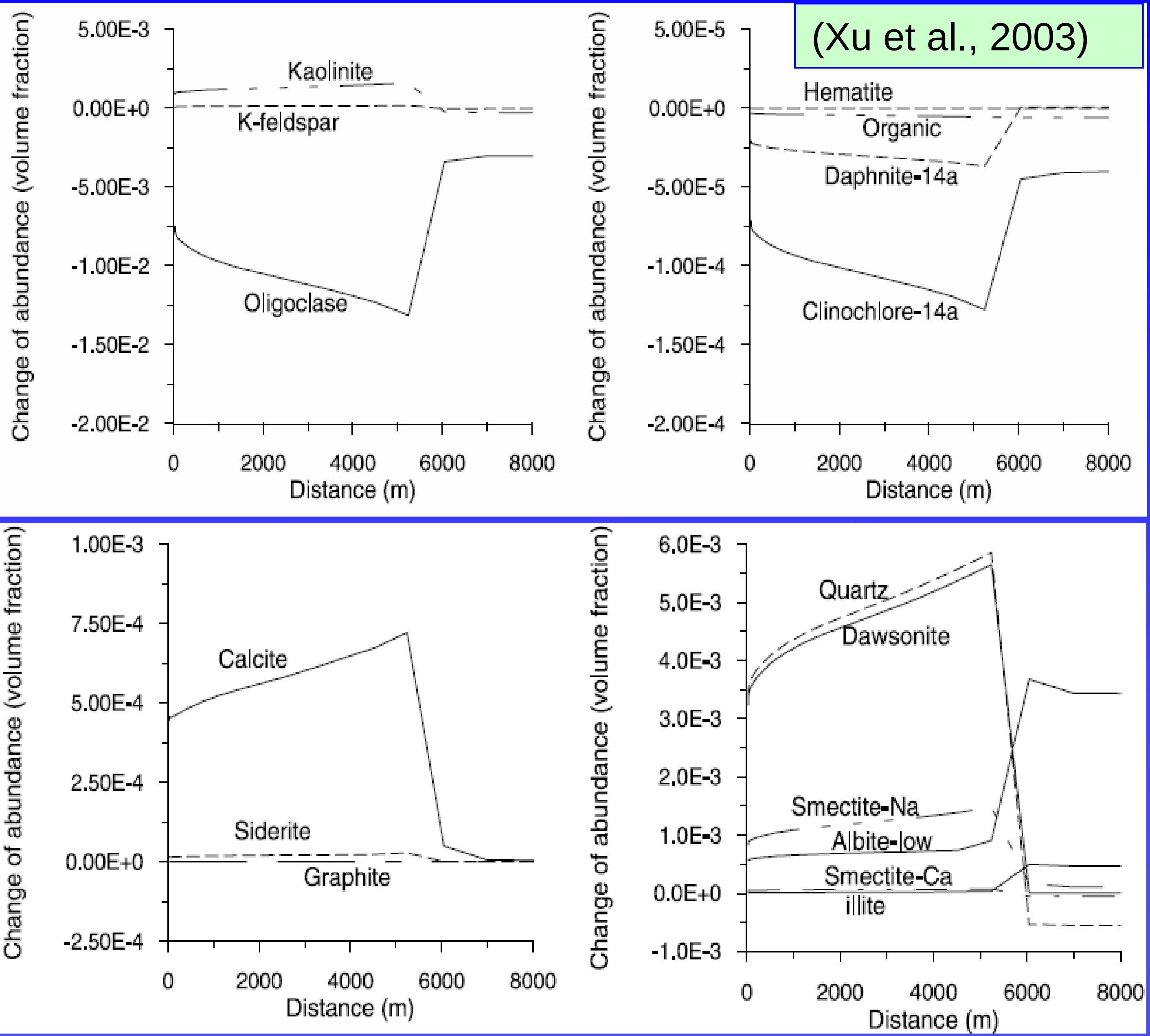
With different time scales, the proportion of different forms of CO2 trapping mechanisms are varying and for different specific injection reservoir, the proportions of CO2 trapping mechanisms are specific due to specific reservoir mineral compositions and formation water chemistry.

Understanding reservoir geochemical responses



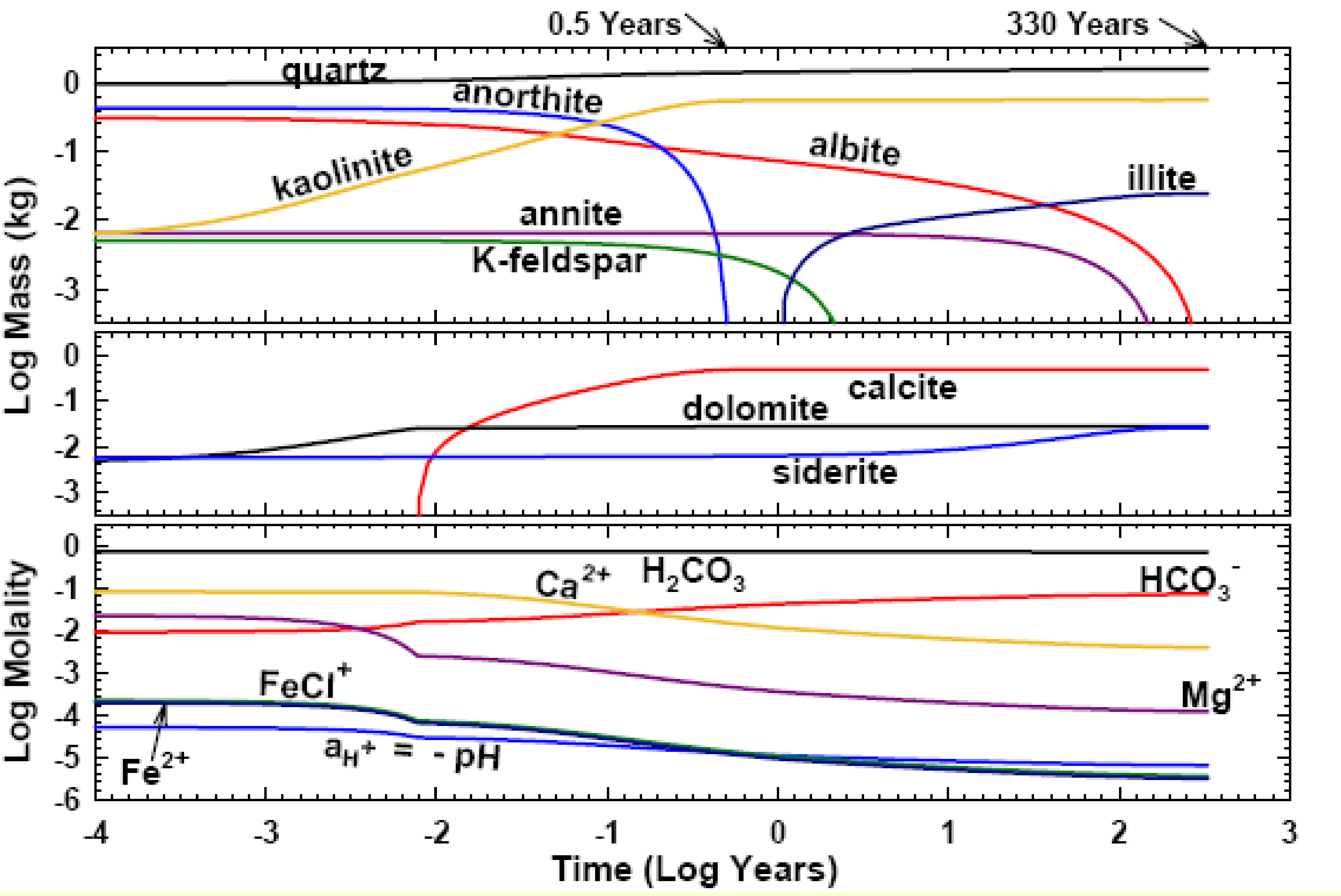

(Li et al., 2010)

Generally speaking, after CO2 is injected into deep saline formations, pH of reservoir water will decrease by 1-2 units and concentrations of chemical components like Al, Si, and HCO_3^- increase significantly. And CO2 would be sequestrated (fixed) mainly by secondary carbonate minerals.



(Xu et al., 2003)

Minerals in the formation water show different evolution tendency due to specific rock compositions and water chemistry. In Xu’s model, CO2 will be trapped by calcite, dolomite ,siderite and dawsonite,which will occur in the presence of high pressure CO2.



(Palandri and Kharaka, 2009)

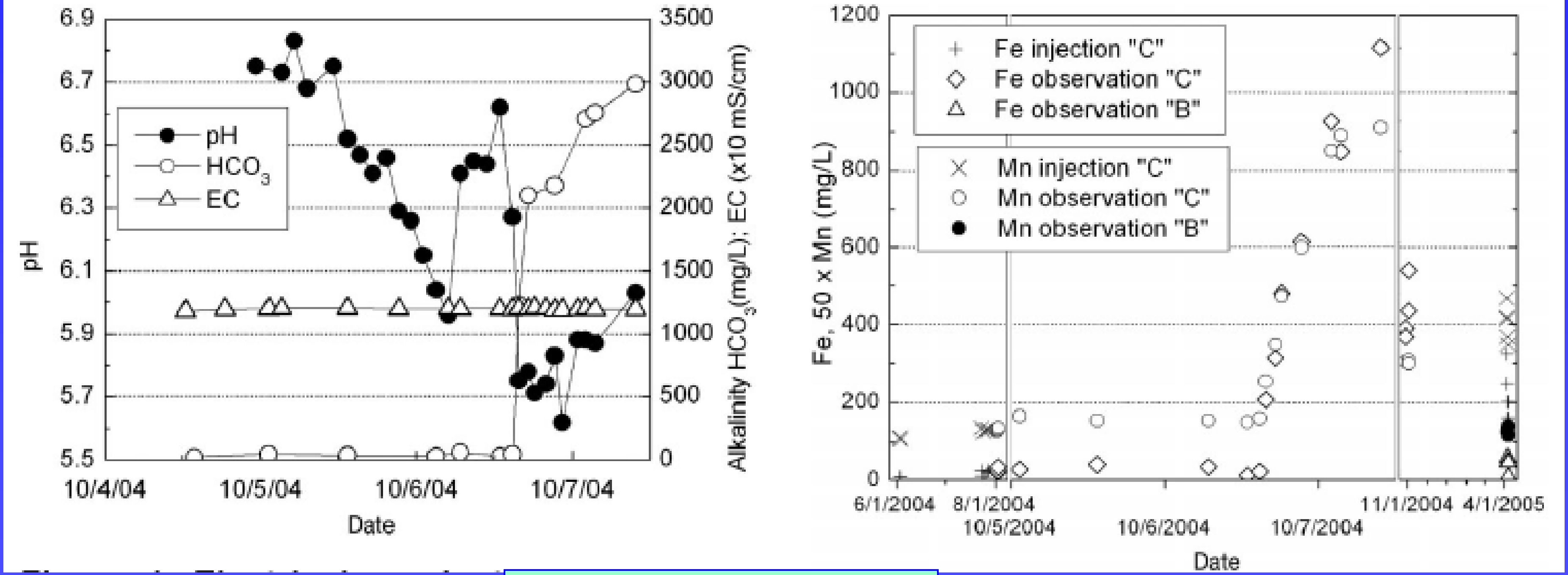
Providing geochemical monitoring indicators

In order to understand the migration path of CO2 plume and what happens after large volume CO2 is injected into the reservoir, effective monitoring needs to be carried out.

Although geophysical monitoring is very efficient, it’s expensive and is difficult to apply.

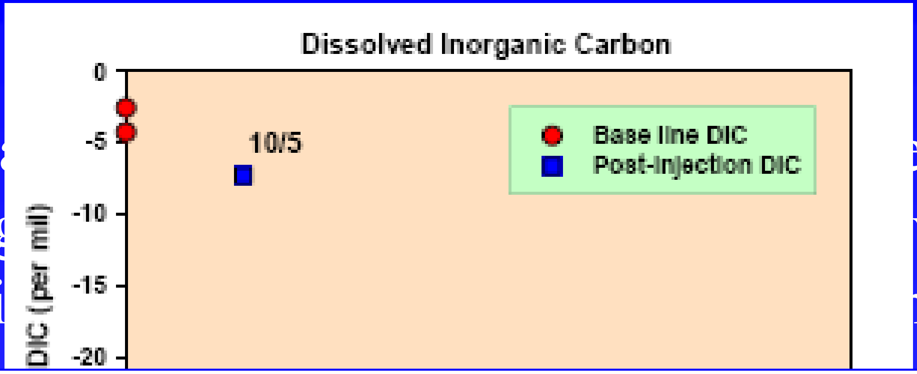
Geochemical monitoring is effective if appropriate monitoring indicators are identified.

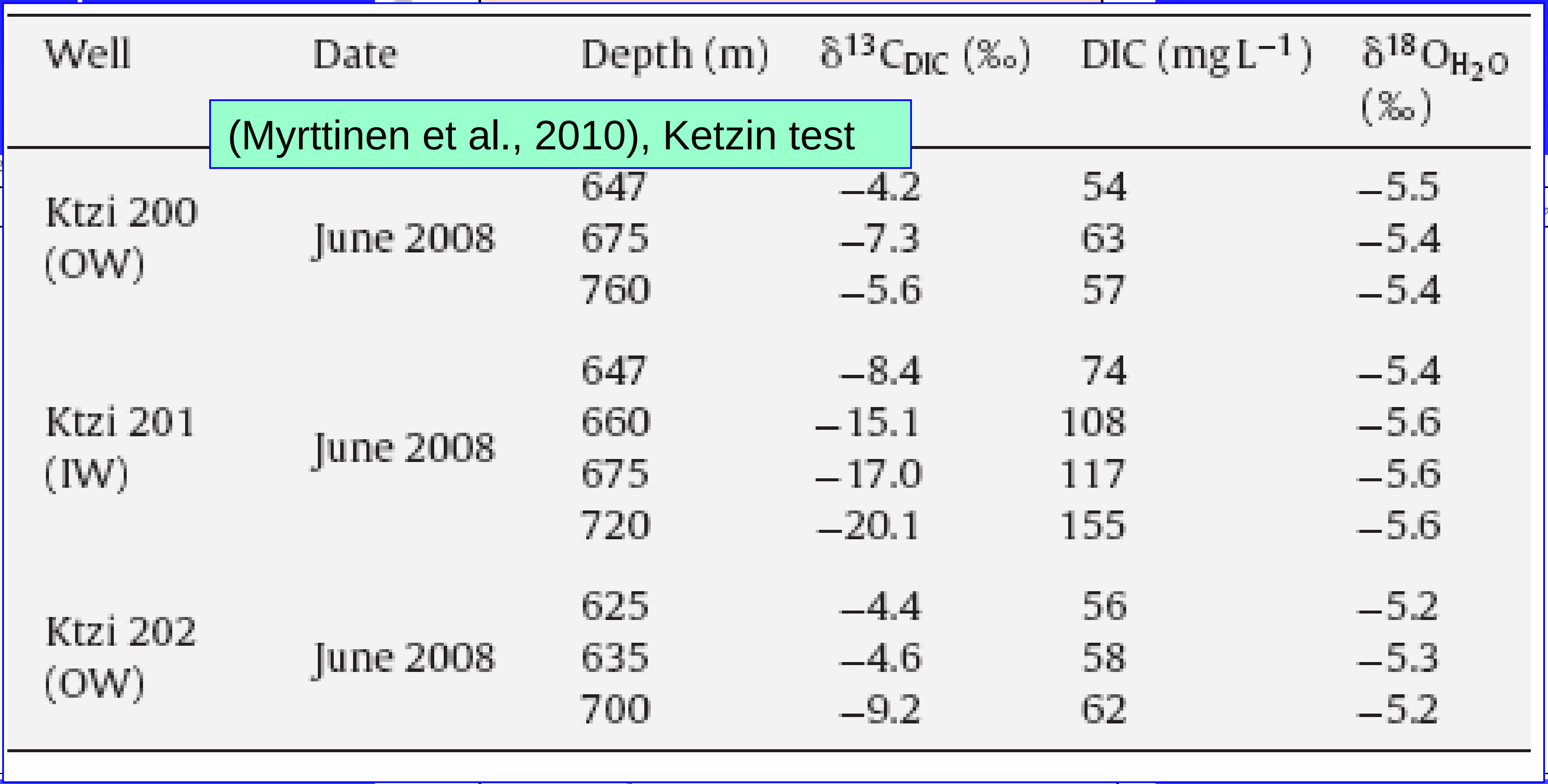
Results from experiments, field tests and numerical simulation indicate that pH, ion concentrations of HCO3-, Fe, Mn will increase even by magnitudes and these geochemical constitutes can be effective monitoring targets.



(Kharaka et al., 2006)

Isotopes of forma… emical
indicators since g… ved in CO2
injection due to i… n water, CO2





(Myrttinen et al., 2010), Ketzin test

Well	Date	Depth (m)	$\delta^{13}C_{DIC}$ (‰)	DIC ($mg\,L^{-1}$)	$\delta^{18}O_{H_2O}$ (‰)
Ktzi 200 (OW)	June 2008	647	−4.2	54	−5.5
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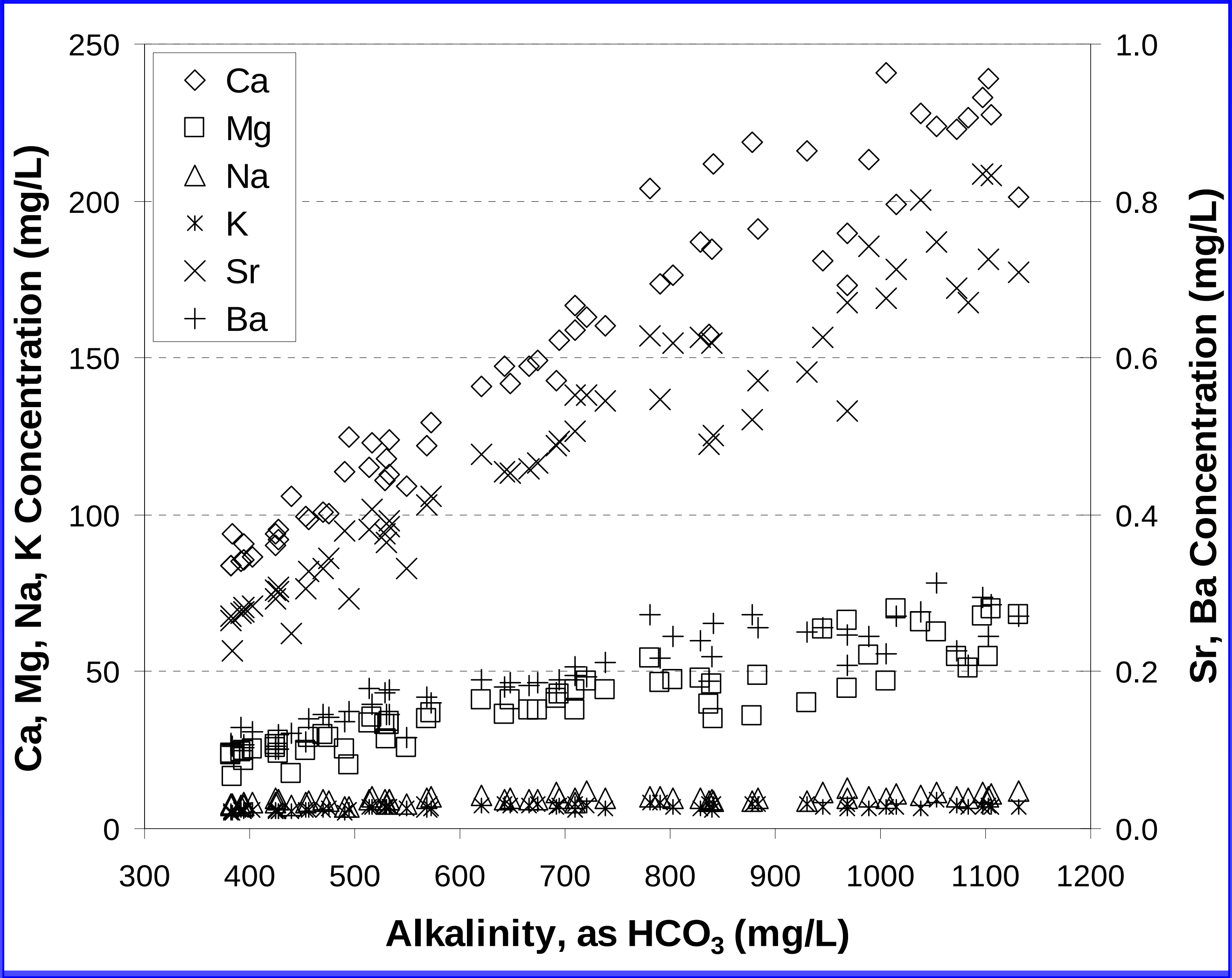
		635	−4.6	58	−5.3
		700	−9.2	62	−5.2

ngon and Mayer, 2011)

Investigating impact of CO2 storage on groundwater systems

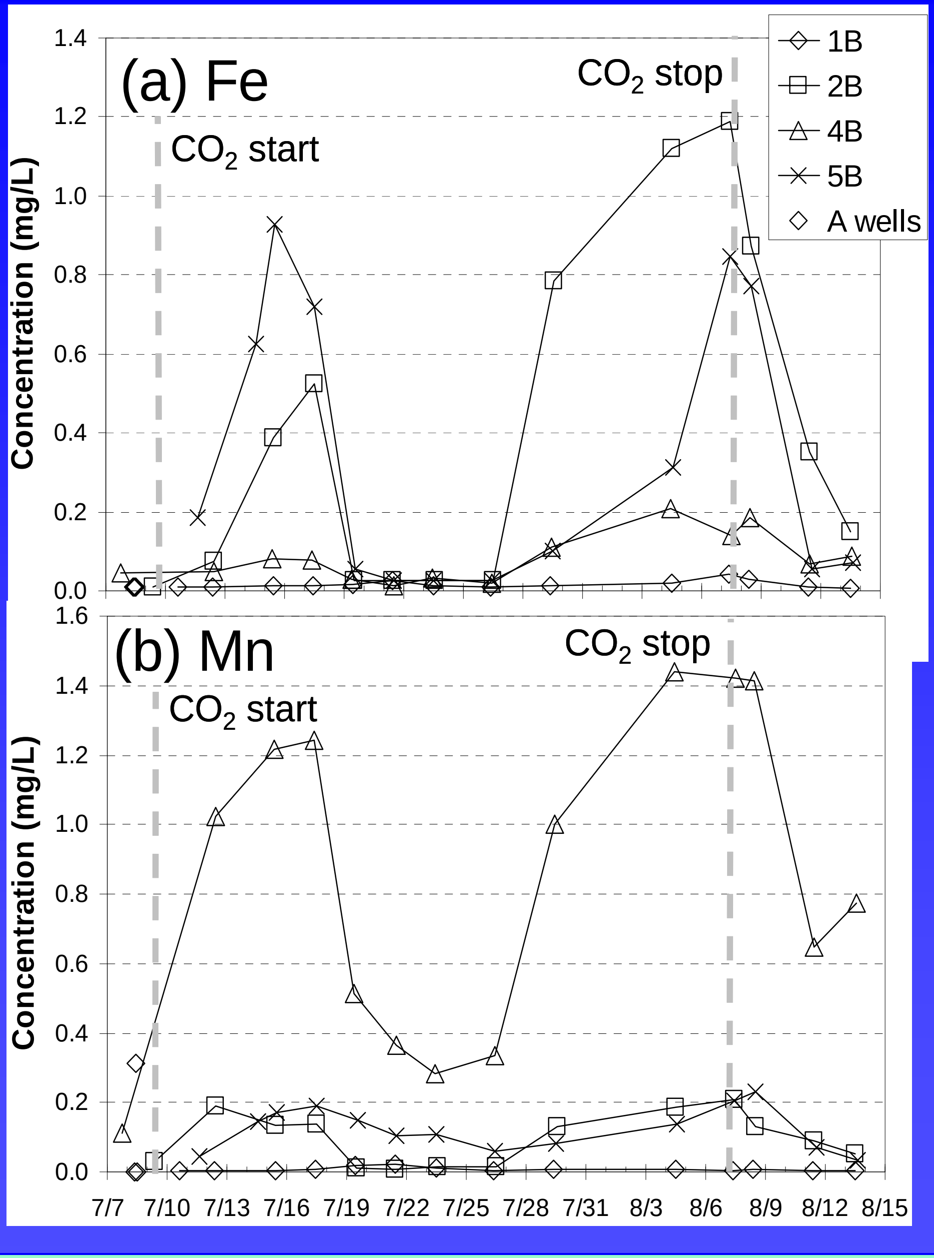
Once injected, CO2 could accelerate water-rock interaction and cause pH decrease and mobilization of metals and hazardous inorganic and organic constituents which could lead to groundwater quality deterioration.

When CO2 migrates from a deep saline formation, e.g. via local high-permeability pathways such as permeable faults or degraded wells, it will arrive in shallow groundwater systems and change the geochemical conditions in the aquifer and will cause secondary effects, contaminating shallow groundwater resources.



Concentrations of major cations in groundwater from the ZERT wells. Note the relatively constant concentrations of Na and K, but the general increases in the concentrations of divalent cations with water alkalinities, possibly indicating dissolution of carbonate minerals.

Results from Research Project on CO2 Geological Storage and Groundwater Resources from Earth Sciences Division, LBNL.



When CO2 is injected into groundwater, concentration of Fe and Mn show an increase.

The low Fe and Mn concentrations during July 20 to July 26 could be attributing to the oxidizing conditions possibly caused by percolating oxygenated water from rainfall events.

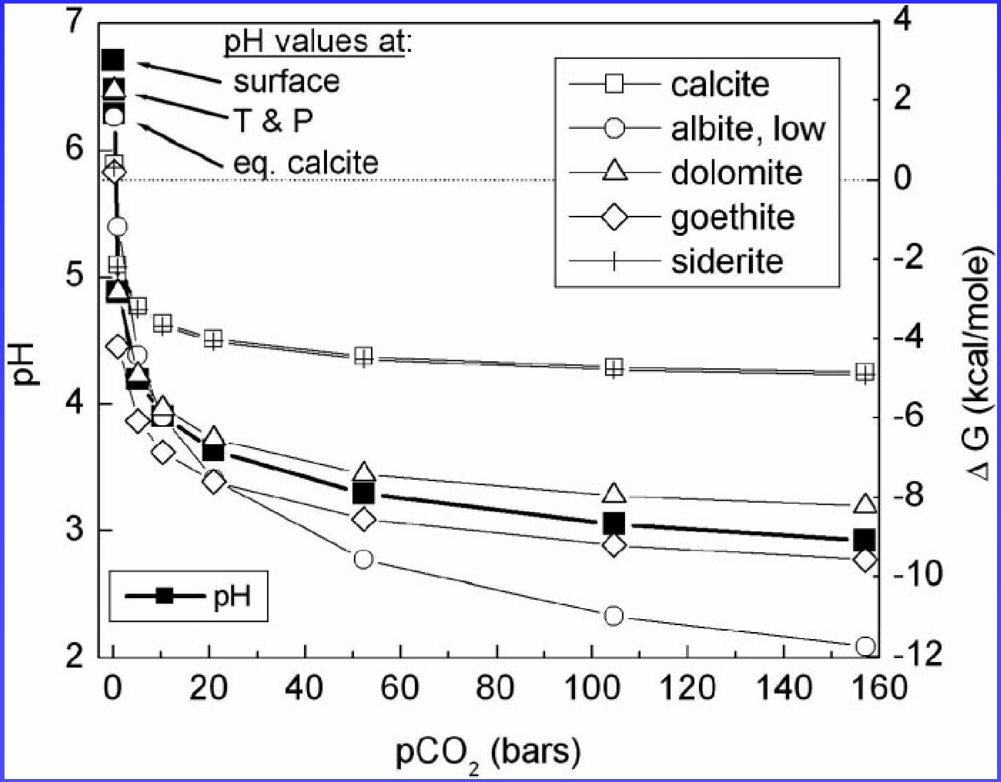
Results from Research Project on CO2 Geological Storage and Groundwater Resources from Earth Sciences Division, LBNL.

Typical water-rock-CO_2 interactions for CO_2 geological storage

$CO_2 + H_2O \leftrightarrow H_2CO_3$ (aq)
H_2CO_3 (aq) $\leftrightarrow H^+ + HCO_3^-$
Calcite + $H^+ \leftrightarrow Ca^{2+} + HCO_3^-$
Dolomite+ $2H^+ \leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^-$
Chlorite+ $16H^+ \leftrightarrow 5Mg^{2+} + 2Al^{3+} + 3SiO_2$ (aq) $+12H_2O$
Albite + $4H^+ \leftrightarrow Na^+ + Al^{3+} + 3SiO_2$ (aq) $+2H_2O$
Dawsonite + $4H^+ \leftrightarrow Na^+ + Al^{3+} + CO_2$ (aq) $+3H_2O$
Anorthite+ $8H^+ \leftrightarrow Ca^{2+} + 2Al^{3+} + 2SiO_2$ (aq) $+4H_2O$

……….

In the Frio test, the observed increases in concentrations of HCO3 and Ca likely result from the rapid dissolution of calcite (1); the increases of Fe are likely caused by dissolution of the observed iron oxyhydroxides (2),this is the same for Mn; another dominant reaction is aluminosilicate mineral dissolution .



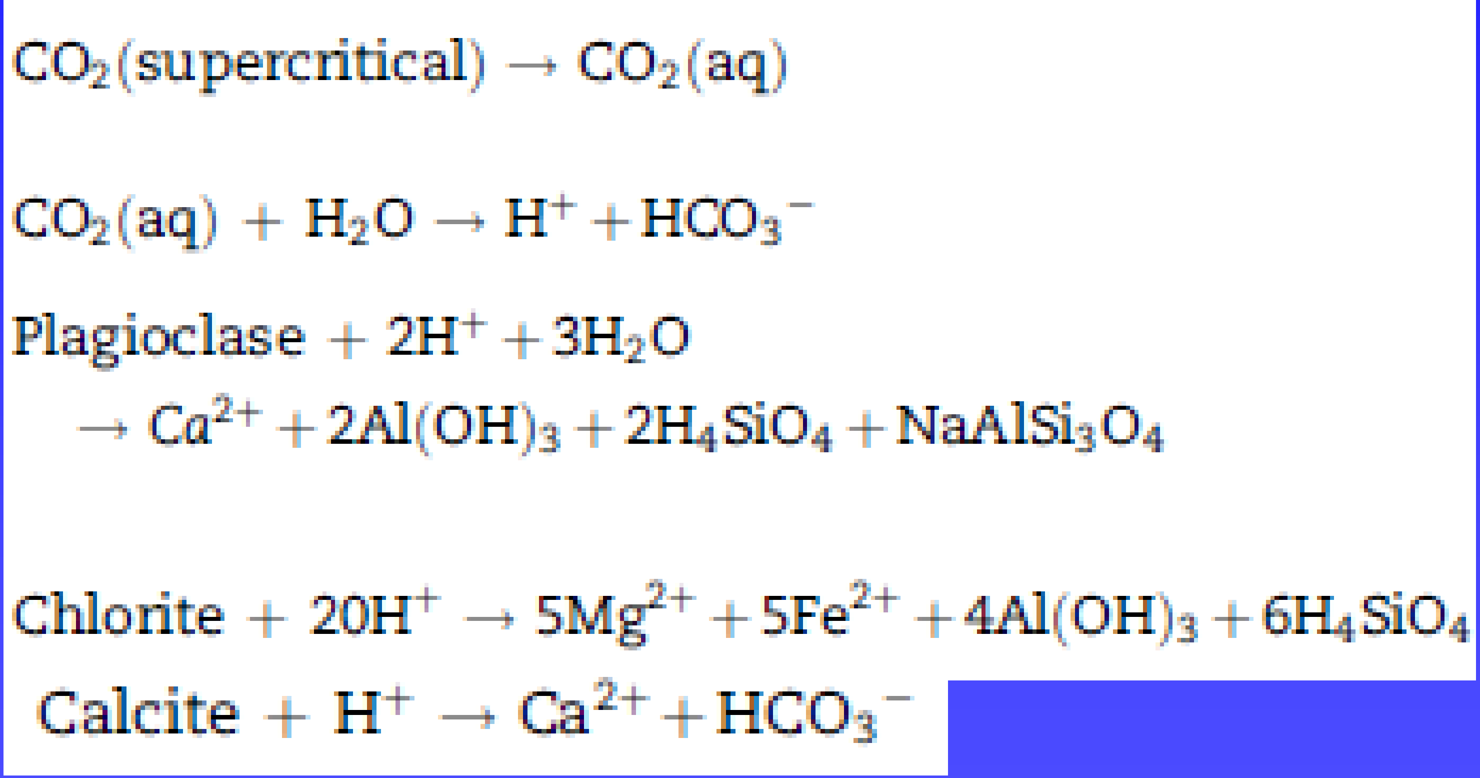
(Kharaka et al., 2006) Frio test

$$CO_2(g) + H_2O + CaCO_3(s) \Leftrightarrow Ca^{2+} + 2HCO_3^-. \quad (1)$$

$$8Fe(OH)_3(s) + CH_3COOH^0 + 14H^+ \leftrightarrow 8Fe^{2+} + 2HCO_3^- + 20H_2O. \quad (2)$$

$$0.4H^+ + Ca_{0.2}Na_{0.8}Al_{1.2}Si_{2.8}O_8(s) + 0.8CO_2(g) + 1.2H_2O \Leftrightarrow 0.2Ca^{2+} + 0.8NaAlCO_3(OH)_2(s) + 0.4Al(OH)_3(s) + 2.8SiO_2(s). \quad (3)$$

The following reactions are proposed to summarize the geochemical processes at Nagaoka during the early stage of CO2 storage at the reservoir (Mito et al., 2008).



$$CO_2\,(\text{supercritical}) \rightarrow CO_2\,(aq)$$

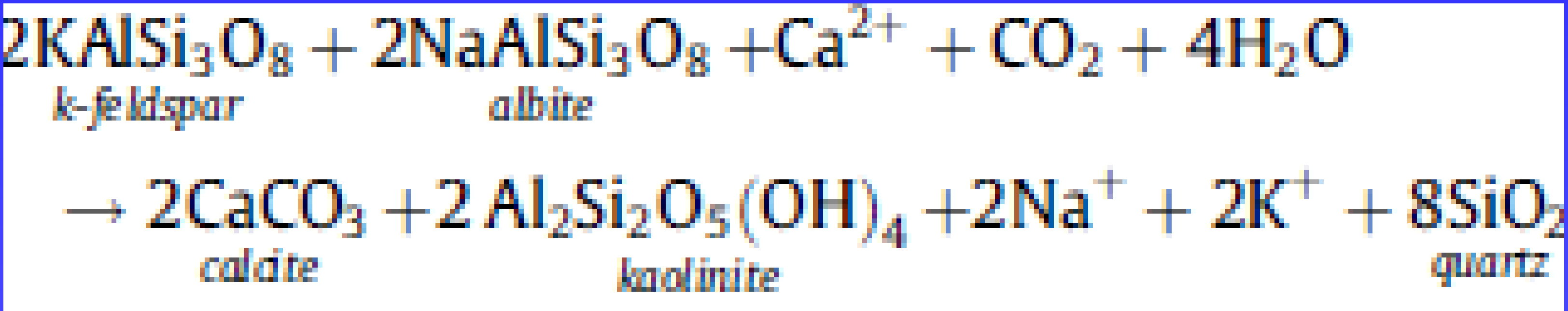
$$CO_2\,(aq) + H_2O \rightarrow H^+ + HCO_3^-$$

$$\text{Plagioclase} + 2H^+ + 3H_2O$$
$$\rightarrow Ca^{2+} + 2Al(OH)_3 + 2H_4SiO_4 + NaAlSi_3O_4$$

$$\text{Chlorite} + 20H^+ \rightarrow 5Mg^{2+} + 5Fe^{2+} + 4Al(OH)_3 + 6H_4SiO_4$$

$$\text{Calcite} + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

The low pH and under-saturation of the solution promoted extensive calcite cement dissolution in all samples. The overall alterations after the initial acidification and dissolution of carbonates are represented by the following reactions (Ketzer et al., 2009):



$$\underset{\text{k-feldspar}}{2KAlSi_3O_8} + \underset{\text{albite}}{2NaAlSi_3O_8} + Ca^{2+} + CO_2 + 4H_2O \rightarrow \underset{\text{calcite}}{2CaCO_3} + 2\,\underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4} + 2Na^{+} + 2K^{+} + \underset{\text{quartz}}{8SiO_2}$$

Methods for water-rock-CO_2 interaction study

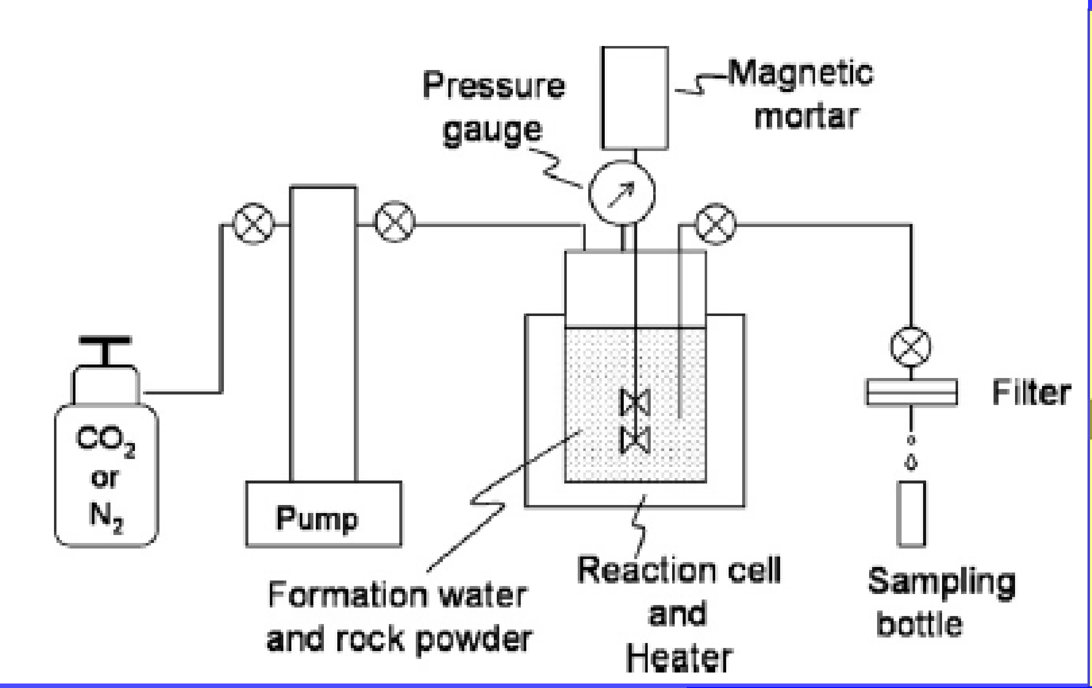
- Experiments of Water-rock-CO_2 interactions in laboratory
- Numerical simulation of a specific site
- Field test and corresponding monitoring

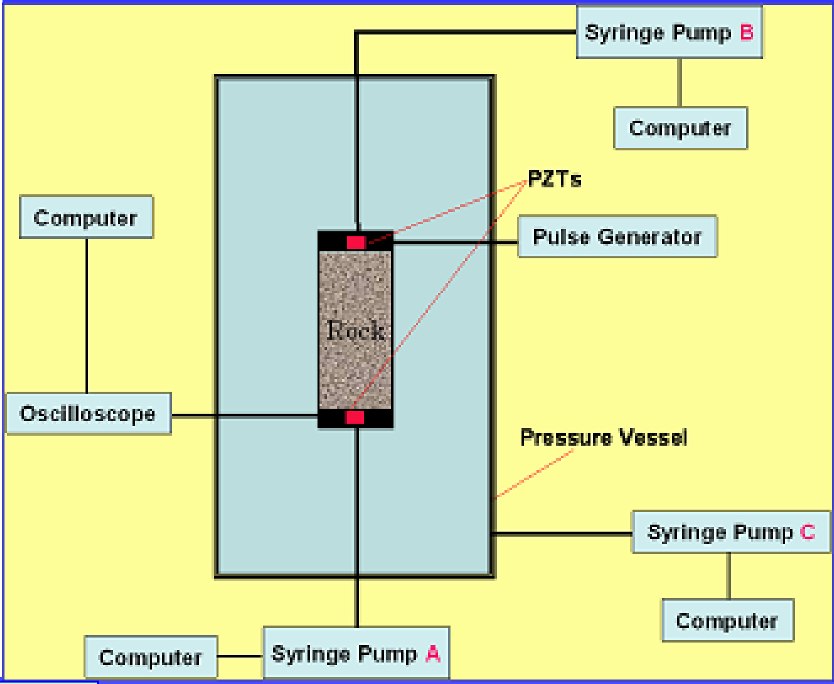
Physical modeling of water-rock-CO2 interaction for Nagaoka test site of Japan

Reaction conditions: 50℃ and 10MPa;

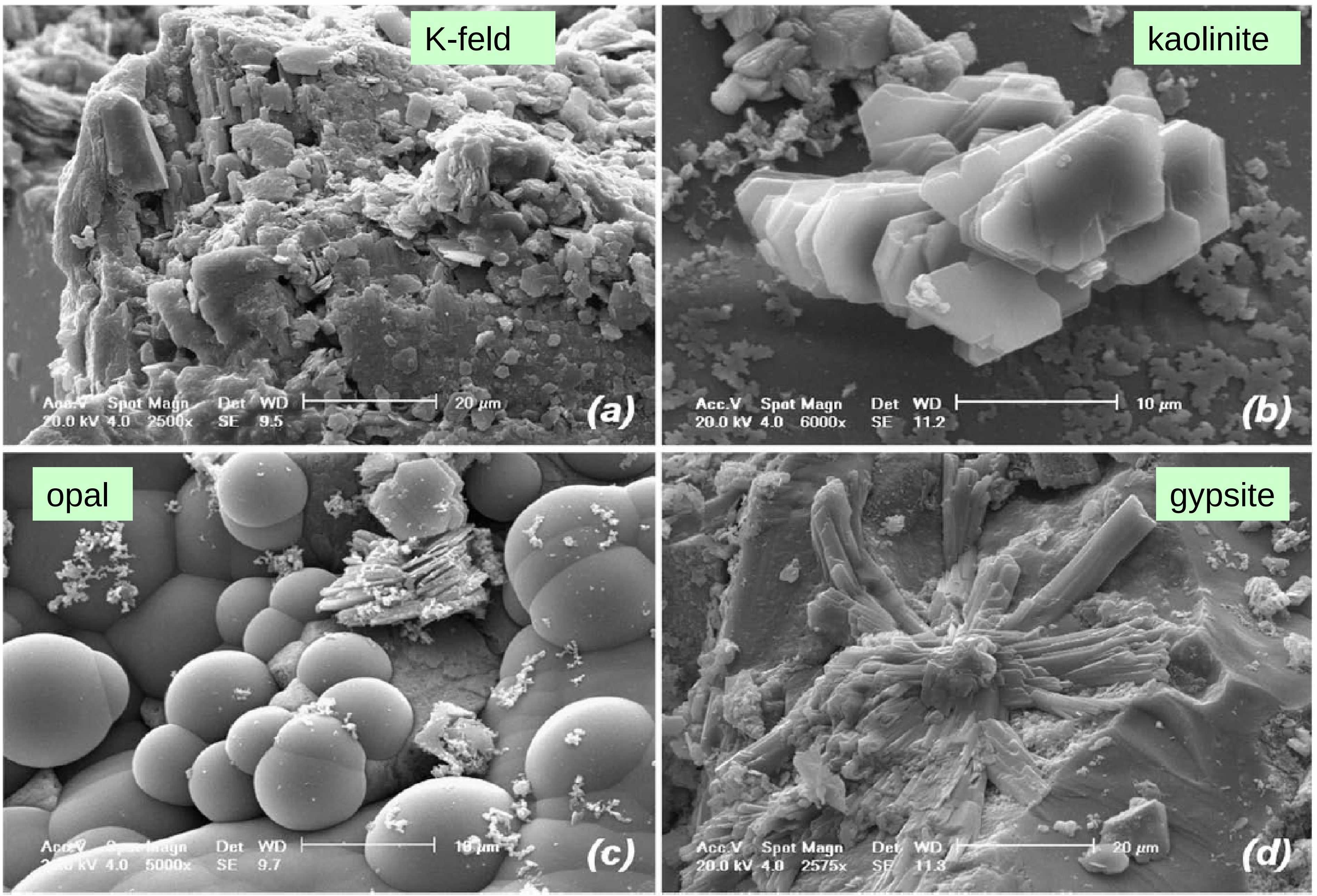
Reaction time: 15 days;

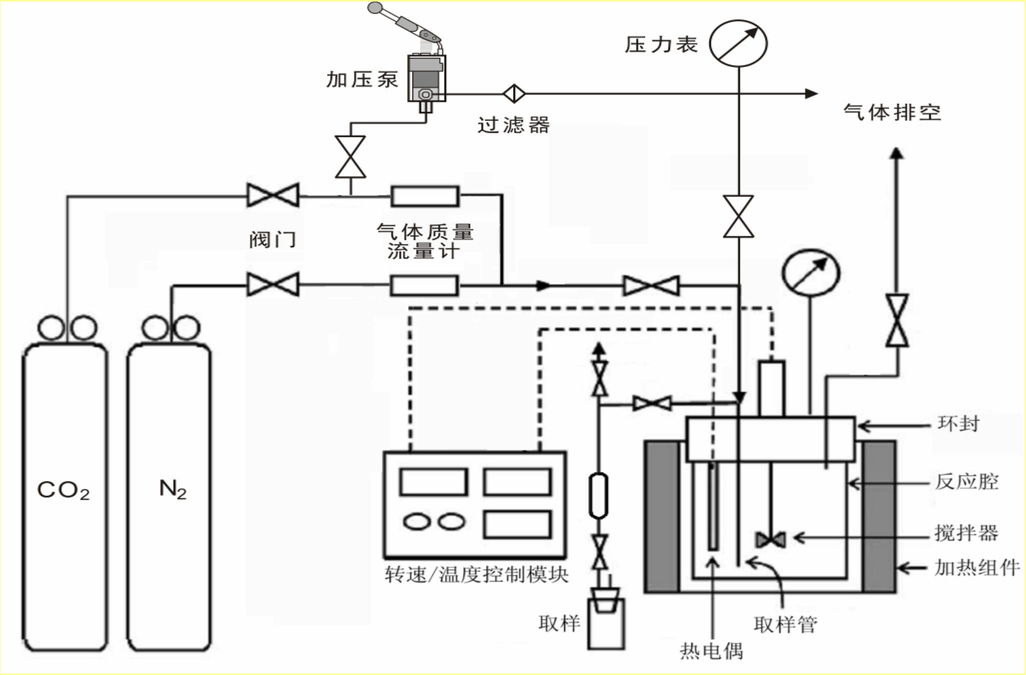
Reactants: formation water stored for two years and 4g rock powers;





(Mito S. et al., 2008)


K-feld
Acc.V Spot Magn Det WD 20 µm
20.0 kV 4.0 2500x SE 9.5
(a)
kaolinite
Acc.V Spot Magn Det WD 10 µm
20.0 kV 4.0 6000x SE 11.2
(b)
opal
Acc.V Spot Magn Det WD 10 µm
20.0 kV 4.0 5000x SE 9.7
(c)
gypsite
Acc.V Spot Magn Det WD 20 µm
20.0 kV 4.0 2575x SE 11.3
(d)



Water-rock-CO2 interaction study for CO2 sequestration in the Guantao formation of the Bohai Bay Basin, NE China

200℃ and 20MPa;

15 days;

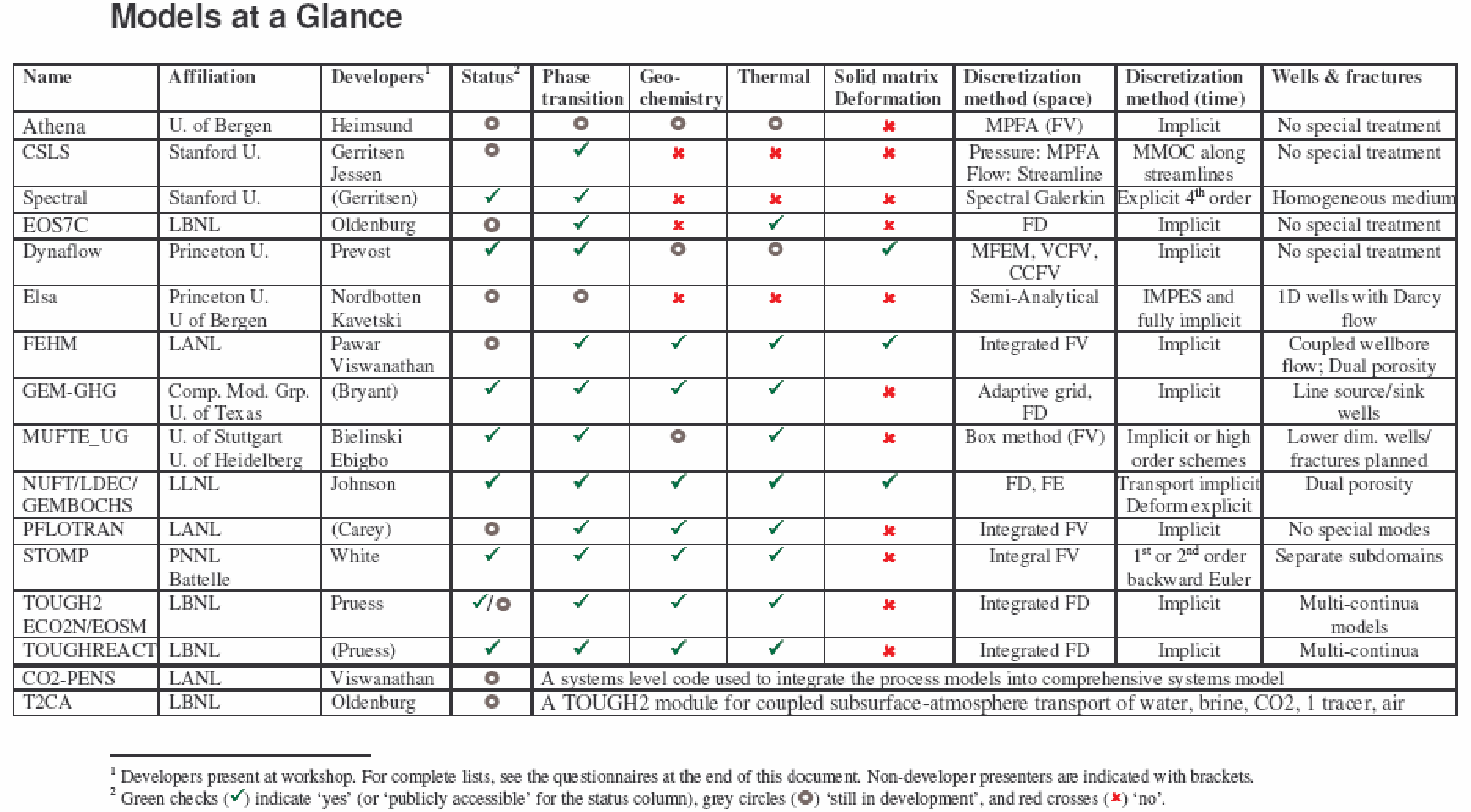
Formation water and rock ;

Methods for water-rock-CO_2 interactions study

- Experiments of Water-rock-CO_2 interactions in laboratory
- Numerical simulation based on specific site
- Field test and corresponding monitoring

Numerical simulations on specific site

List of numerical codes (Study performed by Geogreen)



Models at a Glance

Name	Affiliation	Developers[1]	Status[2]	Phase transition	Geo-chemistry	Thermal	Solid matrix Deformation	Discretization method (space)	Discretization method (time)	Wells & fractures
Athena	U. of Bergen	Heimsund	○	○	○	○	✗	MPFA (FV)	Implicit	No special treatment
CSLS	Stanford U.	Gerritsen Jessen	○	✓	✗	✗	✗	Pressure: MPFA Flow: Streamline	MMOC along streamlines	No special treatment
Spectral	Stanford U.	(Gerritsen)	✓	✓	✗	✗	✗	Spectral Galerkin	Explicit 4th order	Homogeneous medium
EOS7C	LBNL	Oldenburg	○	✓	✗	✓	✗	FD	Implicit	No special treatment
Dynaflow	Princeton U.	Prevost	✓	✓	○	○	✓	MFEM, VCFV, CCFV	Implicit	No special treatment
Elsa	Princeton U. U of Bergen	Nordbotten Kavetski	○	○	✗	✗	✗	Semi-Analytical	IMPES and fully implicit	1D wells with Darcy flow
FEHM	LANL	Pawar Viswanathan	○	✓	✓	✓	✓	Integrated FV	Implicit	Coupled wellbore flow; Dual porosity
GEM-GHG	Comp. Mod. Grp. U. of Texas	(Bryant)	✓	✓	✓	✓	✗	Adaptive grid, FD	Implicit	Line source/sink wells
MUFTE_UG	U. of Stuttgart U. of Heidelberg	Bielinski Ebigbo	✓	✓	○	✓	✗	Box method (FV)	Implicit or high order schemes	Lower dim. wells/ fractures planned
NUFT/LDEC/ GEMBOCHS	LLNL	Johnson	✓	✓	✓	✓	✓	FD, FE	Transport implicit Deform explicit	Dual porosity
PFLOTRAN	LANL	(Carey)	○	✓	✓	✓	✗	Integrated FV	Implicit	No special modes
STOMP	PNNL Battelle	White	✓	✓	✓	✓	✗	Integral FV	1st or 2nd order backward Euler	Separate subdomains
TOUGH2 ECO2N/EOSM	LBNL	Pruess	✓/○	✓	✓	✓	✗	Integrated FD	Implicit	Multi-continua models
TOUGHREACT	LBNL	(Pruess)	✓	✓	✓	✓	✗	Integrated FD	Implicit	Multi-continua
CO2-PENS	LANL	Viswanathan	○	A systems level code used to integrate the process models into comprehensive systems model						
T2CA	LBNL	Oldenburg	○	A TOUGH2 module for coupled subsurface-atmosphere transport of water, brine, CO2, 1 tracer, air						

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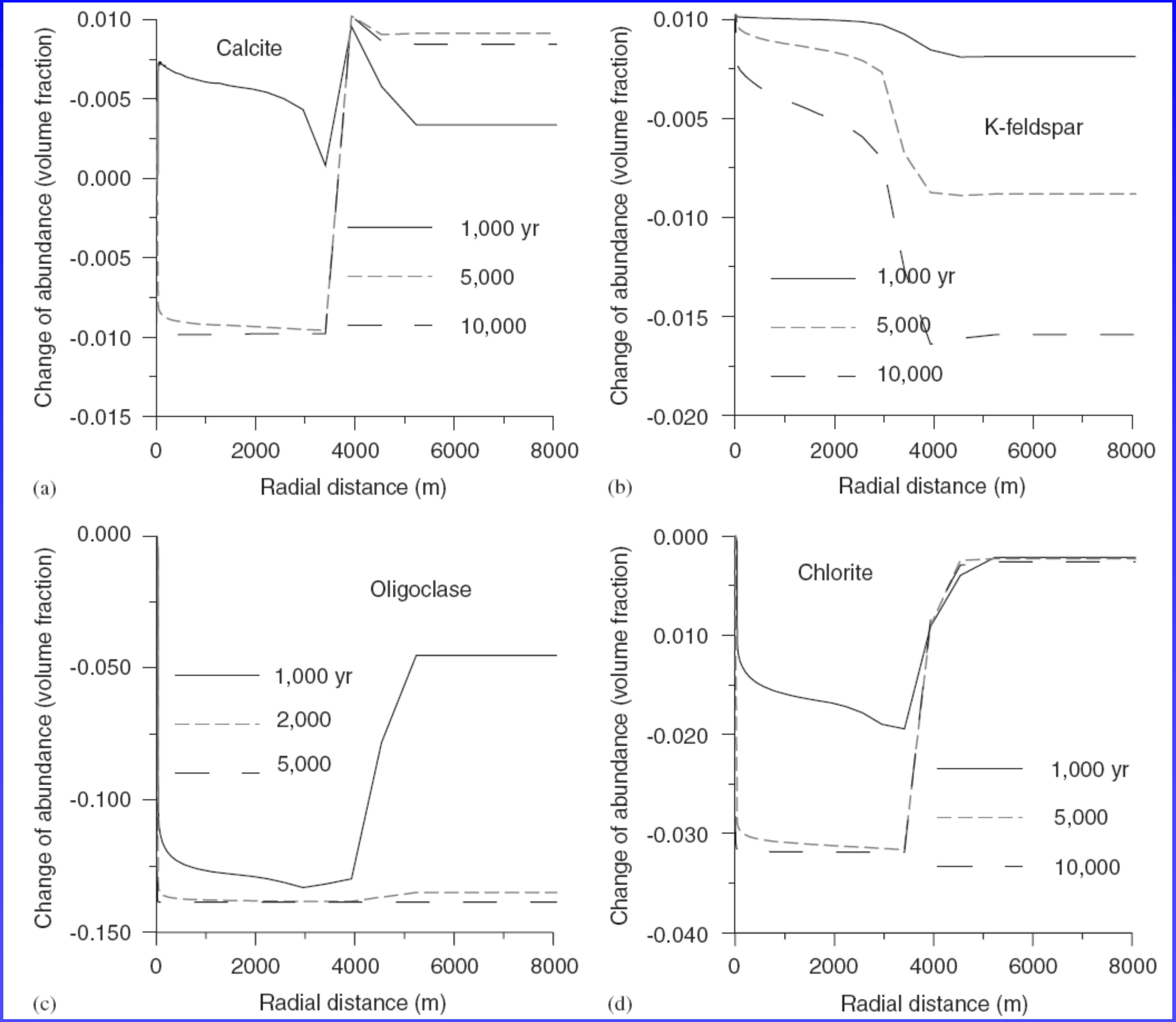
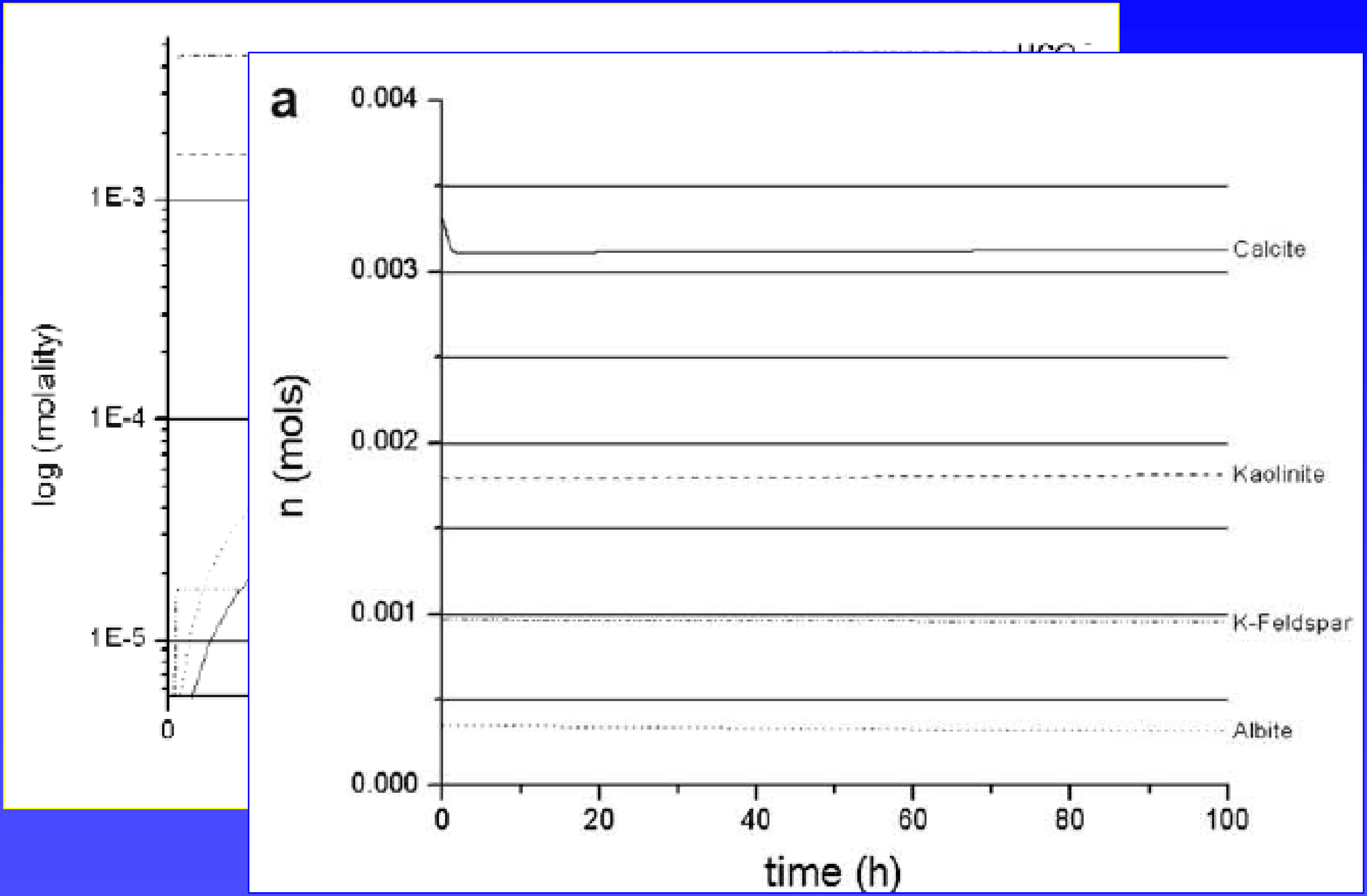
[1] Developers present at workshop. For complete lists, see the questionnaires at the end of this document. Non-developer presenters are indicated with brackets.

[2] Green checks (✓) indicate 'yes' (or 'publicly accessible' for the status column), grey circles (○) 'still in development', and red crosses (✗) 'no'.

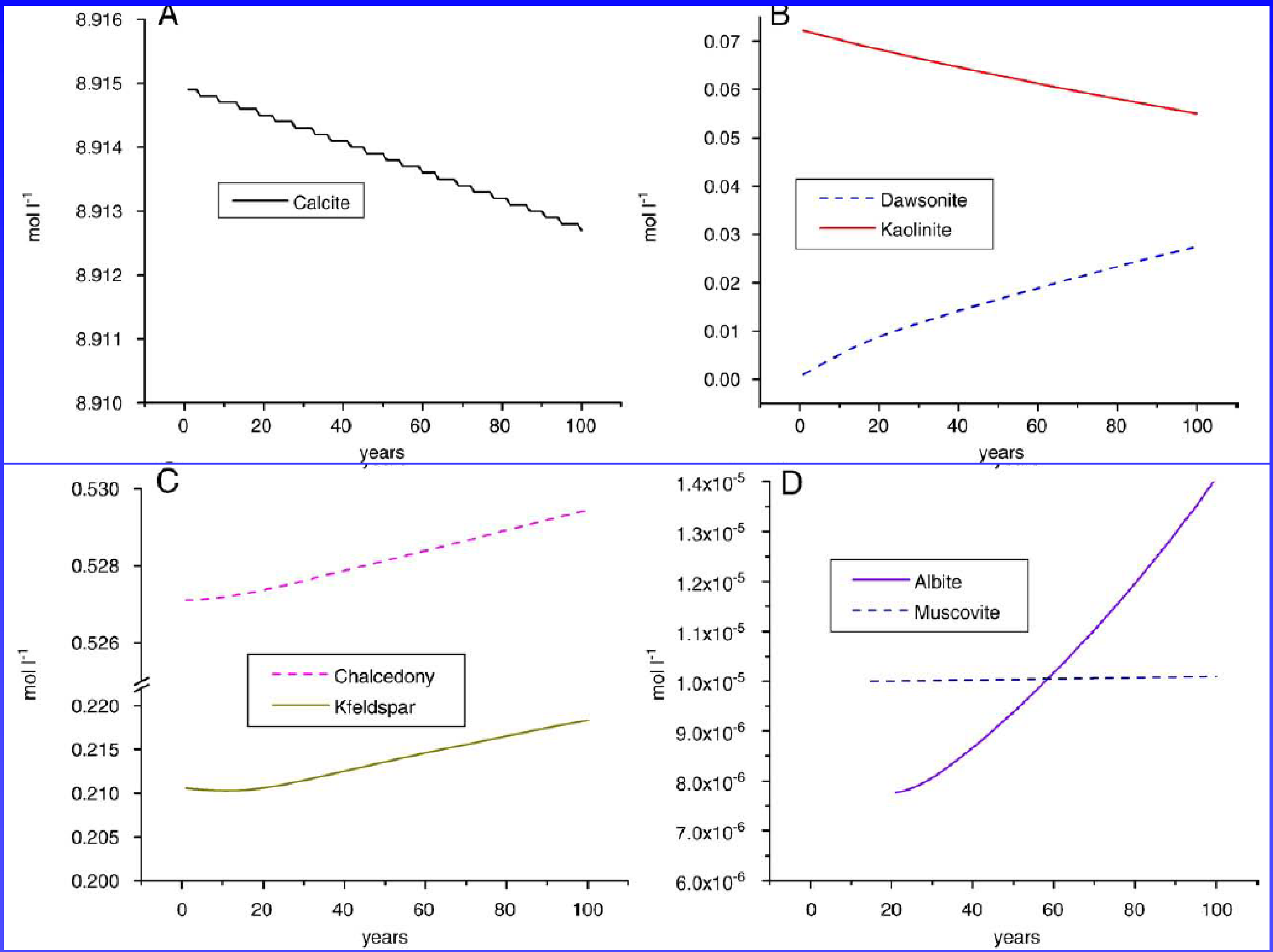


Changes of different kinds of minerals over time scales due to water-rock-CO2 interactions.

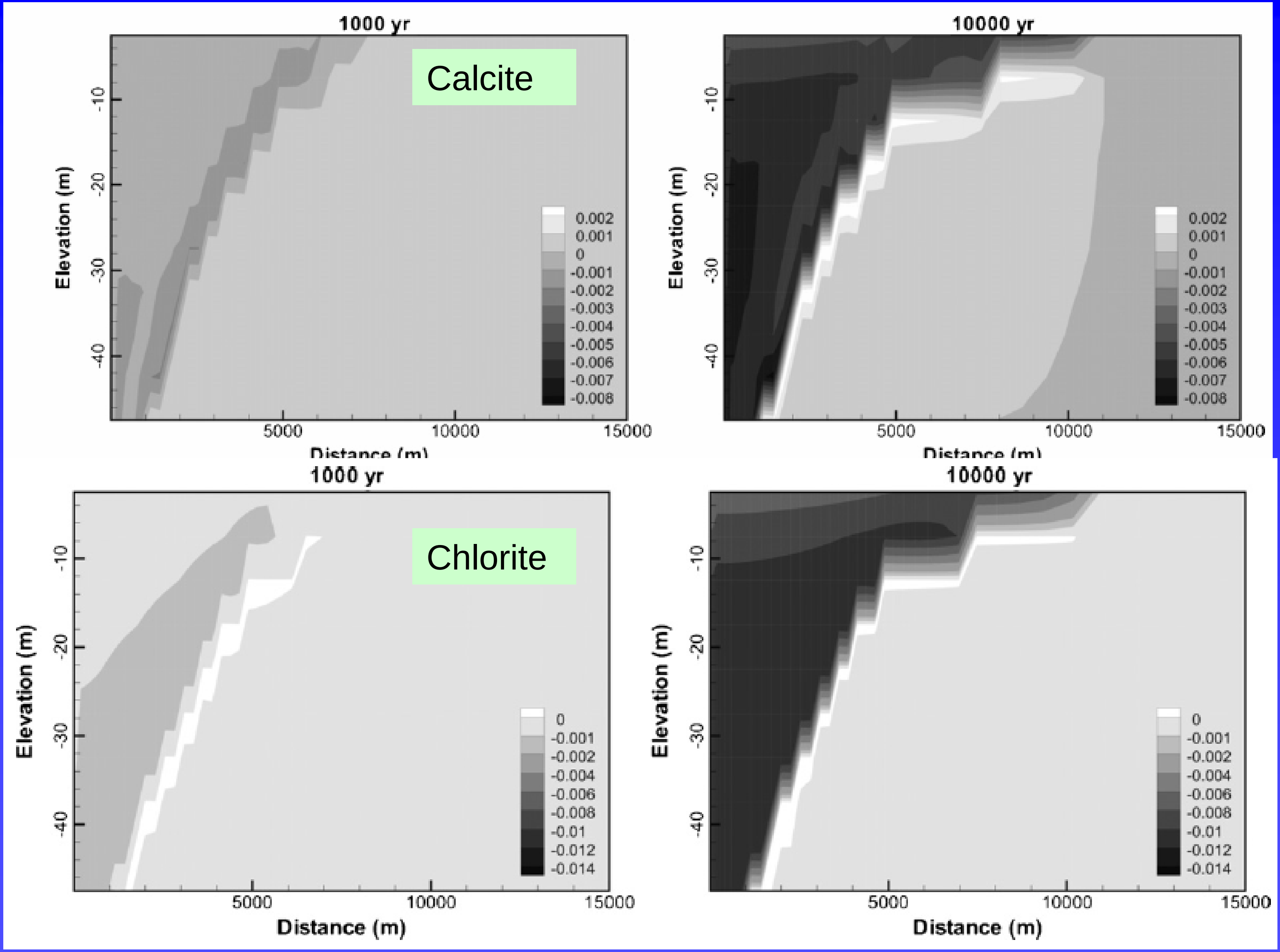
(Xu et al., 2006)



(Ketzer J.M. et al., 2009)



(Barbara et al., 2009)



Calcite

Chlorite

(Zhang et al., 2009)

Methods for water-rock-CO_2 interaction study

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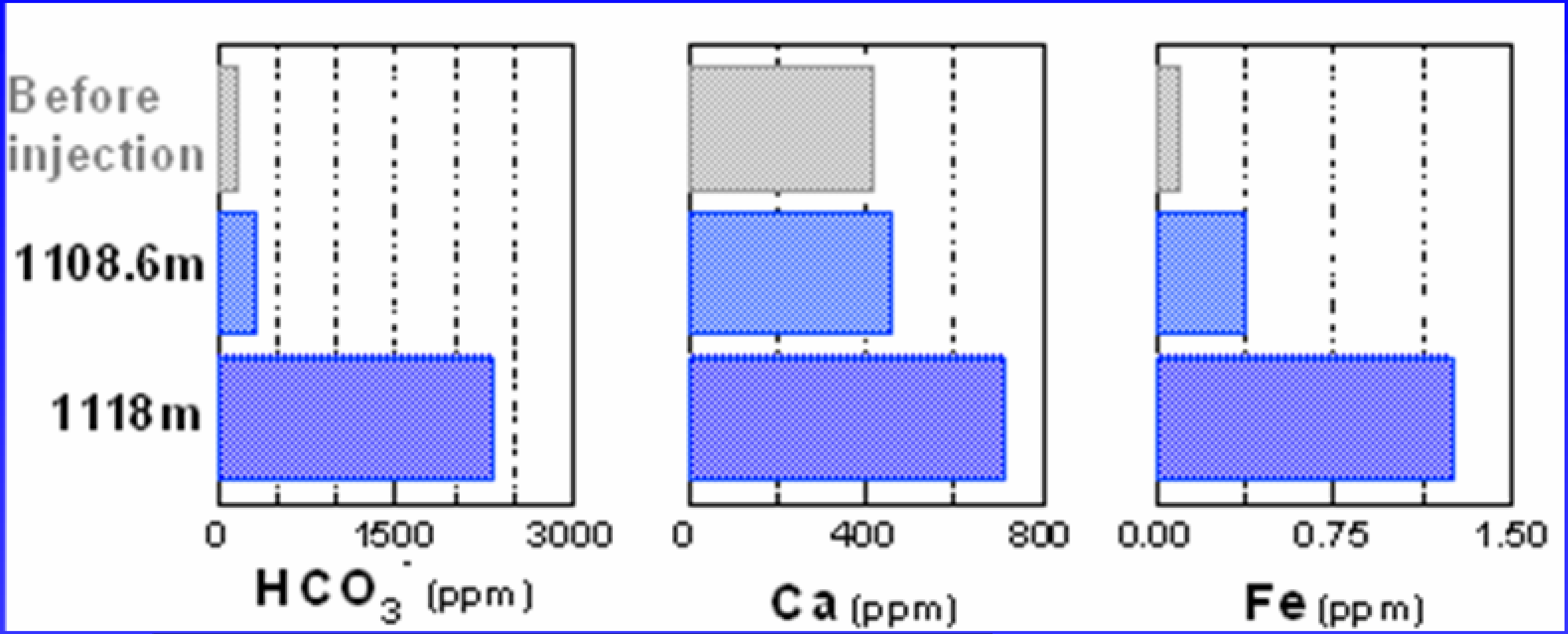
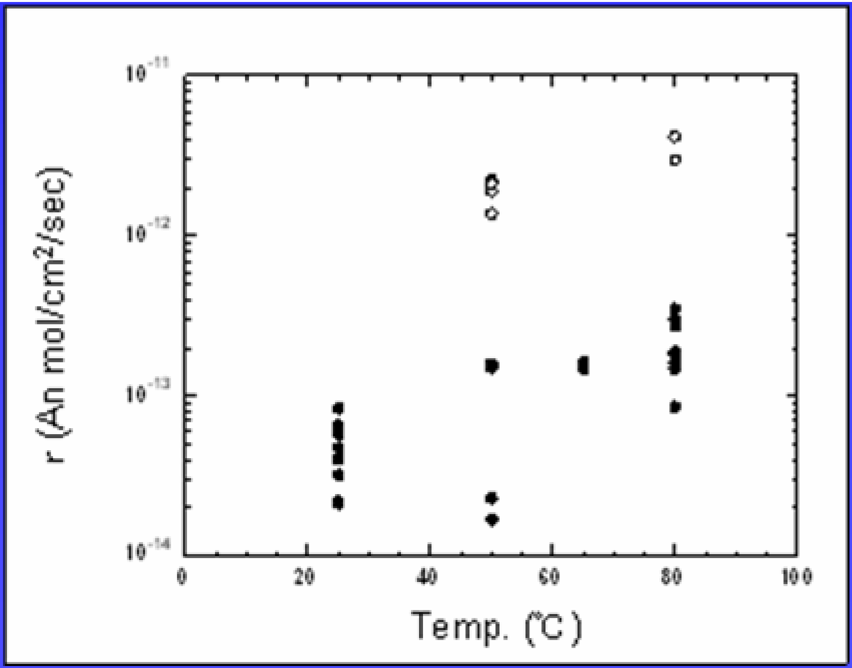
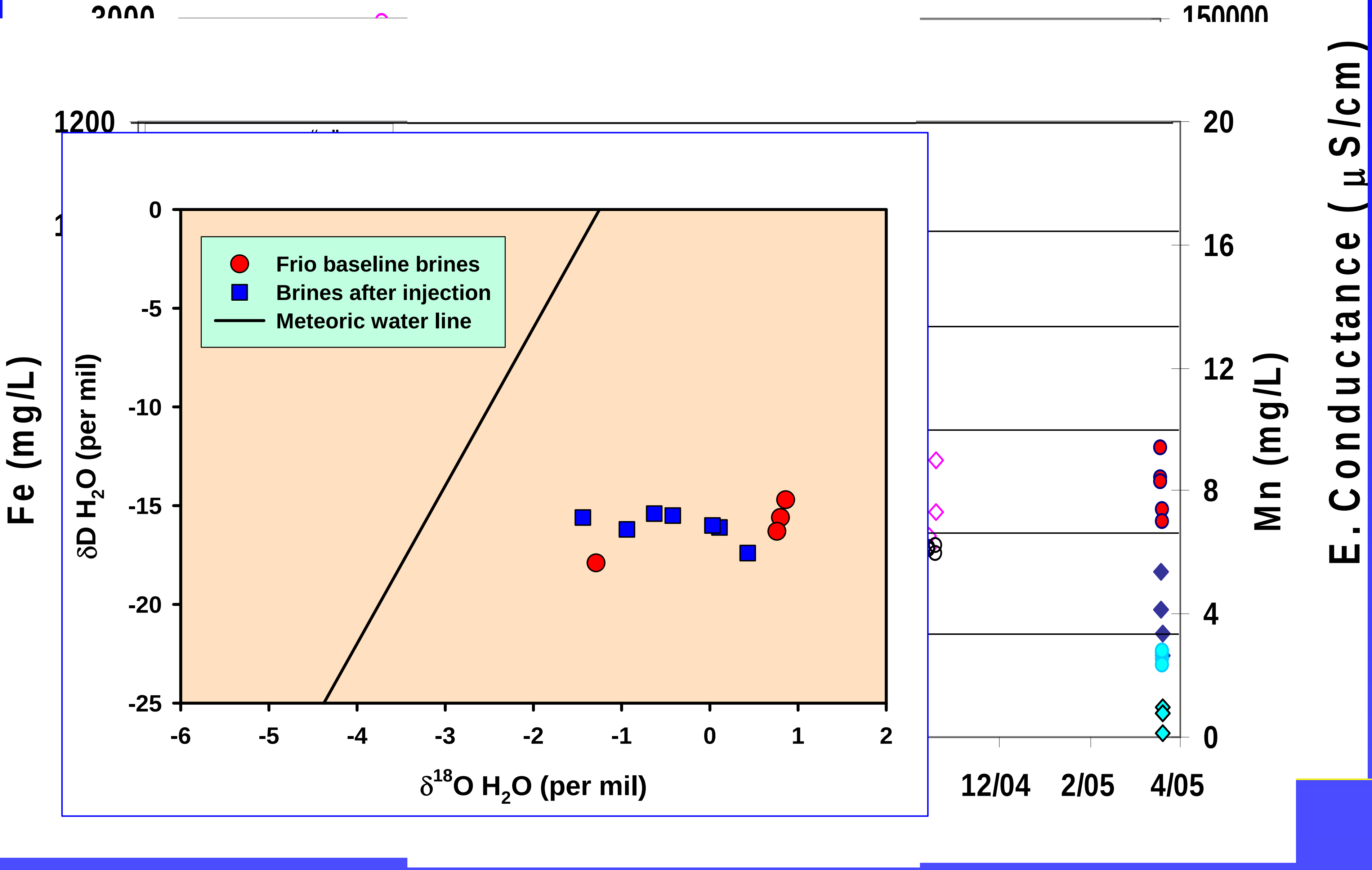


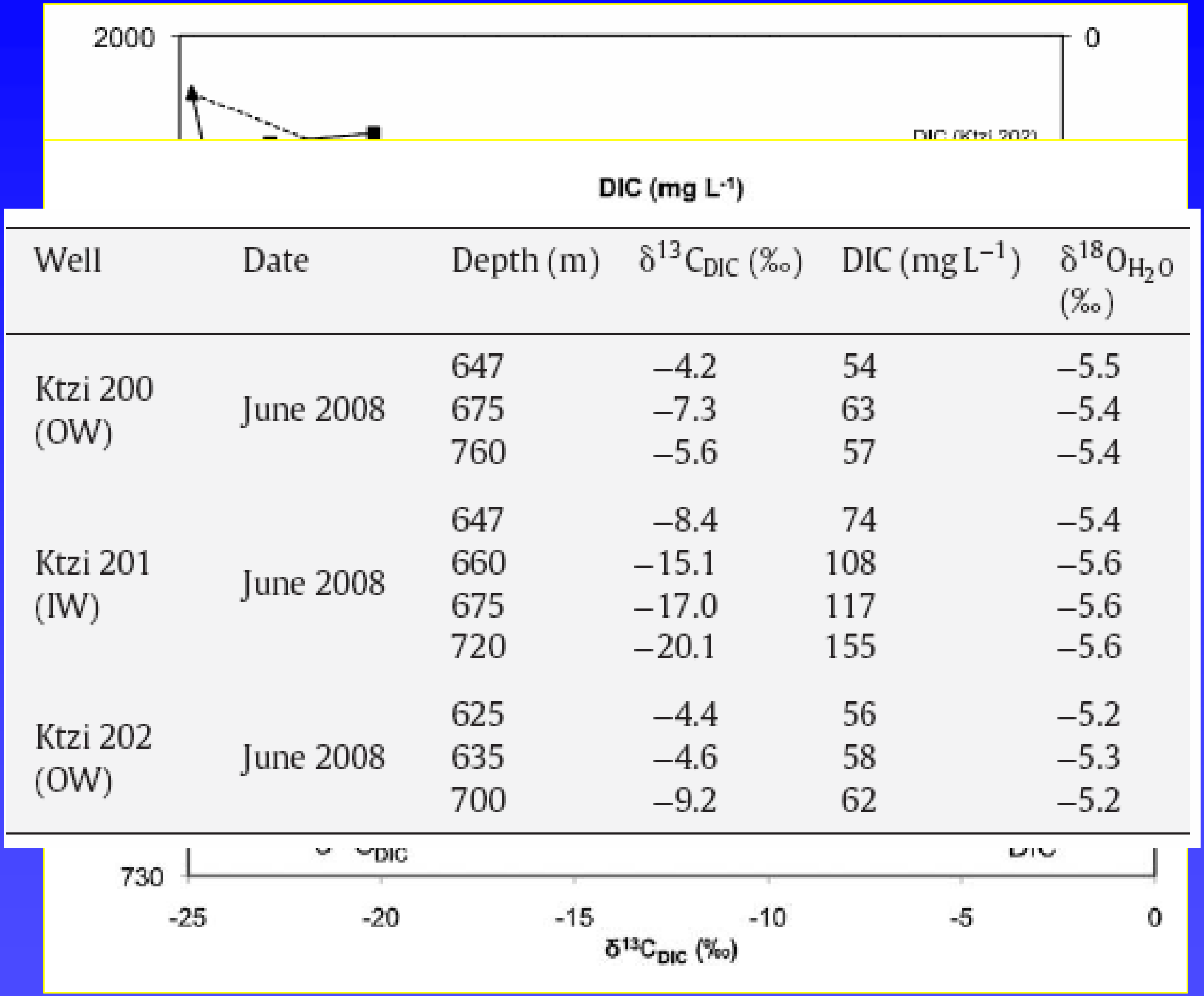


(Mito et al., 2008)

Ions changes and dissolution kinetics of K-feld from the field test of CO2 injection in Nagaoka site.



(Kharaka et al., 2006)



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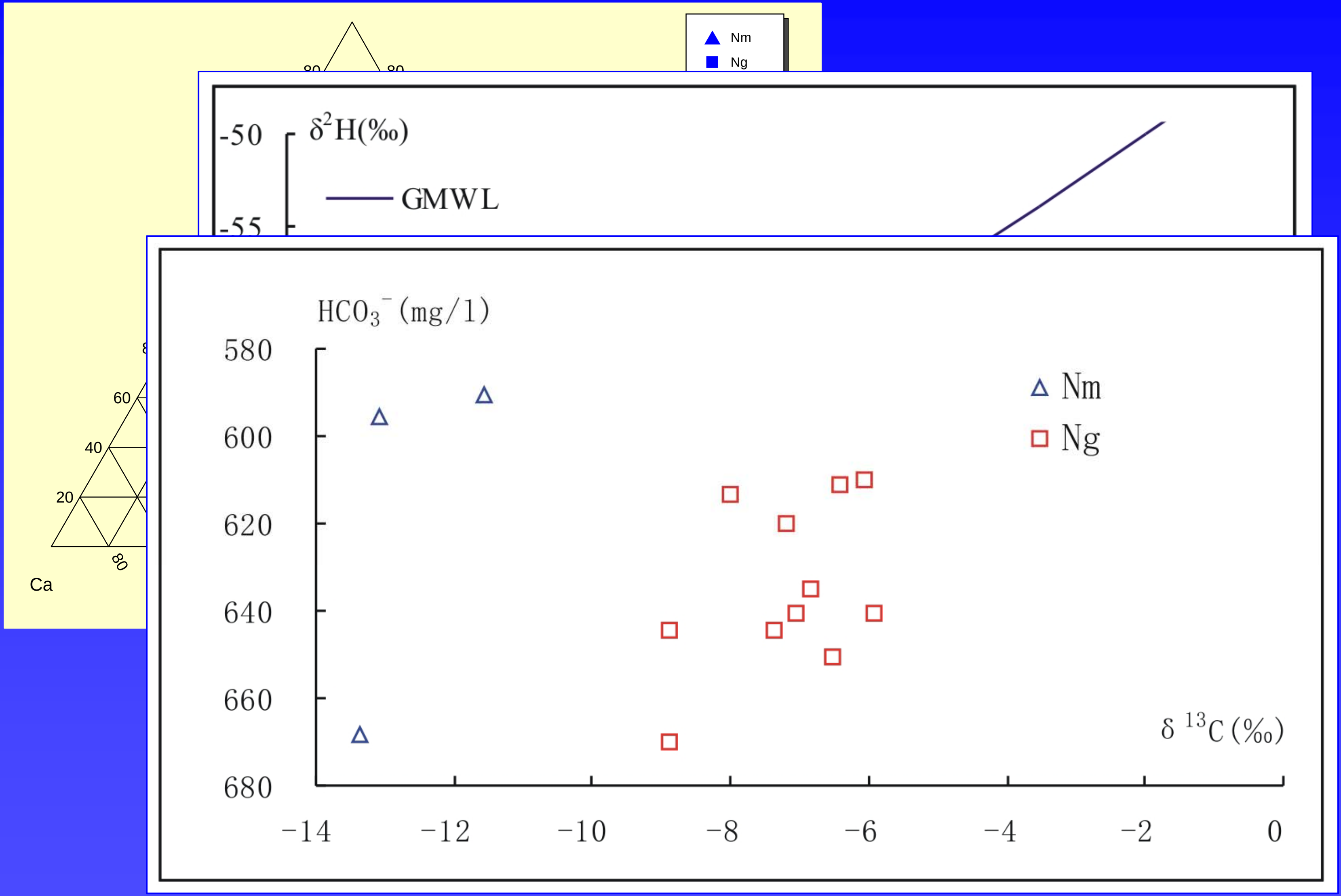
Isotope changes results from Ketzin injection site of Germany.

(Myrttinen et al., 2010)



Geochemical background of formation water from Guantao formation, Bohai Bay Basin.

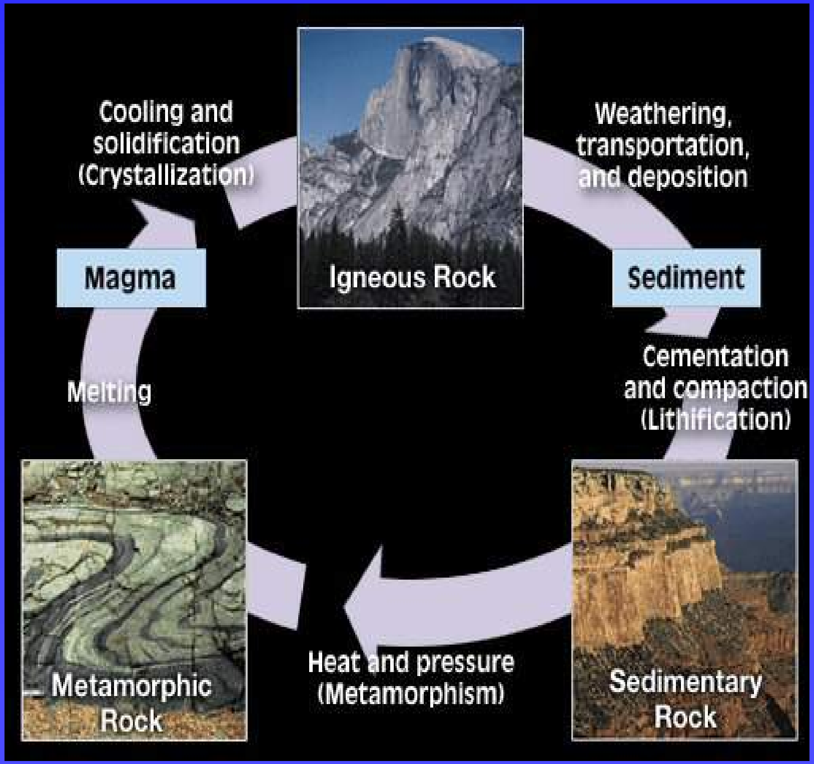
Future focuses

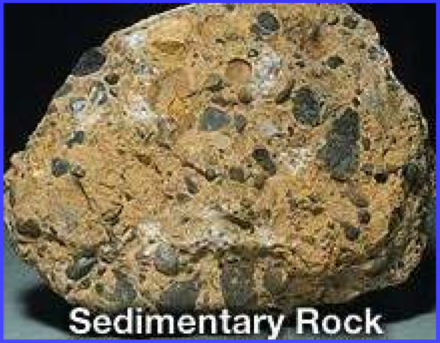
- Water-rock-CO2 interaction for specific reservoir conditions
- Influences of water-rock-CO2 interactions on CO2 storage capacity
- Minerals kinetics in water-rock-CO2 interaction and corresponding influences on reservoir physical properties

Different sedimentary environments can lead to different reservoir and caprock conditions, e.g., continental and marine sedimentary environments.

Different reservoir minerals and formation water chemistry may have great influences on water-rock-CO2 interactions.

Therefore, water-rock-CO2 interaction should be studied for each specific testing site.

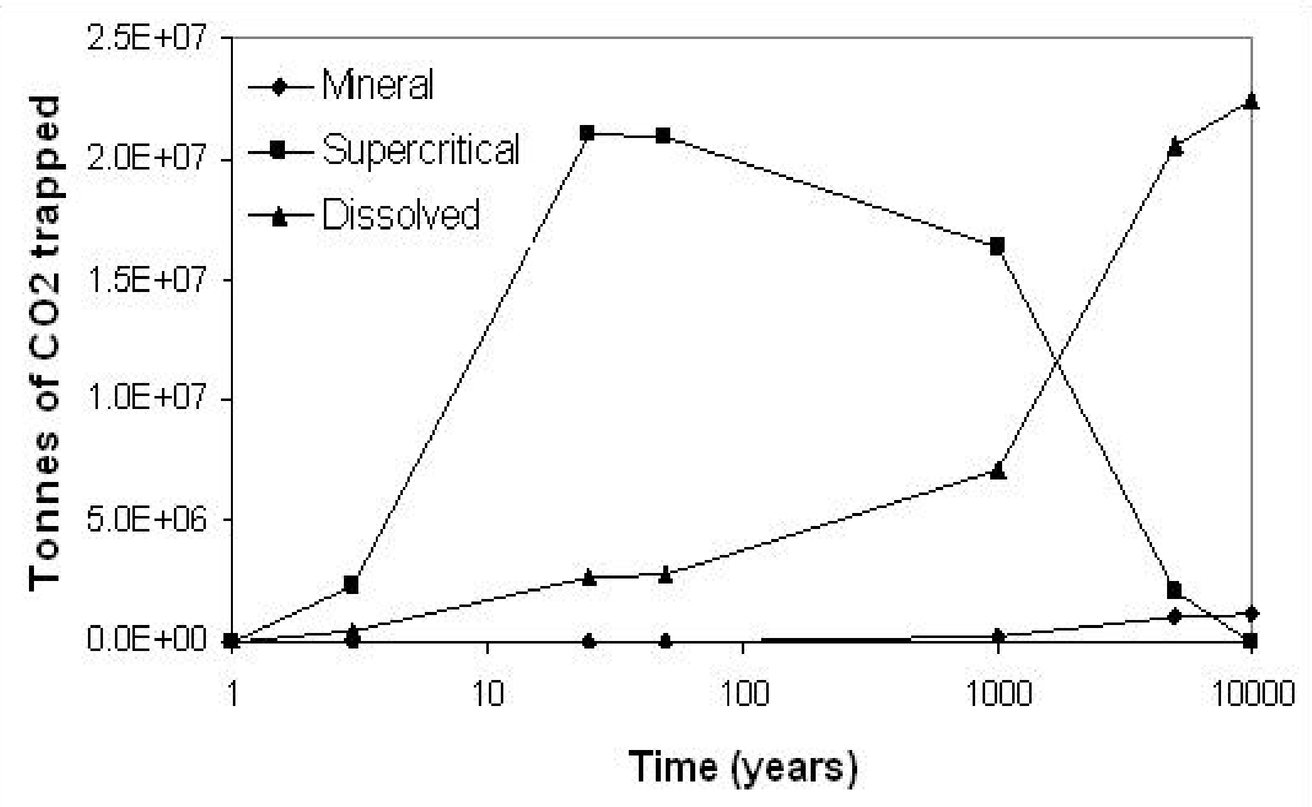




CO2 storage capacity is variable and is mainly controlled by the capacities of mineral, solubility, structural and stratigraphic and residual trappings.

The proportion of different trapping forms is changes with time and so does the total capacity.

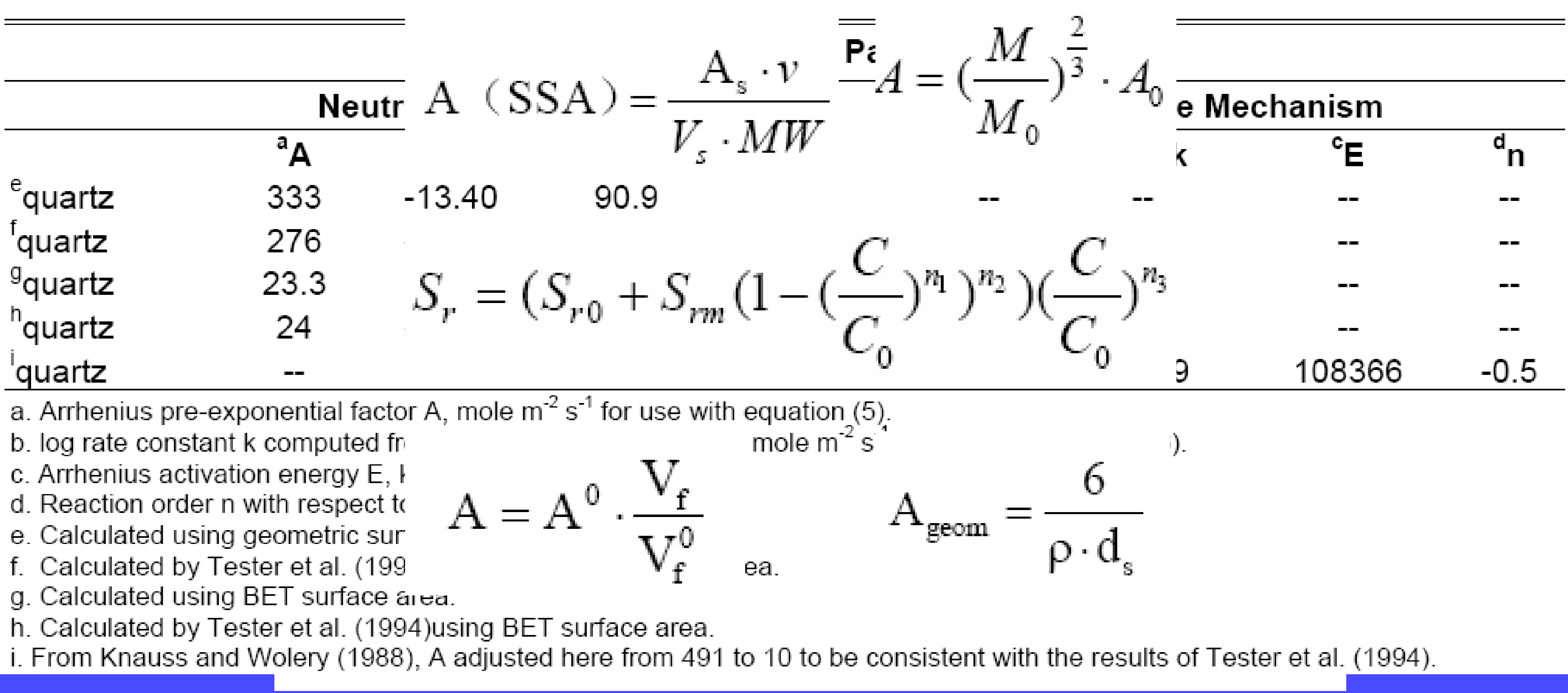
Attention should be paid to CO2 storage capacity at specific time scales.



(Audigane et al., 2007)

Minerals kinetics in water-rock-CO2 interaction

The general rate equation is adopted from Lasaga et al., 1995 and in general, the most well-studied mechanisms are those in pure



	Neutr			Pa		e Mechanism	
	[a]A				k	[c]E	[d]n
[e]quartz	333	-13.40	90.9	--	--	--	--
[f]quartz	276					--	--
[g]quartz	23.3					--	--
[h]quartz	24					--	--
[i]quartz	--				9	108366	-0.5

$$A\ (SSA) = \frac{A_s \cdot v}{V_s \cdot MW}$$

$$A = (\frac{M}{M_0})^{\frac{2}{3}} \cdot A_0$$

$$S_r = (S_{r0} + S_{rm}(1-(\frac{C}{C_0})^{n_1})^{n_2})(\frac{C}{C_0})^{n_3}$$

a. Arrhenius pre-exponential factor A, mole m^{-2} s^{-1} for use with equation (5).

b. log rate constant k computed fr mole m^{-2} s).

c. Arrhenius activation energy E, k

d. Reaction order n with respect t

e. Calculated using geometric sur

f. Calculated by Tester et al. (199 ea.

g. Calculated using BET surface area.

h. Calculated by Tester et al. (1994)using BET surface area.

i. From Knauss and Wolery (1988), A adjusted here from 491 to 10 to be consistent with the results of Tester et al. (1994).

$$A = A^0 \cdot \frac{V_f}{V_f^0}$$

$$A_{geom} = \frac{6}{\rho \cdot d_s}$$

(Transitionary theory by Lasaga et al., 1995)

谢谢！ **Thanks！**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INSTITUTE OF GEOLOGY AND GEOPHYSICS CHINESE ACADEMY OF SCIENCES