Calcium silica speciation and carbonation in cement systems

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Deep disposal concepts for radioactive waste are usually based on a multiple barriers which may involve cementitious materials and thus alkaline media. In such regard, silica and calcium speciation is of major importance for geochemical calculations. The existence of mixed calcium-silica complexes $(CaSiO(OH)_3^+$ and especially $CaSiO_2(OH)_2)$ was inferred in previous works [1, 2]. The present study proposes an assessment for the influence of such complexes on cement hydrates (C-S-H) solubility, with a specific focus on experiment conditions and carbonation, based on a set of lab experiments and measurements, including a short assessment of previous works.

Context

Literature selection, C-S-H in H_2O
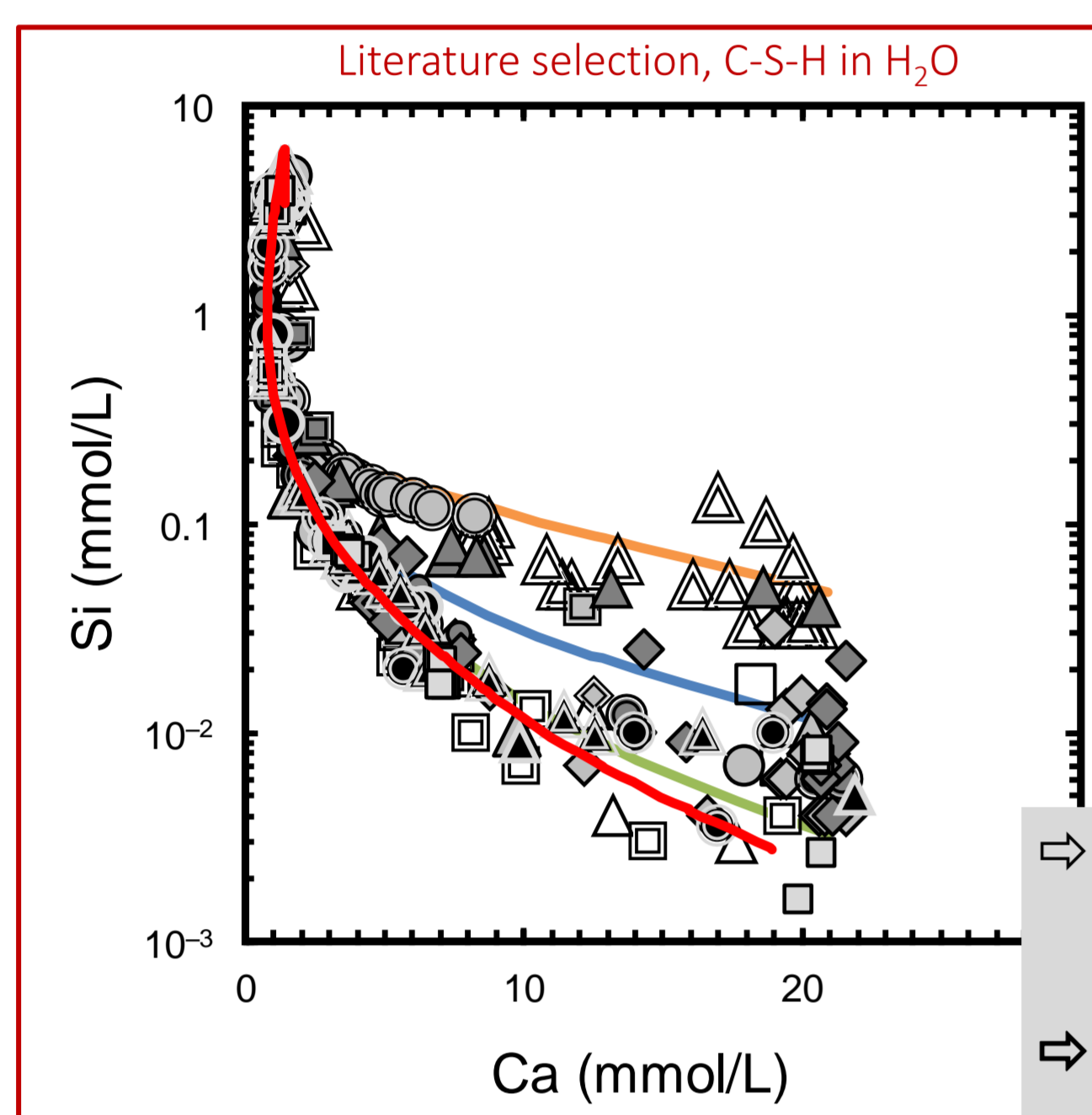
- Comparison with the C-S-H model from Roosz et al [4]
- Considering for the neutral complex
  $Ca^{2+} + SiO_2(OH)_2^{2-} = CaSiO_2(OH)_2^0$
  - $\log_{10}\beta^0 = 4.5$ [1];
  - $\log_{10}\beta^0 = 2.9$ [2];
  - $\log_{10}\beta^0 = 4.0$ [3] or
  - no Ca-Si complex

⇒ Strong influence on C-S-H solubility

⇒ Need to refine complex properties ...

Synthesis of solutions

- Glovebox + NaOH traps
- Na_2SiO_3 solution (Merck®), SiO_2 (Aerosil©), NaOH 1M (Merck®), $Ca(OH)_2$ (Merck®, heated at 1000°C 12h)
- Filtrated at 0.1 μm, ultra filtrated at 10kD, 3kD
- Mother solutions S1-S6 ; C-S-H solutions S7-S10 and S21-S24 ; N-C-S-H solutions S11-S17

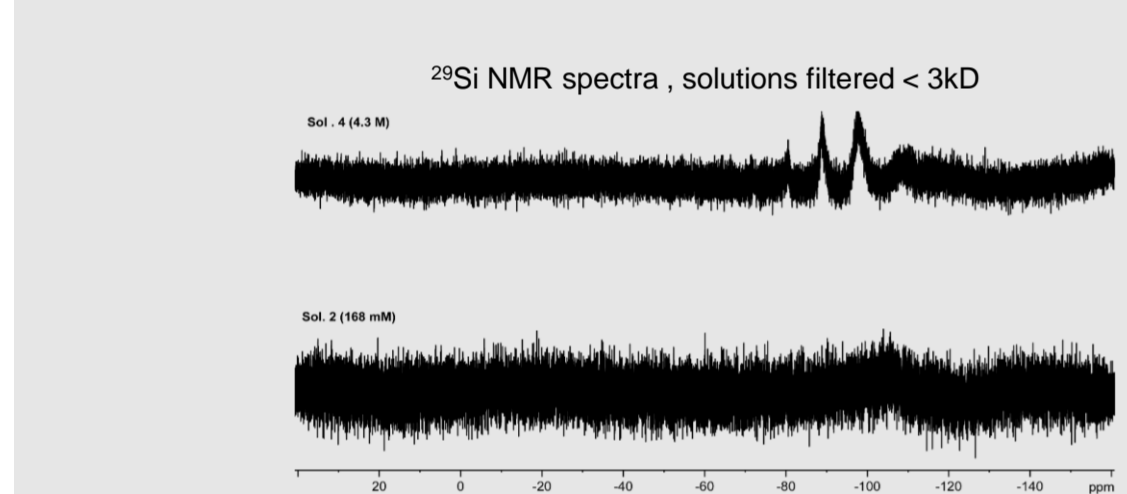Literature selection, C-S-H in H_2O + NaOH
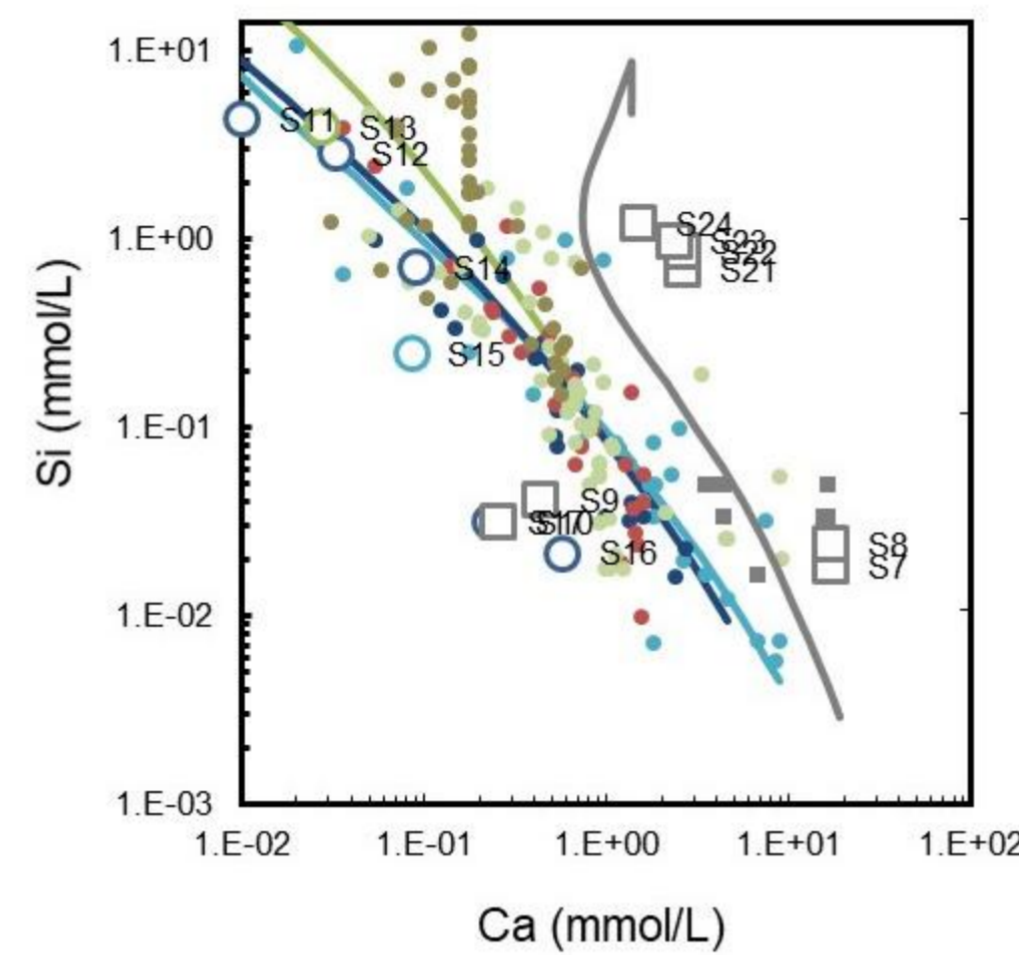
Solution analyses

- pH, T°C, Eh
- Dissolved Si, Ca, Na by ICP-MS and ICP-AES
- After 0.1μm filtration, after 10 and 3 kD filtration
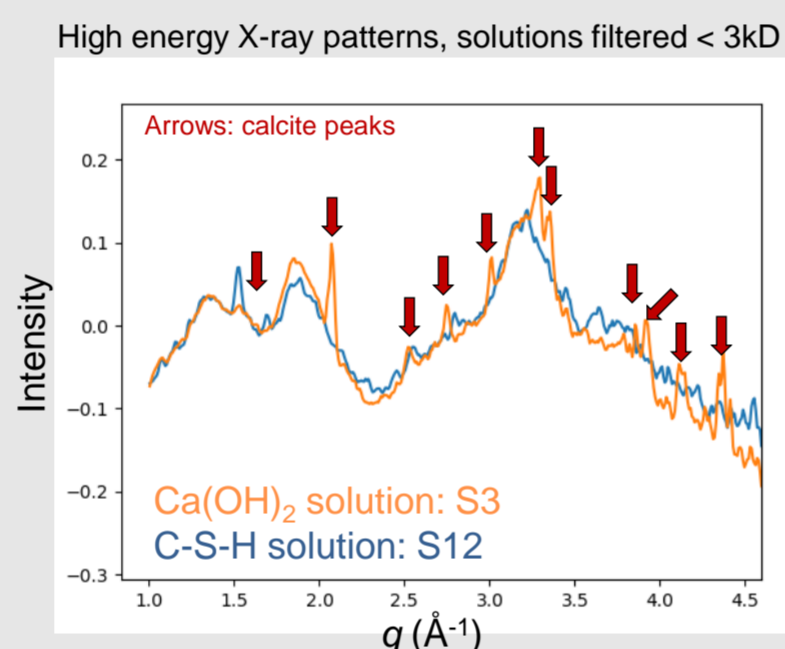- Ca^{2+} ISE electrodes measurements

	Theory (mM)	Ca T (mM)	Ca (< 3 kD, mM)	Δ (mM)	Ca T (mM)	Ca (< 10 kD, mM)	Δ (mM)
S3	20.00	19.93			16.40	18.30	-1.90
S7	19.82	18.98	16.73	2.25	16.70	17.70	-1.00
S8	19.95	19.17	16.88	2.29	16.80	17.40	-0.60
S9	1.00	0.85	0.44	0.41	0.68	0.64	0.04
S10	0.40	0.36	0.25	0.11	0.29	0.25	0.04
S11	8.99	< 0.01	< 0.01		0.15	< 0.17	
S12	0.20	0.03	0.03	0.00	< 0.048	< 0.05	
S13	0.20	0.02	0.03	-0.01	0.06	0.05	0.01
S14	0.99	0.09	0.09	0.00	0.11	0.12	-0.01
S15	0.10	0.09	0.08	0.01	0.12	0.10	0.02
S16	3.00	2.86	0.57	2.29	1.53	1.55	-0.02
S17	1.00	0.96	0.23	0.73	0.23	0.24	-0.01
S21	3.20	2.63	2.59	0.03	2.32	2.33	-0.01
S22	3.20	2.64	2.63	0.02	1.96	2.01	-0.05
S23	2.85	2.36	2.32	0.03	1.87	1.89	-0.02
S24	1.75	1.48	1.48	0.00	1.56	1.61	-0.05
		Brgm			**KIT - INE**		

NMR, High energy HEX-rays

^{29}Si NMR spectra , solutions filtered < 3kD

High energy X-ray patterns, solutions filtered < 3kD

Arrows: calcite peaks

$Ca(OH)_2$ solution: S3
C-S-H solution: S12

^{29}Si NMR and Raman are not sensitive enough, solids are detected by HEX-rays, calcite 10 nm and 0.2 mM

Titrations

Calcite present after < 3 kD filtration, pCO_2 calculated = 10^{-13} atm

$Ca(OH)_2$ solution

C-S-H solution: S7

Solution < 3 kD ⇒ 0.8 mM calcite
Calculated pCO_2 = 10^{-13} atm
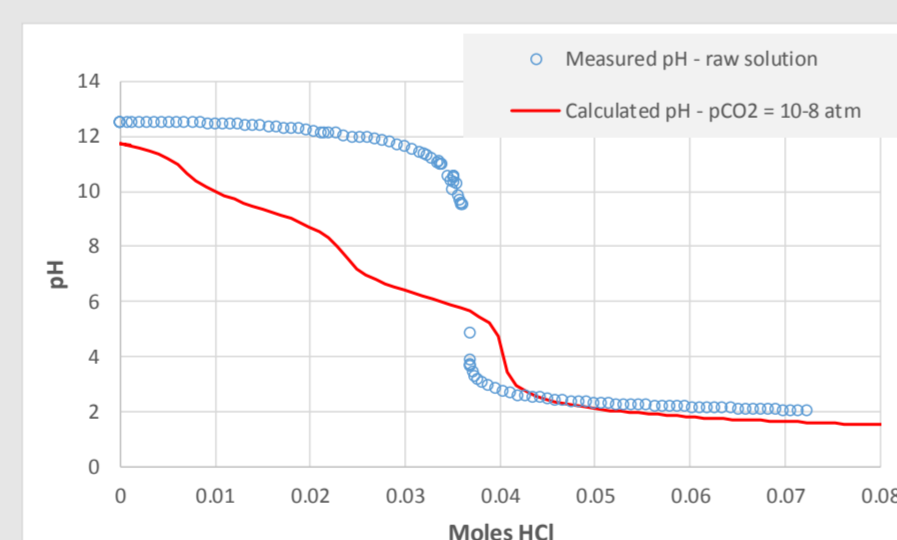
C-S-H solution + 1mM NaOH: S21-S24

Conditions similar to Nicoleau and Schindler [2]
Probable C-S-H precipitation
Weak influence of the $CaSiO_2(OH)_2$ complex

Comparison with previous literature
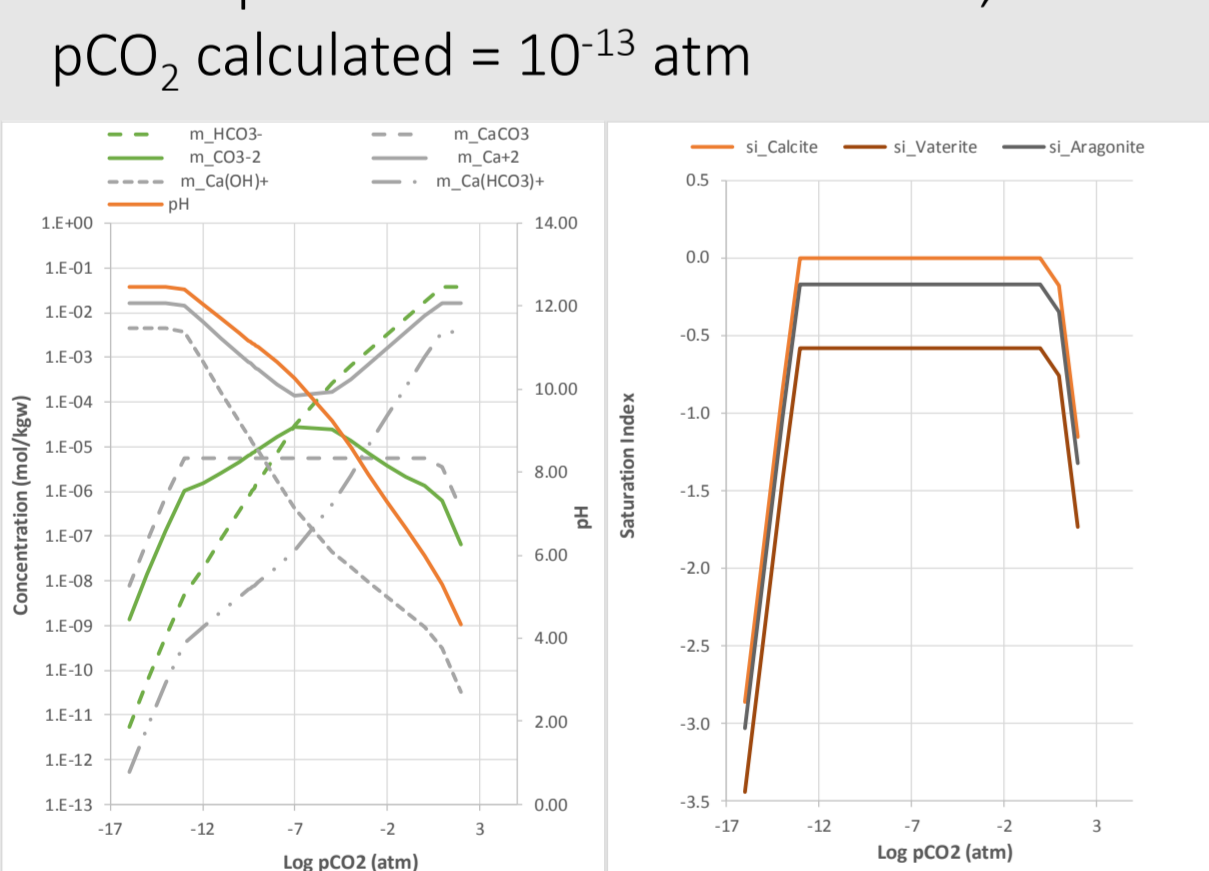
Santschi and Schindler [1]

- Titration in 1M $NaClO_4$
- [Si] = 2.25 mM, pH ranging from 8.3 to 8.9, [Ca] = 150, 200 and 250 mM

- preparation involves dissolved Na_2CO_3
- solids precipitate at the end of the experiment (pH = 8.9)
- no means reported to prevent carbonation
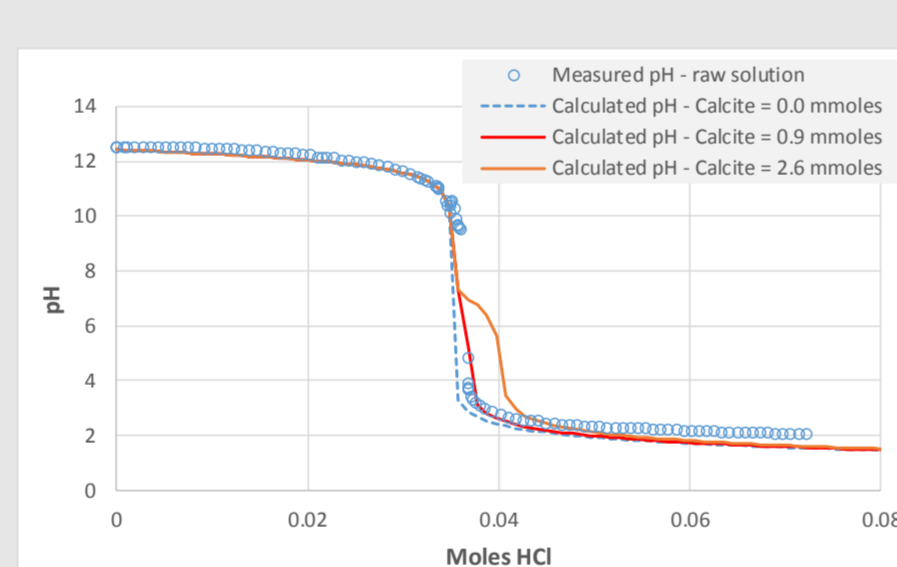- speciation model do not consider carbonates nor calcium hydroxides complexes

A limited carbonation allow reproducing Santschi and Schindler [1] results without considering Ca-Si complexation

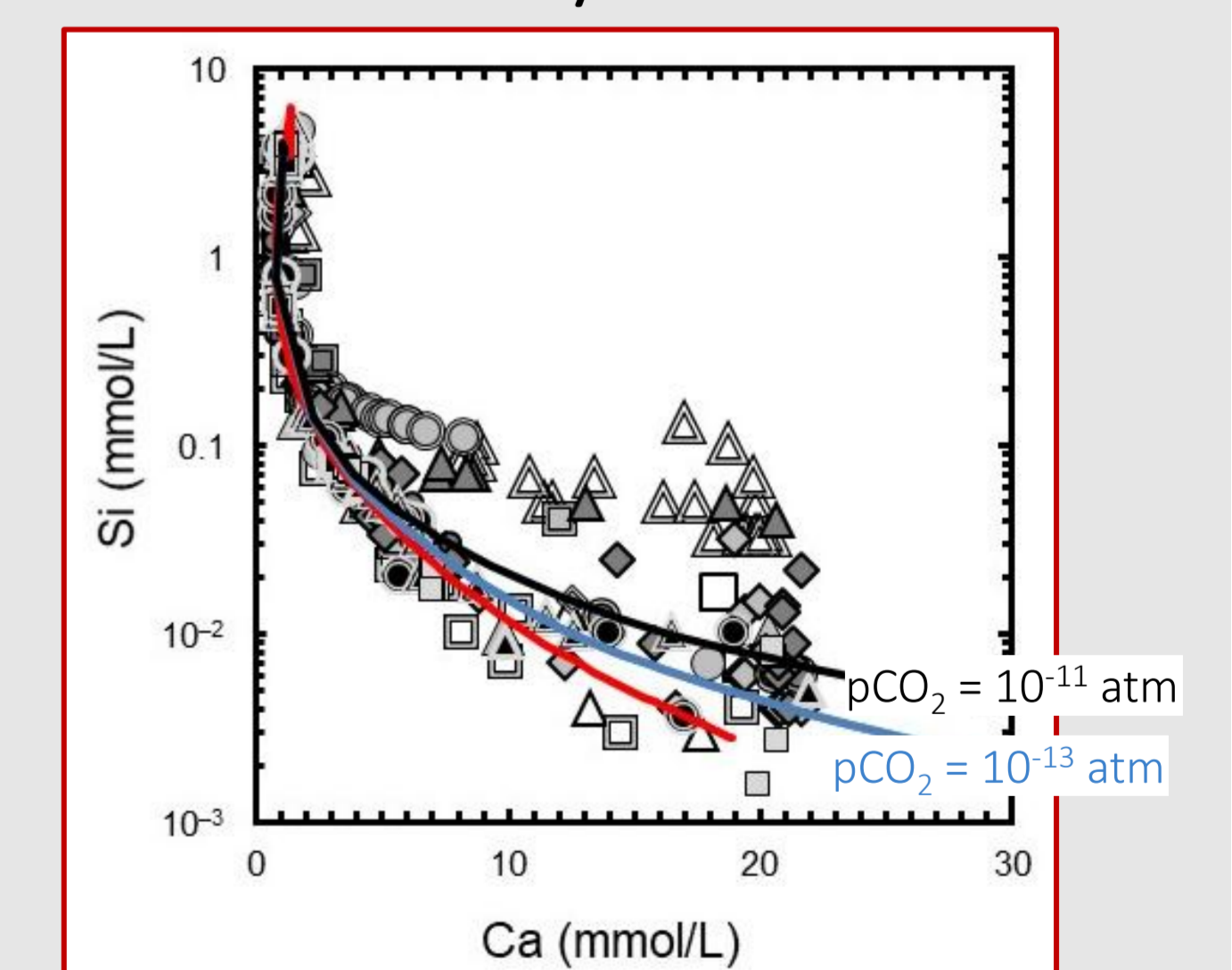### Nicoleau and Schindler [2]

- Ca^{2+} ISE + pH measurements

- Titration by Na_2SiO_3

- [Ca]: 1 to 7 mM
  [Cl]: 2 to 14 mM
  [Na]: 1 to 100 mM
  [Si]: 0.2 to 1.3 mM

- In $N_{2(g)}$ atmosphere

Ca^{2+} activity without Ca-Si complexes
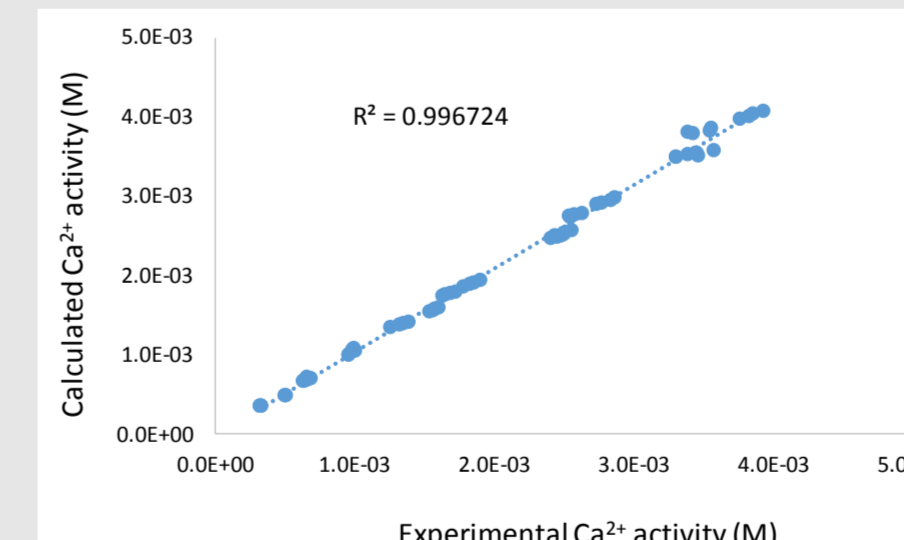
- Including $CaSiO_2(OH)_2$ improves r^2 by 1.36 10^{-4}

- Considering pCO_2 = 10^{-11} atm improves r^2 similarly by 1.22 10^{-4}

Finally ....

pCO_2 = 10^{-11} atm
pCO_2 = 10^{-13} atm

Using Roosz et al. [4] model with pCO_2 = 10^{-13} atm gives results similar to Nicoleau and Schindler [2]

Several analytical technics are used to characterize the filtered solutions (Raman, ^{29}Si NMR, High energy X-ray, acidic titrations, Ca-ISE, ICP). Measurements do not provide unambiguous proof of the presence of mixed calcium-silica complexes in the solutions. Rather, they indicate different sources of uncertainty in analytical methods (ICP) and Ca2+ ICE measurements, especially. Hex-rays results results clearly indicate a partial carbonation of the system. Modelling the titration experiments confirms the carbonation of the system, especially for high pH solutions. Finally, previous works dedicated to calcium-silica complexes are re-investigated and re-assessed regarding for the influence of carbonation. The latter can explain modifications of the overall speciation without involving the presence of mixed silica complexes.

REFERENCES:
[1] Santschi, P.H., Schindler, P.W., 1974. Complex formation in the ternary systems Ca-H4SiO4-H2O and Mg-H4SiO4-H2O. Journal of the Chemical Society, Dalton Transactions, 181-184.
[2] Nicoleau, L., Schreiner, E., 2017. Determination of Ca2+ complexation constants by monomeric silicate species at 25°C with a Ca2+ ion selective electrode. Cement and Concrete Research 98, 36-43.
[3] Walker, C.S., Sutou, S., Oda, C., Mihara, M., Honda, A., 2016. Calcium silicate hydrate (C-S-H) gel solubility data and a discrete solid phase model at 25 °C based on two binary non-ideal solid solutions. Cement and Concrete Research 79, 1-30.
[4] Roosz, C., Vieillard, P., Blanc, P., Gaboreau, S., Gailhanou, H., Braithwaite, D., Montouillout, V., Denoyel, R., Henocq, P., Madé, B., 2018. Thermodynamic properties of C-S-H, C-A-S-H and M-S-H phases: Results from direct measurements and predictive modelling. Applied Geochemistry 92, 140-156.