The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration.

Andrew R. Felmy
Herman Cho
Gregory R. Choppin (FSU)
David A. Dixon
James R. Rustad
Zheming Wang

EMSP presentation, November 5,2001 Richland WA.

Outline

- Background
- Development of Aqueous Model for Polysilicates to High Ionic Strength.
  - NMR identification of new silicate species (enantomers).
  - Development/use of new MD model.
- Complexation and solid formation in Sr solutions.
- Cm(III)-silicate complexation to high base.
- New determinations of the monomeric stability constants of Ni, Co, Eu, Am, U(VI) – FSU.
- Summary

Background

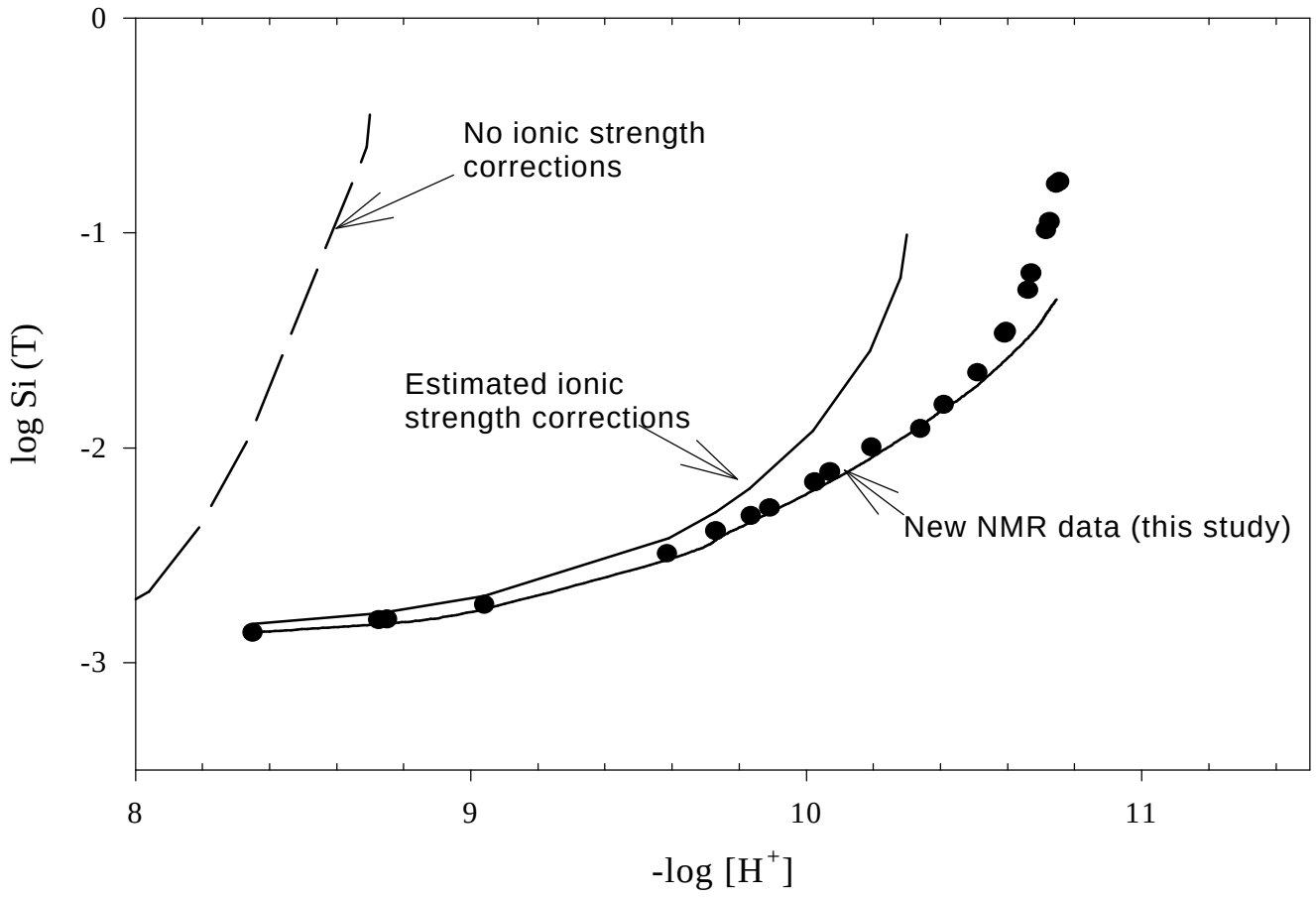
- Project is part of an on-going effort to develop accurate thermodynamic models for concentrated tank waste solutions.
  - Other efforts: major electrolytes (Na-NO_3-NO_2-OH-SO_4-CO_3-F-PO_4-H_2O)- WTP and chelates (EDTA-HEDTA-NTA-oxalate with Sr and actinides) – EMSP.
- Focus of this project is on silica species under basic, high ionic strength conditions.
- Dissolution of silica containing solids in the subsurface:
  - Dramatically lowers the free hydroxide (from as high as 1-3 M to pH 11-12) and releases large concentrations of anionic silica species to solution.
  - Anionic silica species can alter the phase distribution via precipitation reactions with Al, Ca or other components as well as potentially transport radionuclides via complexation reactions.

Background (cont'd)

- Accurate thermodynamic models for polysilicates species valid to high ionic strength are unavailable.
- Silica species present as complex mixtures.
  - Monomers - $H_4SiO_4(aq)$, $H_3SiO_4^-$, $H_2SiO_4^{2-}$
  - Dimers - $Si_2O_2(OH)_2^{2-}$.
  - Trimers - straight chain, cyclo.
  - Tetramers - straight chain, cyclo, other.
  - Pentamers and others – possible.
  - Highly charged (postulated as high as -4 or -6).
- Multiple species binding sites on polymeric species.

Thermodynamic Polysilicate Modeling

- Extensive investigations of polysilcate formation in solution.
  - Late 1950 - early 1960 - EMF measurements by the Swedish group (Ingri, Lagerstrom …).
    - hypothesized several polysilicates based upon fitting the EMF data).
  - Mid 1970's - pioneering work of Harris, Englehardt, and Marsmann.
    - links between the ^{29}Si NMR shifts and the chemical structure of the complexes.
  - Mid -1980's - first realistic thermodynamic models for the polysilicates (Sjöberg et al. ^{29}Si NMR/EMF).
    - Difficulties:
      - No effective corrections for ionic strength.
      - Highly charged species (z^2 in Debye-Hückel huge).
      - NMR analysis could not identify all of the Si (60% of the total Si identified).



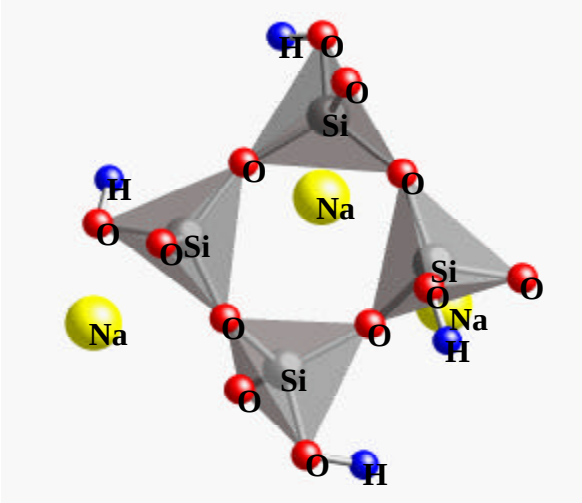
Amorphous silica solubility data of Zarubin and Nemkina (1990) in 1m NaCl

Polysilicate Modeling (Cont'd)

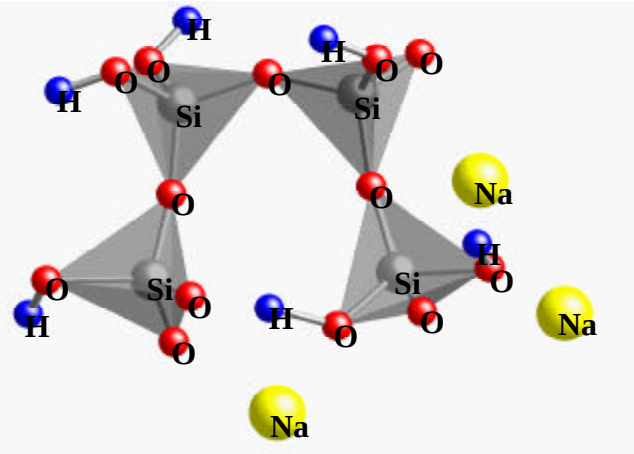
- Approach
  - Test the applicability of the best existing models on more recent data not used in development.
  - Tabulate and analyze ALL existing literature data that appear valid (solubility, EMF, NMR).
  - Develop new experimental data (NMR) where needed.

Solution ID	[NaOH] added	Final pC_{H+}	$[NaNO_3]$	[Si] total	Fraction monomer	Fraction Dimer	Fraction cyclic trimer	Fraction linear trimer	Fraction substituted trimer	Fraction cyclic tetramer	Fraction linear tetramer	Fraction prismatic hexamer
A1	0.06	10.859	0.44	0.06	.653	.084	.013	.011	-	.010	.011	.002
A2	0.07	11.258	0.43	0.06	.605	.084	.017	.015	.014	.008	.011	.003
A3	0.08	11.666	0.42	0.06	.619	.085	.020	.020	.005	.008	.009	.002
A4	0.09	11.856	0.41	0.06	.638	.090	.019	.023	.009	.009	.007	-
A5	0.10	12.019	0.40	0.06	.634	.085	.019	.012	.009	.006	.006	.001
B1	0.18	12.023	2.82	0.15	.295	.054	.019	.017	(.018)	.012	.013	.0071
B2	0.20	12.269	2.80	0.14	.299	.055	.024	.020	(.021)	.013	.010	.0078
B3	0.22	12.433	2.78	0.15	.335	.059	.034	.017	(.024)	.010	.012	.0067
B4	0.24	12.543	2.76	0.15	.368	.060	.024	.018	(.024)	.0092	.010	.0055

(a)



(b)



(a) Cyclic tetramer and (b) linear tetramer, both with associated sodium ions.
Strong intramolecular hydrogen bonding present in the linear trimer closes the gyration radius, giving rise to similar structures for the cyclic and linear tetramers.

Aqueous Species and Equilibrium Constants Used in this Study.

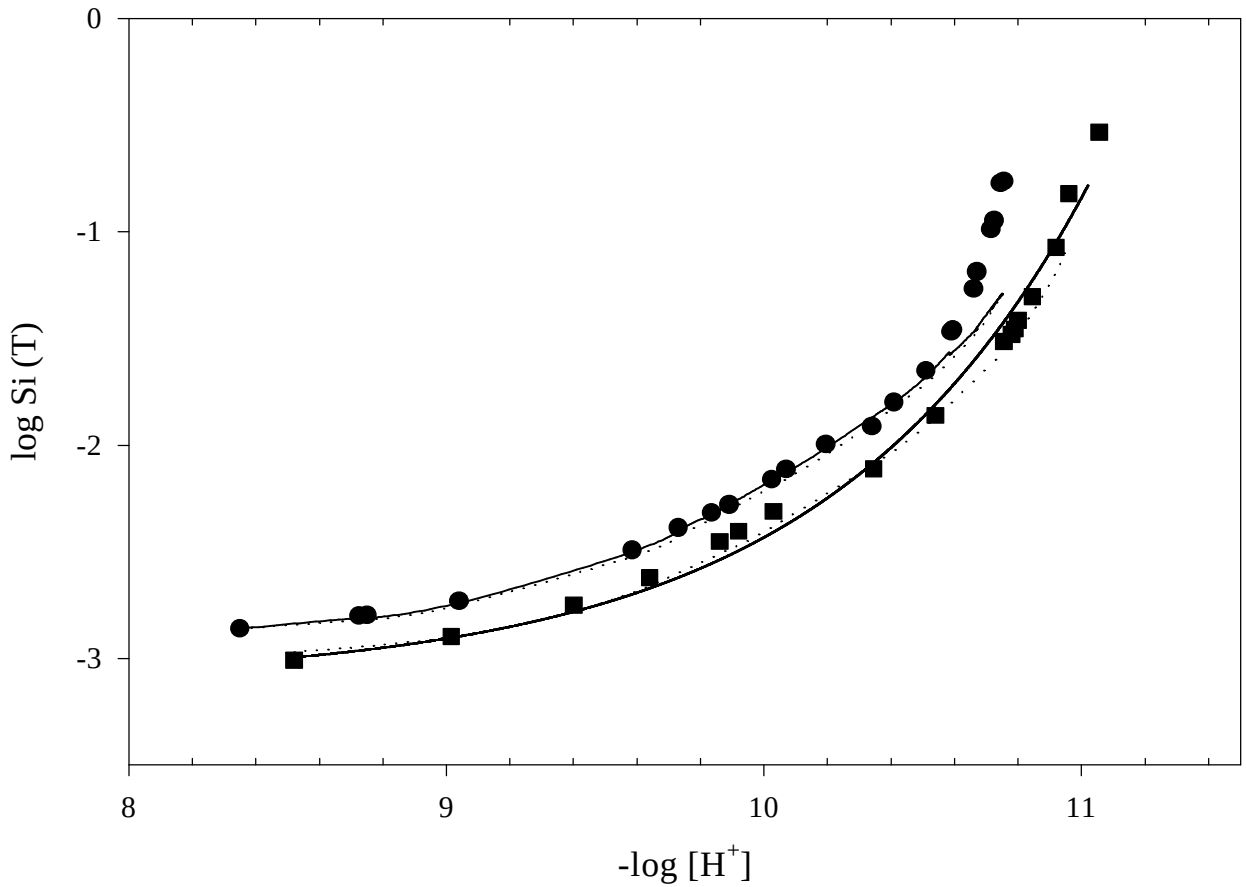
p, q	formula	Log K^0 (final)	Reference
-1, 1	$H_3SiO_4^-$	-9.82	Hershey and Millero (1986)
-2,1	$H_2SiO_4^{2-}$	-23.27	Hershey and Millero (1986)
-1,2	$Si_2O_2(OH)_5^-$	-8.50	This Study[a]
-2,2	$Si_2O_3(OH)_4^{2-}$	-19.4	This Study
-3,3	$Si_3O_6(OH)_3^{3-}$ (cyclo)	-29.3	This Study
-3,3	$Si_3O_5(OH)_5^{3-}$ (lin)	-29.4	This Study
-4,4	$Si_4O_7(OH)_6^{4-}$ (lin)	-39.1	This Study
-4,4	$Si_4O_8(OH)_4^{4-}$ (cyclo)	-39.2	This Study
-4,4	$Si_4O_8(OH)_4^{4-}$ (sub)	-39.1	This Study
-2,4	$Si_4O_6(OH)_6^{2-}$	-15.6	This Study[b]
-6,6	$Si_6O_{15}^{6-}$	-57.9	This Study

[a] Calculated using our value for the formation of the $Si_2O_3(OH)_4^{2-}$ species along with the protonation constant of Sjöberg et al. (1985).

[b] Calculated using our value for the formation of the cyclic tetramer and the protonation constant of Svensson et al. (1986).

Pitzer Ion-Interaction Parameters. The cation is Na^+ in all cases.

anion	ß^0 (est.)	ß^1(est)	ß^0 (final)	ß^1 (final)	Reference (final)
$H_3SiO_4^-$	.043	.24	.043	.24	Hershey and Millero (1986)
$H_2SiO_4^{2-}$	.32	.13	.32	.13	Hershey and Millero (1986)
$Si_2O_2(OH)_5^-$	-	-	-	-	This Study
$Si_2O_3(OH)_4^{2-}$	0.1	1.5	0.13	1.5	This Study
$Si_3O_6(OH)_3^{3-}$ (cyclo)	0.2	4.0	0.49	4.0	This Study
$Si_3O_5(OH)_5^{3-}$ (lin)	0.2	4.0	0.52	4.0	This Study
$Si_4O_8(OH)_4^{4-}$ (cyclo)	0.5	11.0	1.2	11.0	This Study
$Si_4O_6(OH)_6^{2-}$ (cyclo)	0.1	1.5	0.1	1.5	This Study
$Si_4O_7(OH)_6^{4-}$ (lin)	0.5	11.0	1.2	11.0	This Study
$Si_6O_{15}^{6-}$ (pris.)	1.3	30.	4.4	30.0	This Study
H_4SiO_4(aq)	$?_{Na}+ = .0925$				Azaroual et al. (1997)



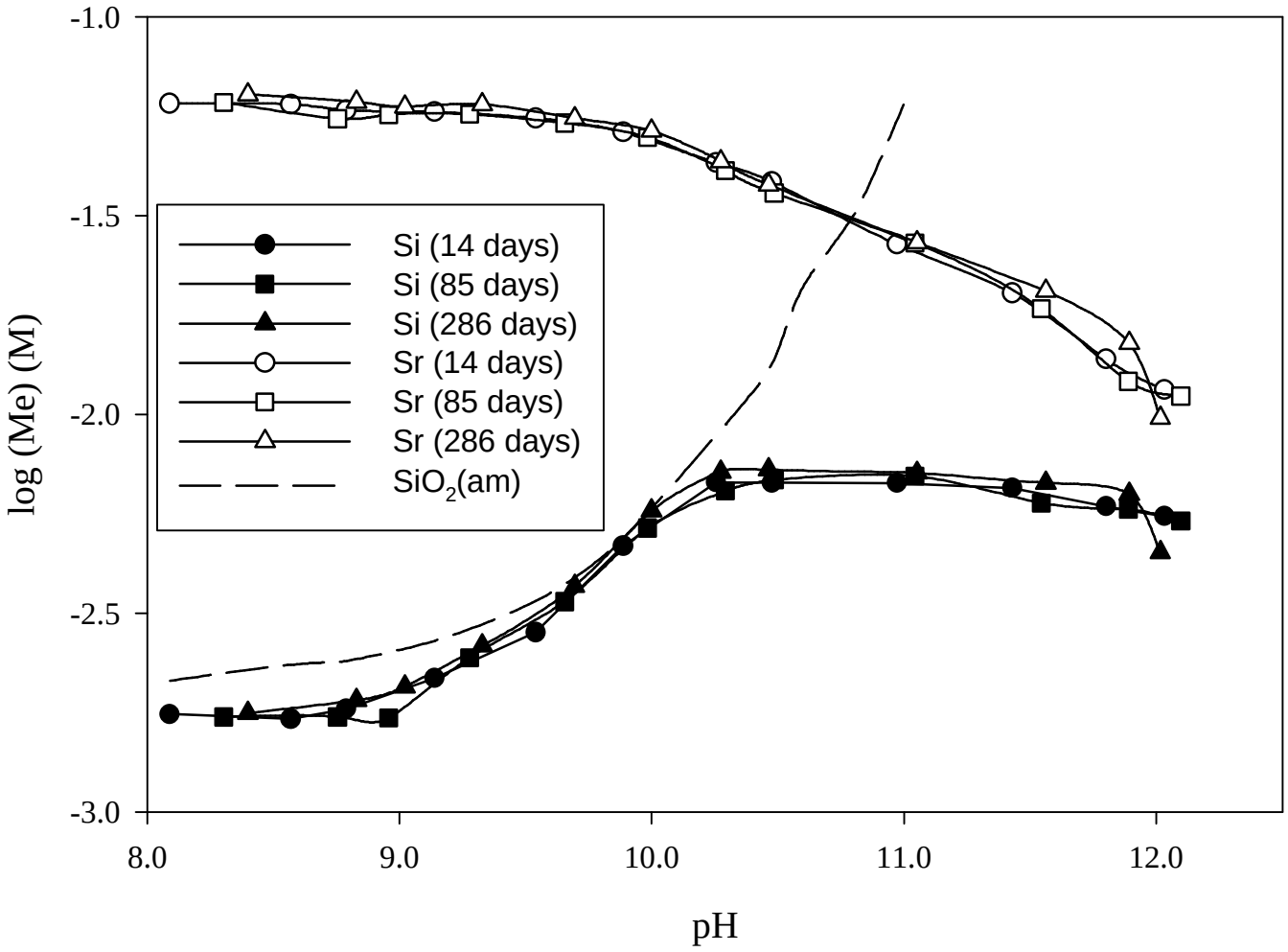
Calculated and experimental amorphous silica solubilities in 1m and 3m NaCl. Experimental data of Zarubin and Nemkina (1990)

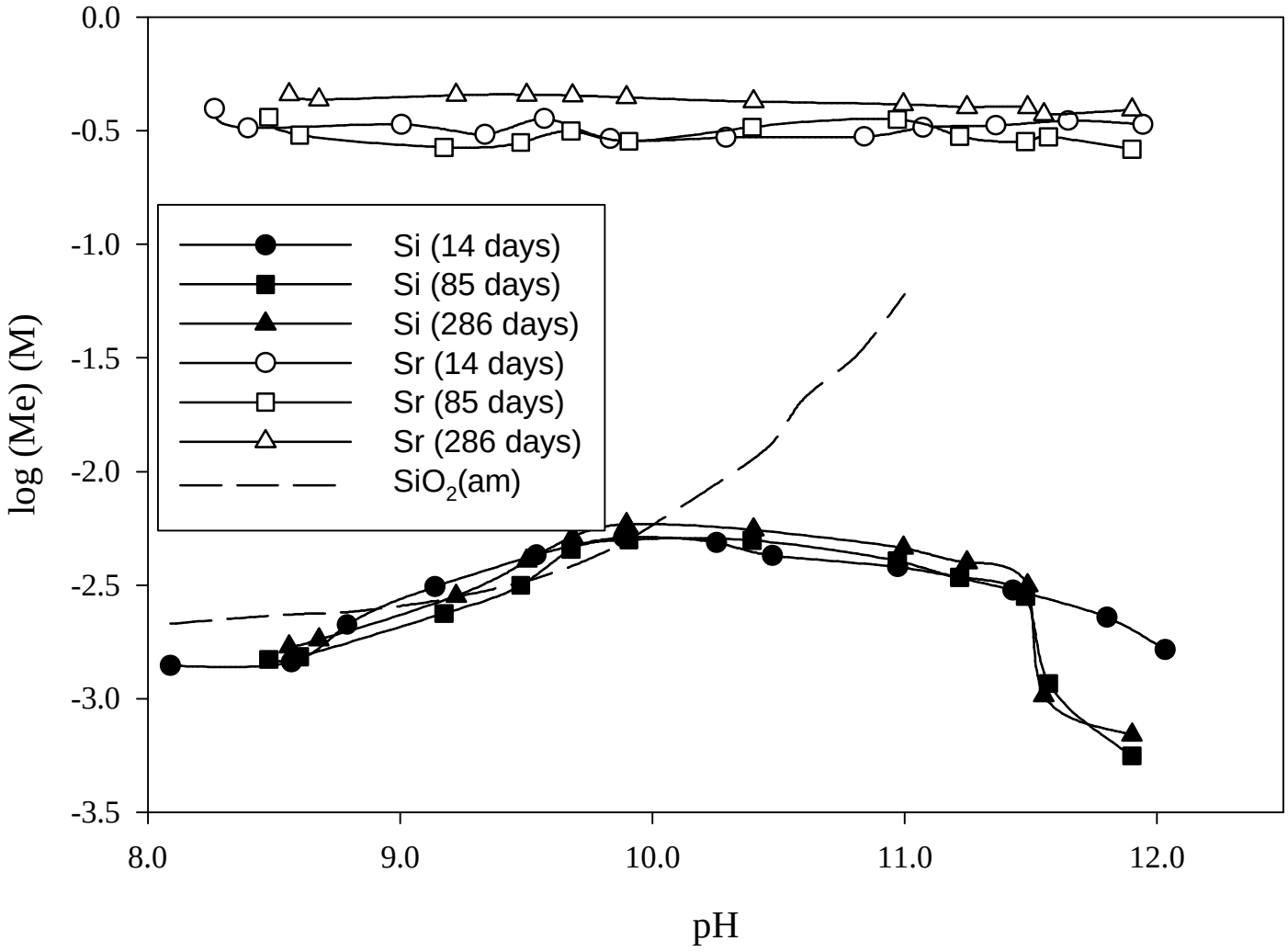
Sr Precipitation/Complexation

- No stability constants published for Sr silicate aqueous species.
- Divalent cation interacting with highly charged silicate species.
  - Strong interaction expected.
- Precipitation or complexation?

Sr-silicate Interactions

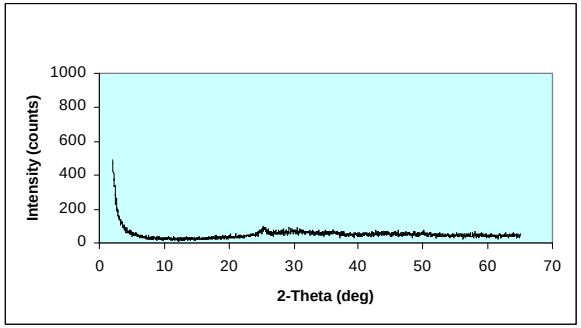
- Tested several series of Sr and Si concentrations to identify where polysilicates and Sr were present at high concentration.
  - High silica – Sr too low to effect ^{29}Si NMR signals for any species.
  - High Sr – silica too low to see any polynuclear complexation.
- Amorphous Sr-silicate precipitate forms.
  - Maintains the highest possible Sr and Si concentrations in solution.


-1.0
-1.5
-2.0
-2.5
-3.0
log (Me) (M)
8.0
9.0
10.0
11.0
12.0
pH
Si (14 days)
Si (85 days)
Si (286 days)
Sr (14 days)
Sr (85 days)
Sr (286 days)
SiO2(am)



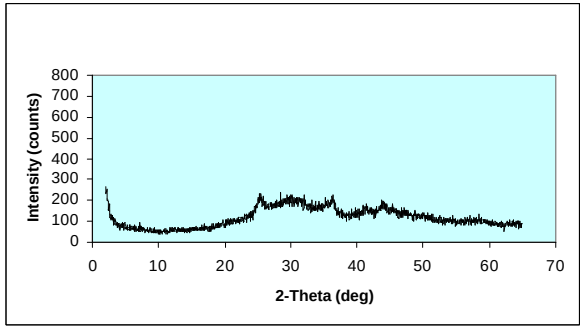
Sr and Si Solubilities as a function of pH Dissolution into 0.4M $Sr(NO_3)_2$ Solution

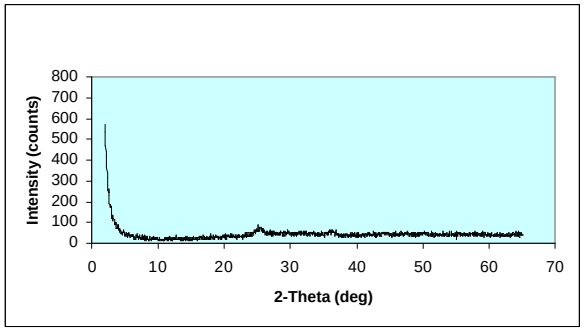
0.0 added Si **0.4m added Si**



pH=11.1

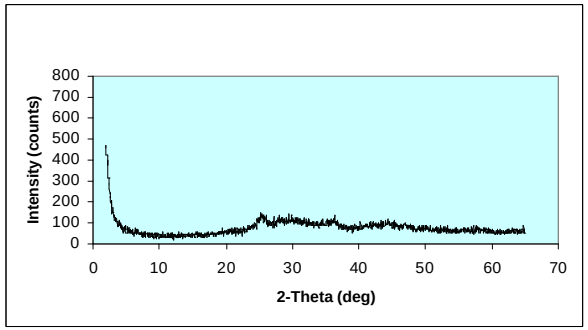
pH=11.2

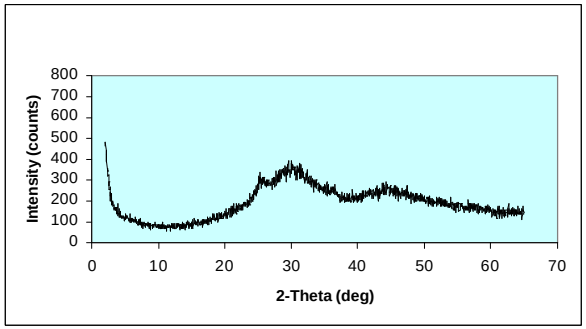




pH=11.6

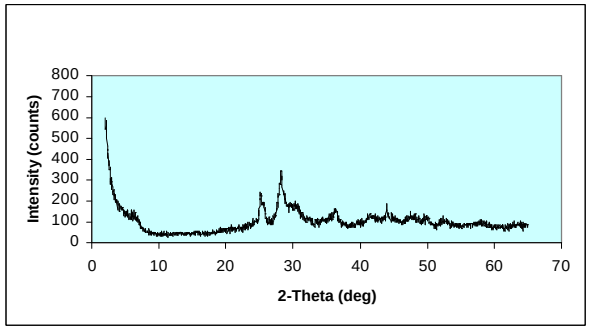
pH=11.5

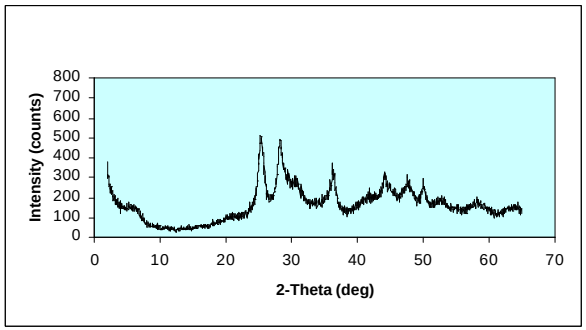




pH=11.9

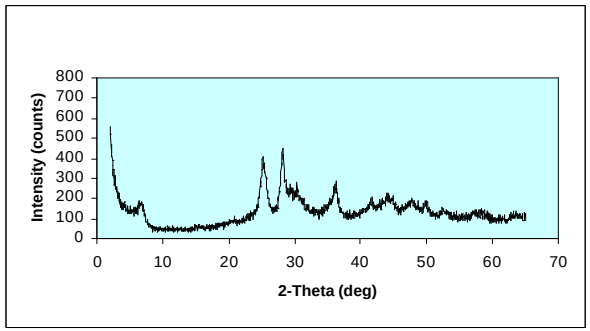
pH=11.6

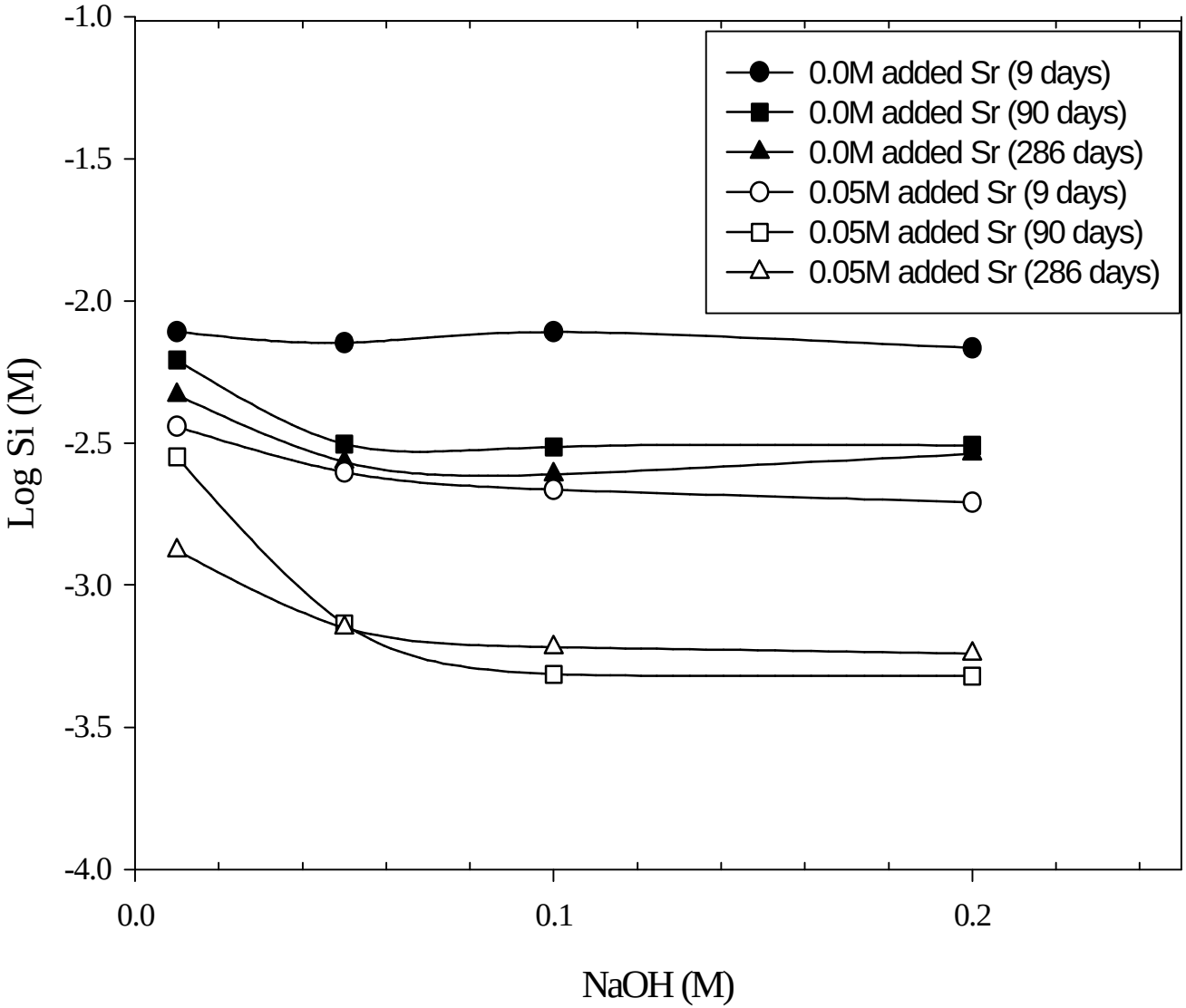




pH=12.0

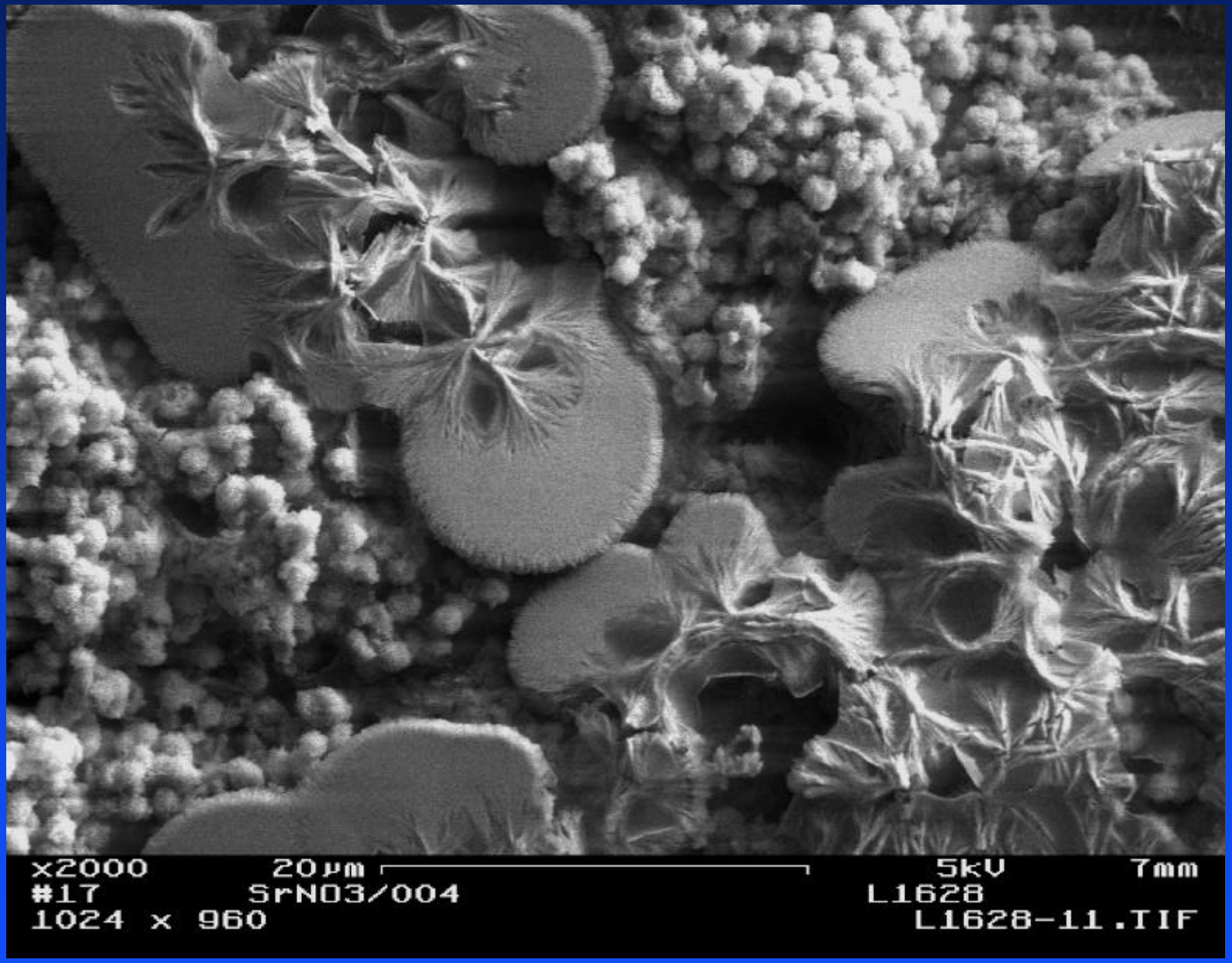
pH=11.9

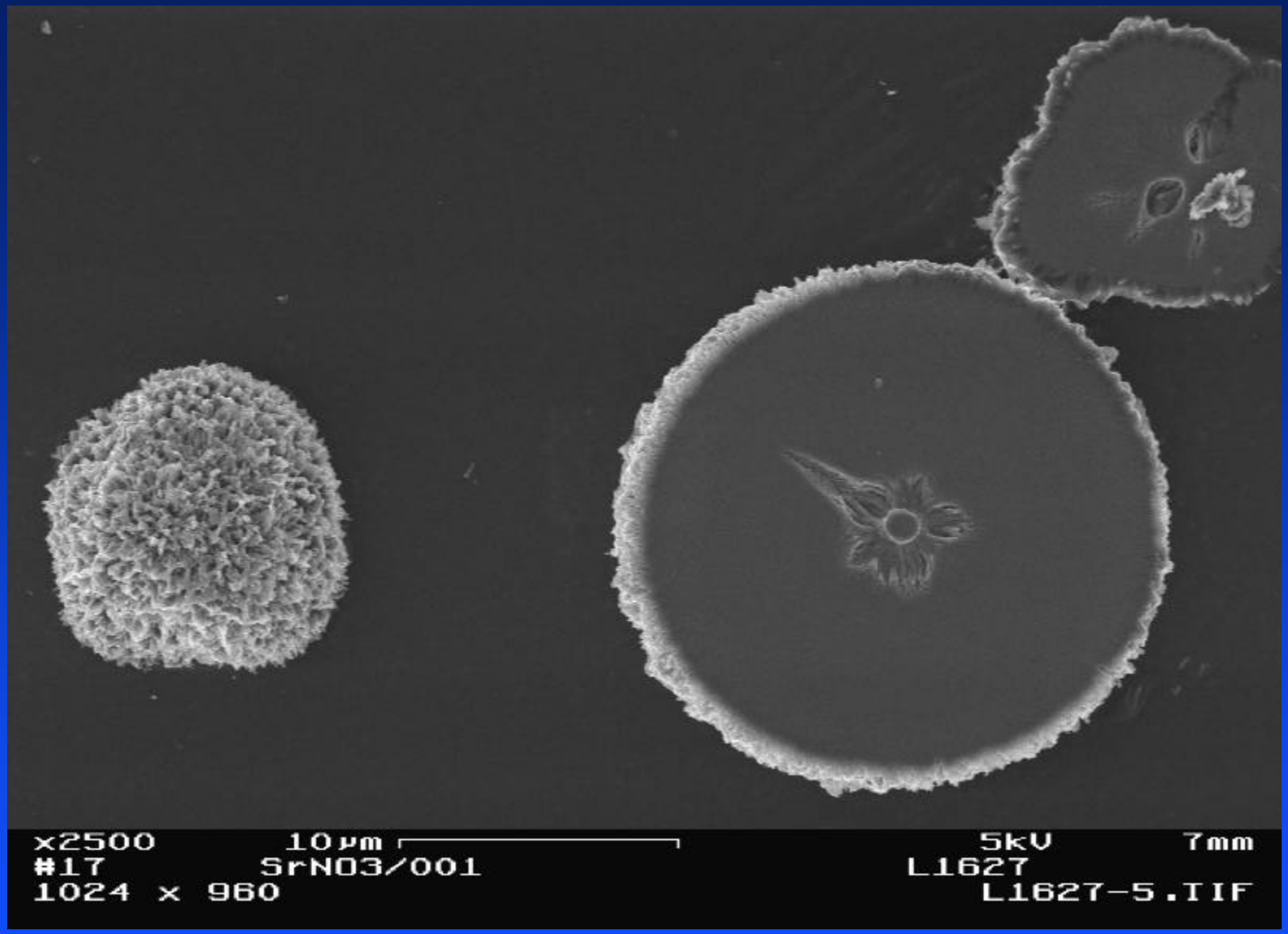


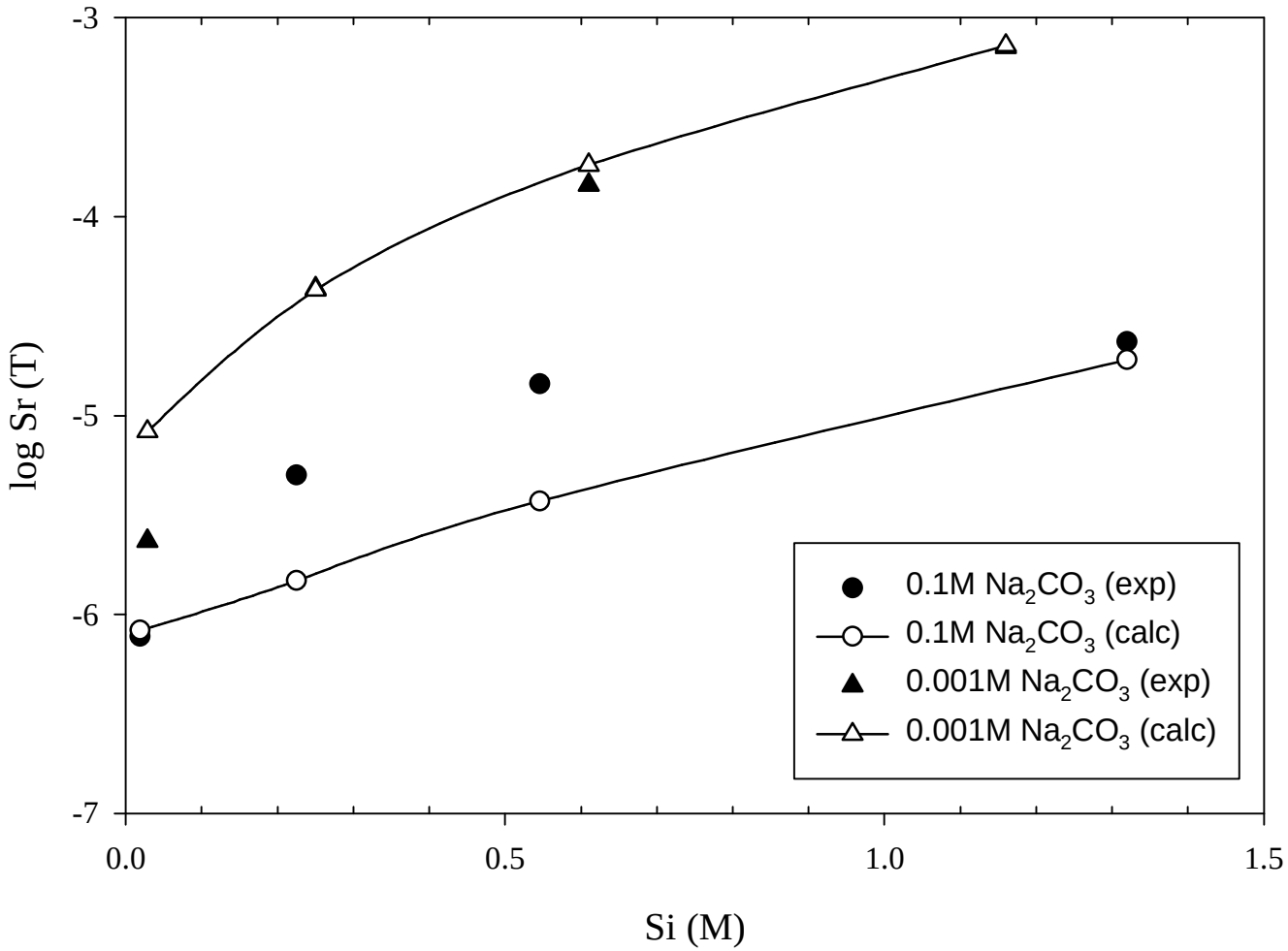

-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
Log Si (M)
0.0
0.1
0.2
NaOH (M)
0.0M added Sr (9 days)
0.0M added Sr (90 days)
0.0M added Sr (286 days)
0.05M added Sr (9 days)
0.05M added Sr (90 days)
0.05M added Sr (286 days)

Sr-silicate Interactions

- New phase identified - $Sr_5Si_6O_{16}(OH)_2 \cdot 5H_2O$.
  - Chemical analysis, XRD, TGA.
  - Tobermorite like structure.
  - Calculated a solubility product and estimated a stability constant for $SrH_2SiO_4(aq)$.
    - Log K = 2.86 compares (Ca = 3.09 and Mg = 4.17).
  - Dissolution features exhibit “sheaf of wheat” nucleation centers.
- Thermodynamic models for Sr speciation are reasonable even to high (1.2m Si).


x2000
20µm
5kV
7mm
#17
SrNO3/004
L1628
1024 x 960
L1628-11.TIF


x2500 10µm 5kV 7mm
#17 SrNO3/001 L1627
1024 x 960 L1627-5.TIF

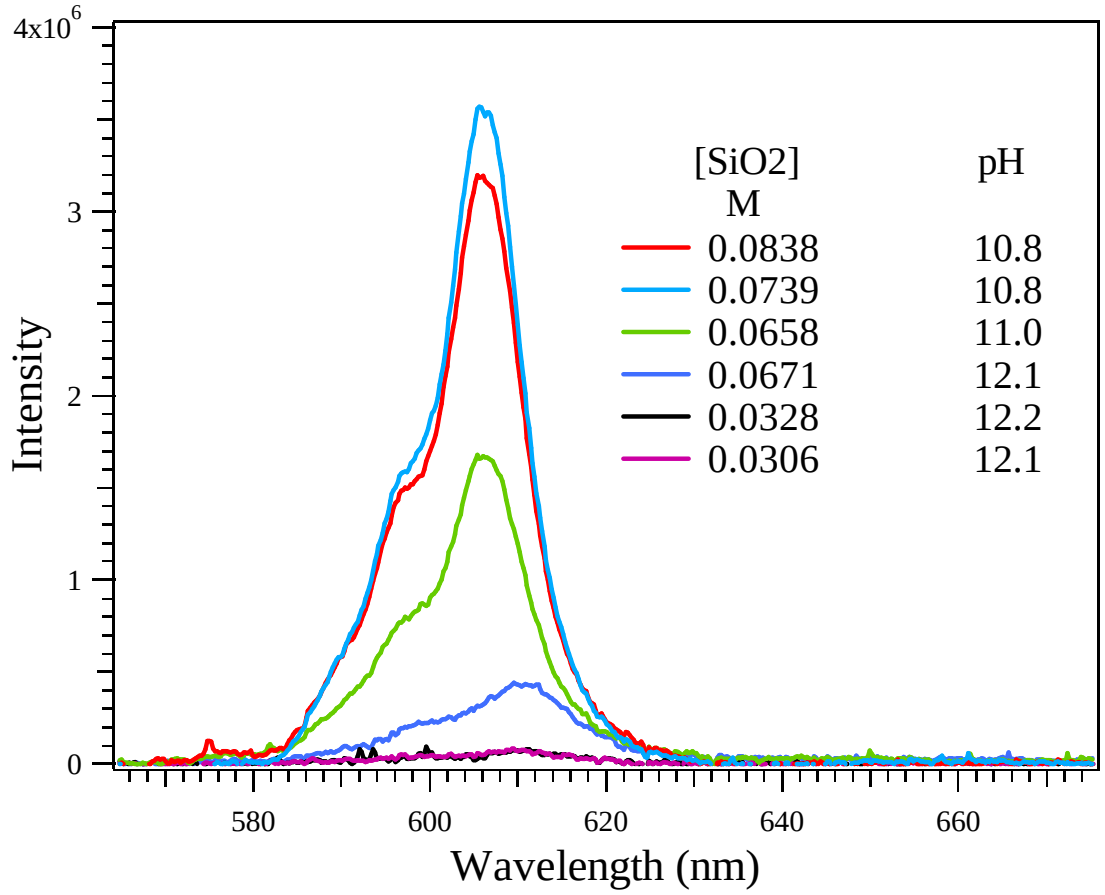


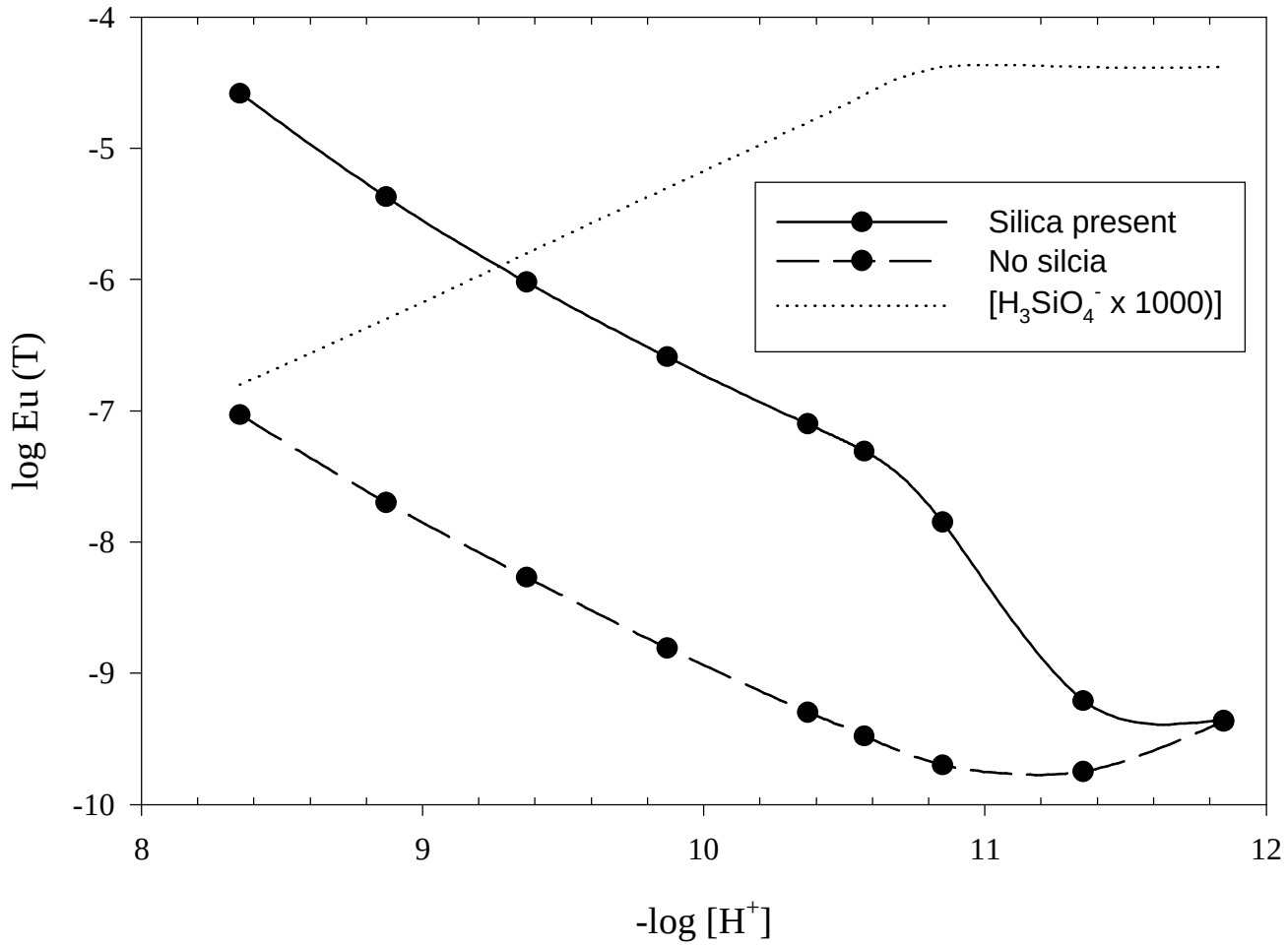
The Solubility of $SrCO_3(c)$ in Na_2CO_3 – NaOH Solutions with added SiO_2

Cm-silica Complexation

- TRLFS measurements of ^{248}Cm in silica containing solutions to high base.
- Results indicate silica complexation dominates to pH ~12.
  - Modeling results (FSU data on monomeric complexation) does not indicate polysilicate complexation.

Fluorescence spectra of Cm(III) at different silica concentration after filtration: filter cut-off = 30,000 NMWL, pore size = 3.6 nm





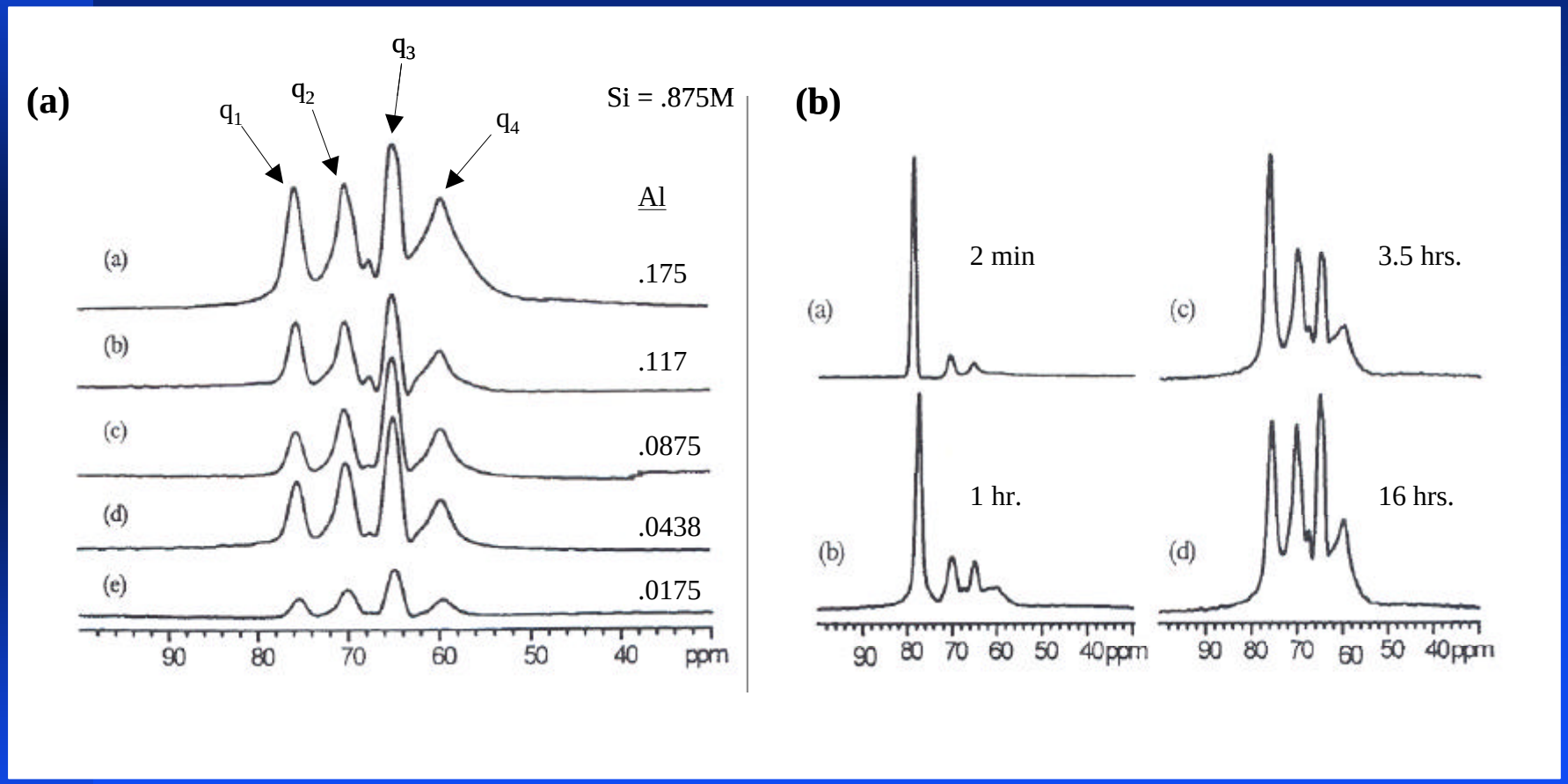
Calculated and Experimental Solubilities of $Eu(OH)_3$ in the Presence (0.1M max) and Absence of Silica

Monomeric o-silicate complex stability constants determined by solvent extraction (FSU)

Table 1. **Stability constants for metal – *o*-silicate complexes**

Metal ion	log β_1	log β_2	*I*, M	References
UO_2^{2+}	6.79 ± 0.25 7.6 – 6.8	12.85 ± 0.28	0.20 0.1 – 0.2	*This work* [1 – 3]
Am^{3+}	7.46 ± 0.22 7.3		0.20 0.2	*This work* [4]
Eu^{3+}	7.04 ± 0.15 7.26	11.7	0.20 0.10	*This work* [5]
Co^{2+}	4.85 ± 0.25		0.20	*This work*
Ni^{2+}	5.41 ± 0.23		0.20	*This work*

Summary

- Polysilicate model is complete (25^0C).
- Monomeric complexation studies are complete (FSU).
- Sr - high Si complexation studies complete – support only monomeric complexation.
  - New phase identified.
- Initial results for Cm at high silica also support monomeric complexation.
- Thermodynamic database developed for use in reactive transport simulation (Yabusaki, Lichtner).
- Future Studies: Complete polysilicate complexation studies (Cm, U, Al, …) examine higher temperatures.

Al-silicate aqueous species dominate speciation at high Al/Si