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Experimental Determination of Solubility Constants of Saponite at Elevated Temperatures in High Ionic Strength Solutions: Applications to Nuclear Waste Isolation

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OUTLINE OF PRESENTATION

- Introduction
- Objective of This Work
- Experimental Methodology
  - Synthesis of Saponite
  - Experimental Set-ups
- Experimental Results
- Summary

INTRODUCTION

- Salt formations are ideal for nuclear waste isolation, as recommended by National Academy of Science as early as 1950's (National Academy of Science, 1957).
- Brines associated with salt formations usually have high concentrations of magnesium, as exemplified by the examples in the following slides.
- When high level waste (HLW) glass is corroded in Mg-rich solutions, Mg-containing clay minerals such as saponite, $Mg_4Al_2Si_2O_{10}(OH)_2 \bullet 4H_2O$, form (i.e., Grambow and Muller, 1990).
- When saponite form, it may impact the near-field chemistry of a geological repository in salt formations:
  - Governing the chemical compositions, including hydrogen ion concentrations, of the resulting solutions
  - Forming protective layer on surfaces of HLW glass, preventing or reducing the further corrosion of HLW glass

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Grambow, B. and R. Muller (1990). CHEMISTRY OF GLASS CORROSION IN HIGH SALINE BRINES. Scientific Basis for Nuclear Waste Management Xiii. Pittsburgh, Materials Research Soc. **176:** 229-240.

National Academy of Sciences Committee on Waste Disposal. 1957. *The Disposal of Radioactive Waste on Land*. Publication 519. Washington, DC: National Academy of Sciences–National Research Council.

INTRODUCTION (Continued)

- However, thermodynamic properties of saponite are not well-defined:
  - It is difficult to make reliable and accurate predictions for the evolution of chemical compositions of the solutions interacting with glass.
- The accurate knowledge of its thermodynamic properties is the prerequisite for modeling the glass corrosion in $MgCl_2$-dominated solutions in salt formations.
- Examples of well characterized brines associated with salt formations
  - Brines from Waste Isolation Pilot Plant (WIPP), New Mexico, USA
    - the Generic Weep Brine, GWB
    - Energy Research and Development Administration (WIPP Well) 6, ERDA-6
  - Asse, Germany
    - Q-brine (Schuessler et al., 2001)

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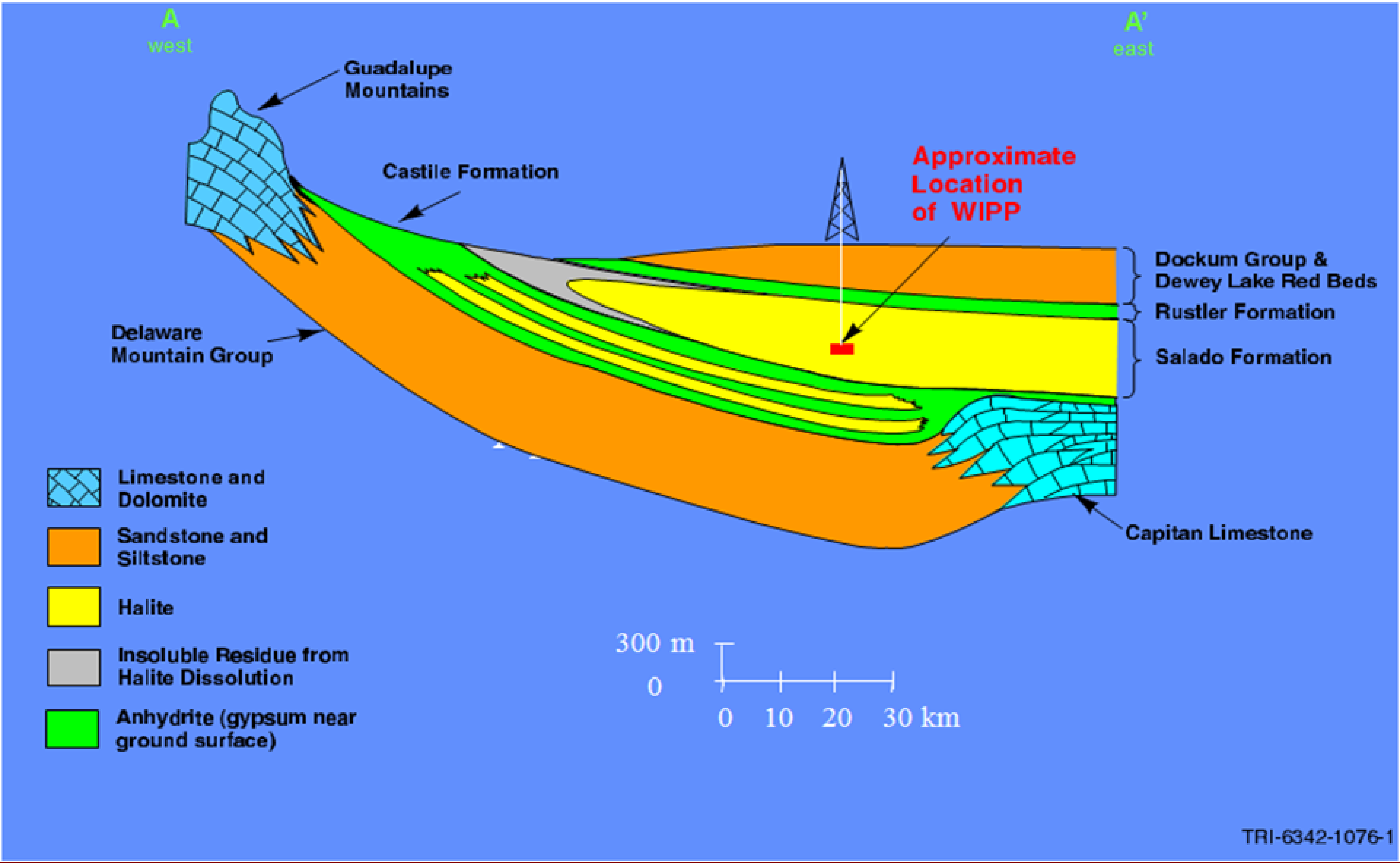
Schuessler, W., Kienzler, B., Wilhelm, S., Neck, V. and Kim, J.I. (2001) Modeling of Near Field Actinide Concentrations in Radioactive Waste Repositories in Salt Formations: Effect of Buffer Materials. Mat. Res. Soc. Symp. Proc. Vol. 663, p. 791.

INTRODUCTION (Continued), WIPP



INTRODUCTION (Continued): WIPP Brines

Appendix B
Concentration Scales in Molarity (Moles/L Solution) and Molality ($Moles/kg\ H_2O$) for Synthetic Salado (GWB) and Castile (ERDA-6) Brines

Chemical Species	GWB Moles/L sol'n	GWB Moles/kg H_2O	ERDA-6 Moles/L sol'n	ERDA-6 Moles/kg H_2O
Na^+	3.53	3.98	4.85	5.44
K^+	0.467	0.526	9.70×10^{-2}	0.109
Li^+	4.48×10^{-3}	5.05×10^{-3}	None	None
Ca^{2+}	1.38×10^{-2}	1.56×10^{-2}	1.20×10^{-2}	1.34×10^{-2}
Mg^{2+}	1.02	1.15	1.90×10^{-2}	2.13×10^{-2}
Cl^-	5.61	6.32	4.64	5.20
Br^-	2.66×10^{-2}	3.00×10^{-2}	1.10×10^{-2}	1.23×10^{-2}
SO_4^{2-}	0.178	0.200	0.167	0.187
$B_4O_7^{2-}$	3.95×10^{-2}	4.45×10^{-2}	1.57×10^{-2}	1.76×10^{-2}

From Xiong (2008)

INTRODUCTION (Continued), Asse, Q-brine

Chemical Species	mole/kg H_2O
Na^+	0.377
K^+	0.966
Mg^{2+}	4.47
Cl^-	10.1
SO_4^{2-}	0.178

From Schuessler et al. (2001)

OBJECTIVE OF THIS STUDY

- To synthesize saponite according to the well-established procedure (Shao and Pinnavaia, 2010).
- To investigate solubility constants of saponite at elevated temperatures

Shao, H. and Pinnavaia, T.J., 2010. Synthesis and properties of nanoparticle forms saponite clay, cancrinite zeolite and phase mixtures thereof. *Microporous and Mesoporous Materials*, *133*(1), pp.10-17.

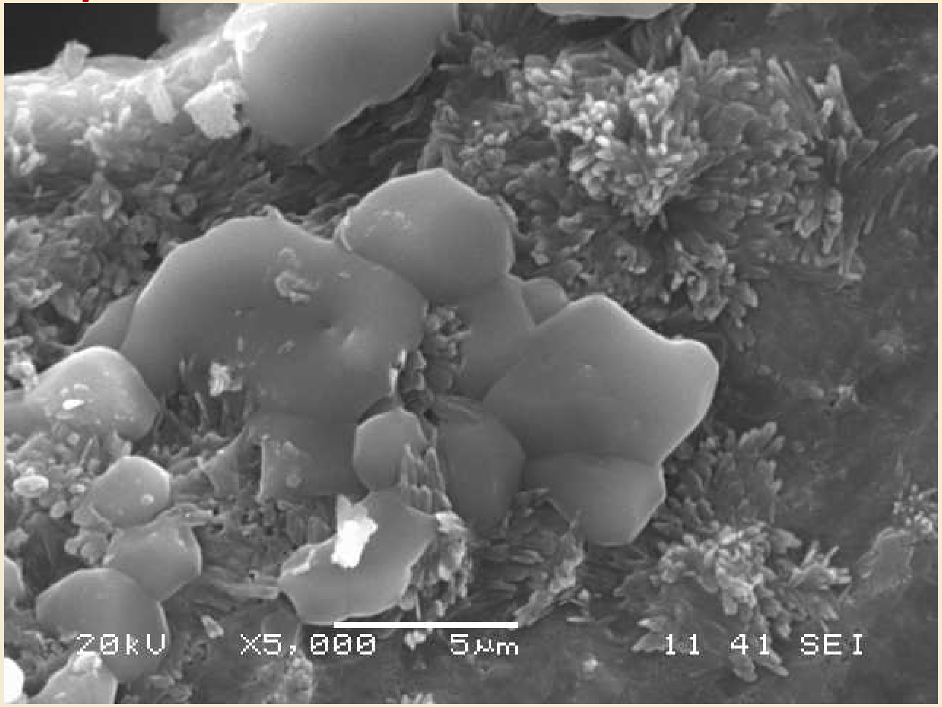
EXPERIMENTAL METHOD

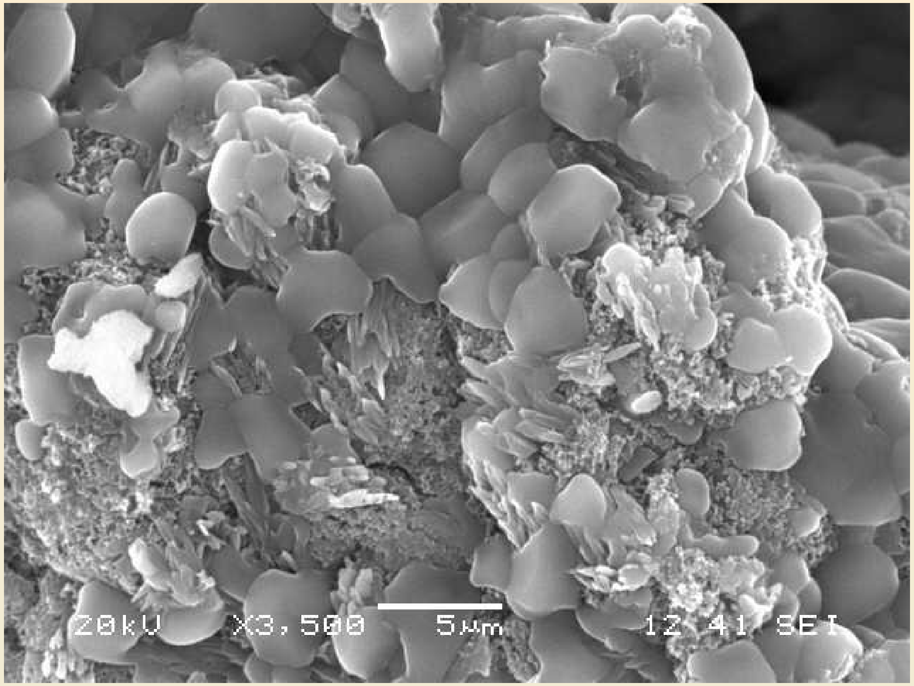
- Saponite was synthesized at 90^{o}C using the following chemicals with reagent grade:
  - Na_2SiO_3•$9H_2O$, $Al(NO_3)_3$•$9H_2O$, NaOH, $Mg(NO_3)_2$•$6H_2O$, and DI water
- Approaching equilibrium from both supersaturation and undersaturation:
  - Supersaturation experiments:
    - Saponite equilibrates with the original solutions from which saponite was precipitated and synthesized
  - Undersaturation experiments:
    - Saponite was filtered out from the original solution
    - Saponite was dried
    - Dried saponite equilibrates with desired supporting solutions at temperatures of interest
- pH measurements: pH's of experiments were measured at the experimental temperatures
  - pH buffers (at least three pH buffers) were first equilibrated at the experimental temperatures.
  - pH meter was calibrated with the pH buffers.
  - Experimental solutions were measured with respect to pH.

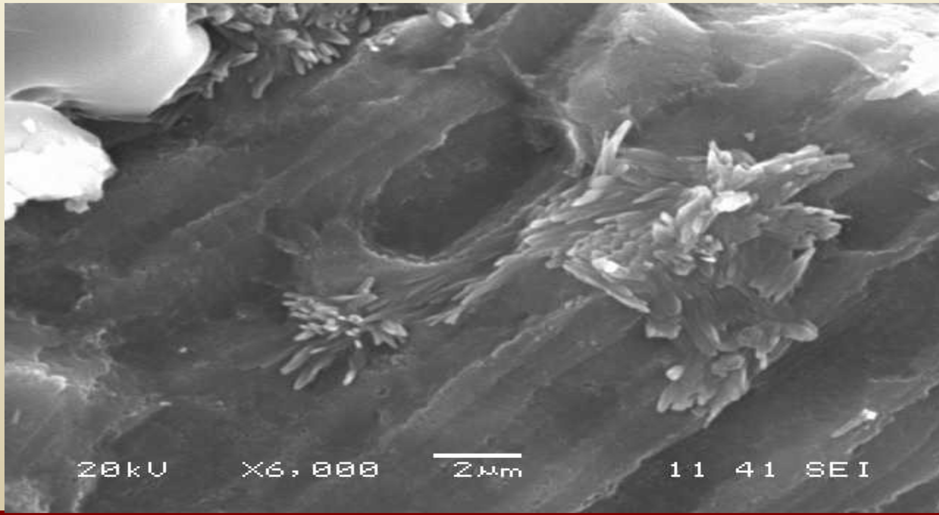
EXPERIMENTAL METHOD(Continued)

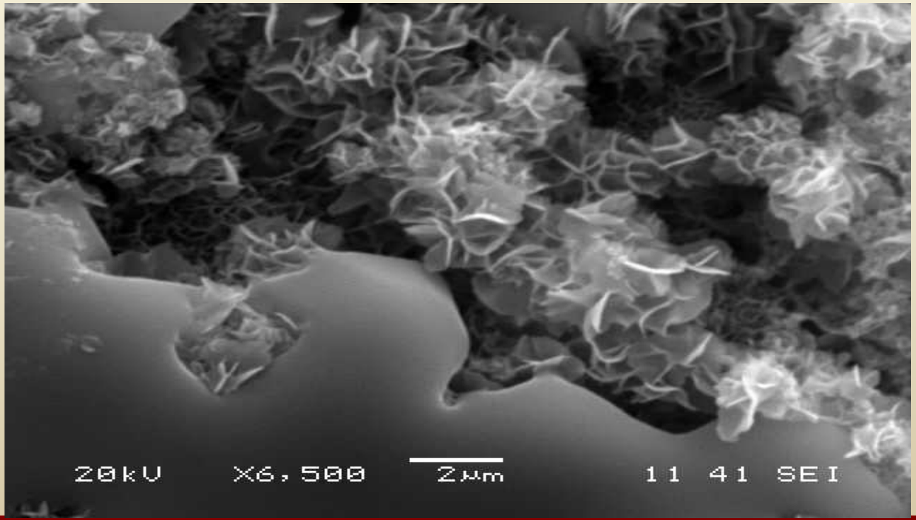
- Solution samples were filtered with 0.2 μm filters.
- Solution samples were with trace metal grade HNO_3.
- Solution samples were diluted to desired concentrations for analyses.
- Solution samples were analyzed for Al, Mg, Na and Si using inductively coupled plasma atomic emission spectrometer (ICP-AES).
- Solid samples were characterized with scanning electron microprobe (SEM) with energy-dispersive X-ray spectroscopy (EDS).
- Phase identifications for solid samples was done by using Bruker D8 Advance X-ray diffractometer.

Experimental Results: SEM Images

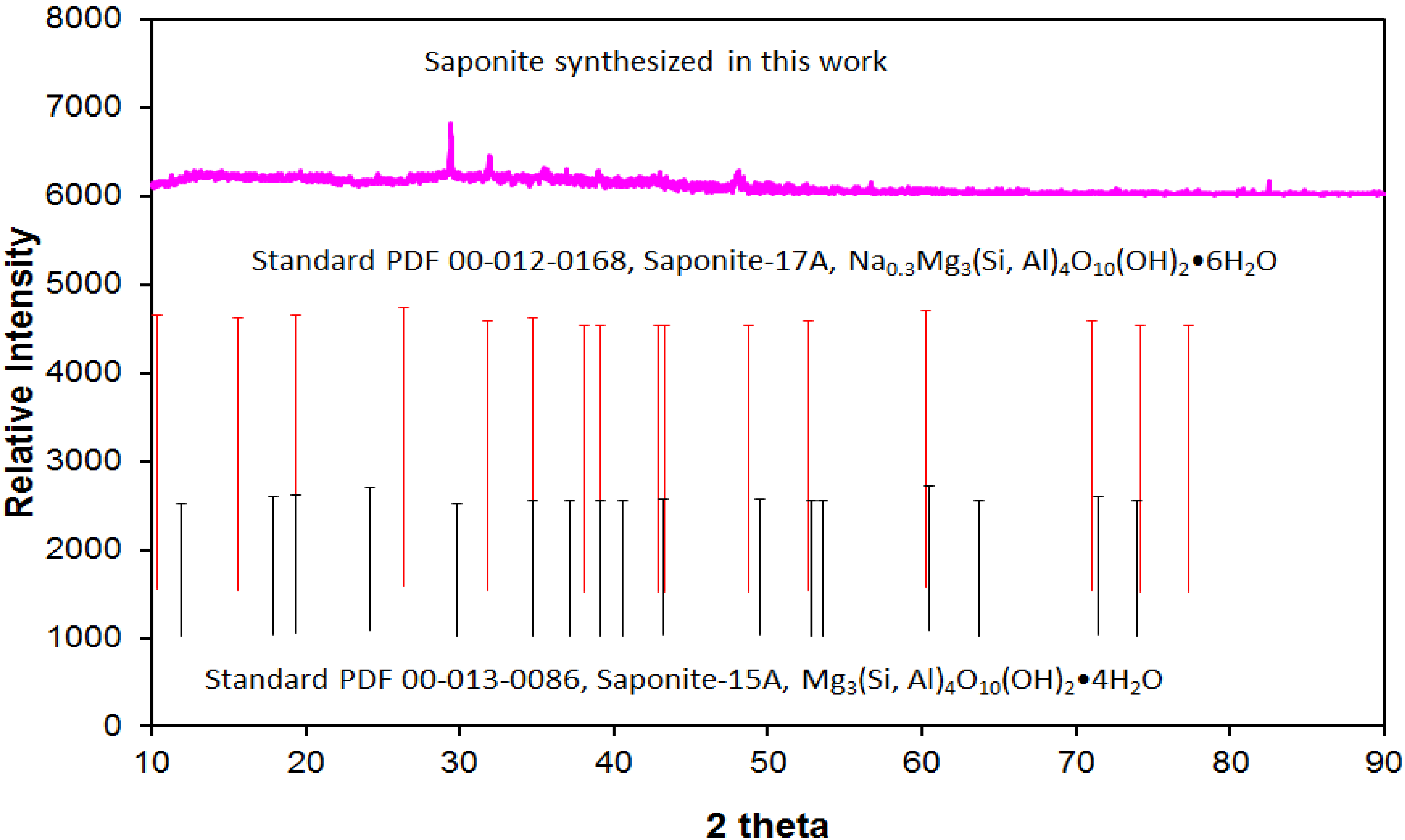




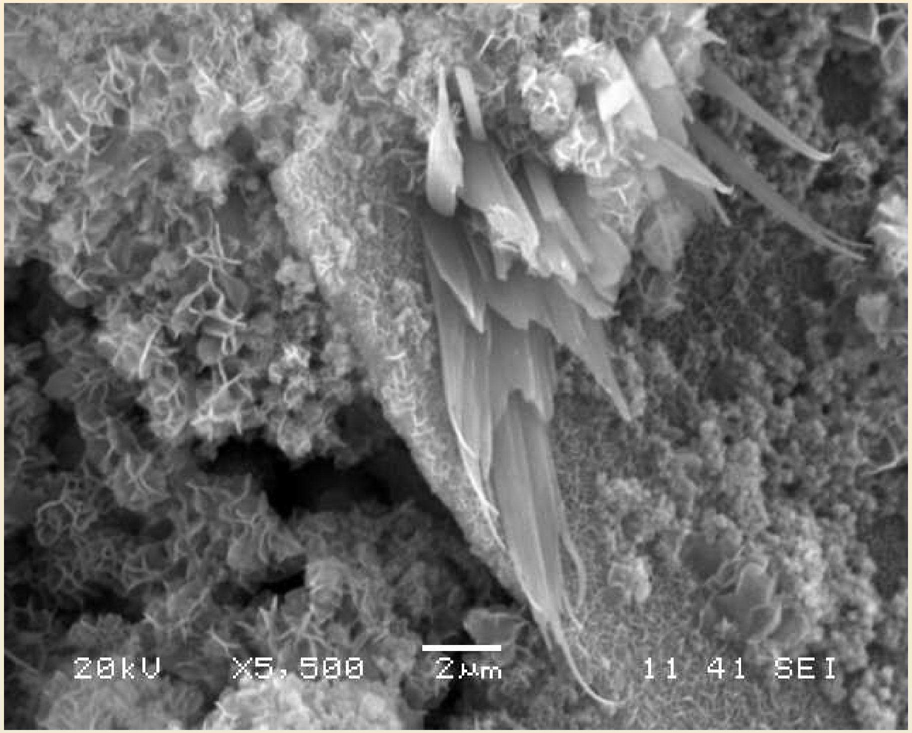


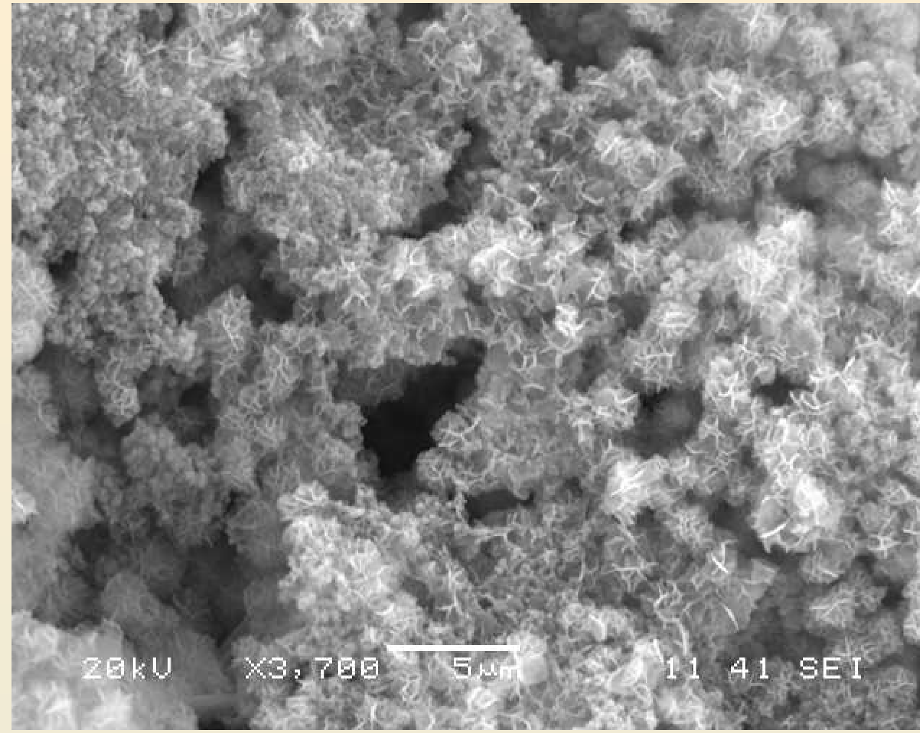


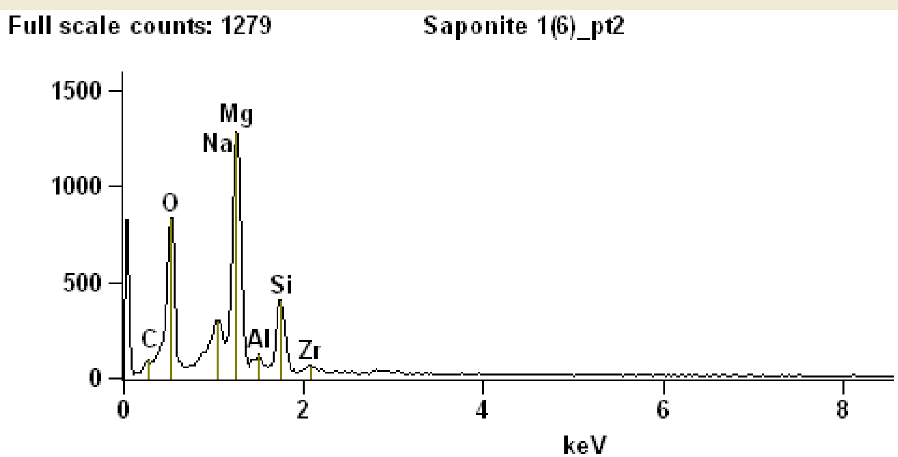
Experimental Results: XRD patterns

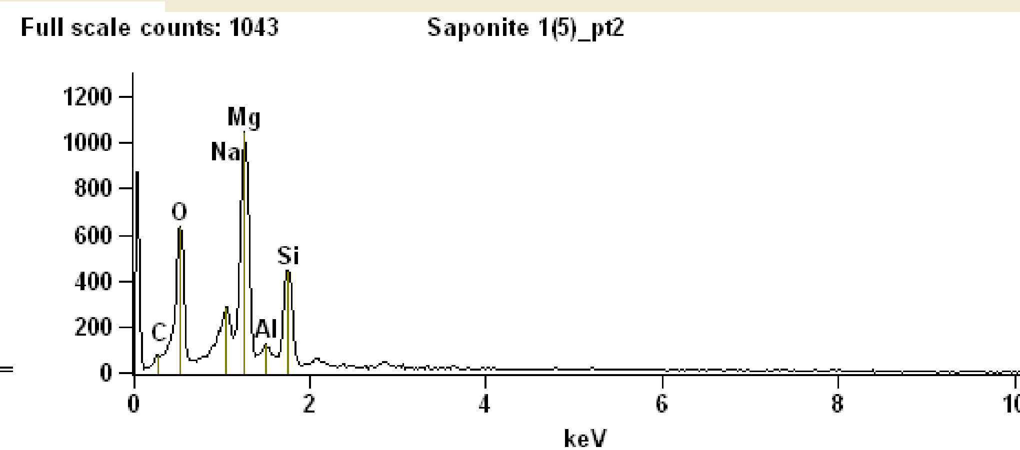


Experimental Results: SEM-EDS

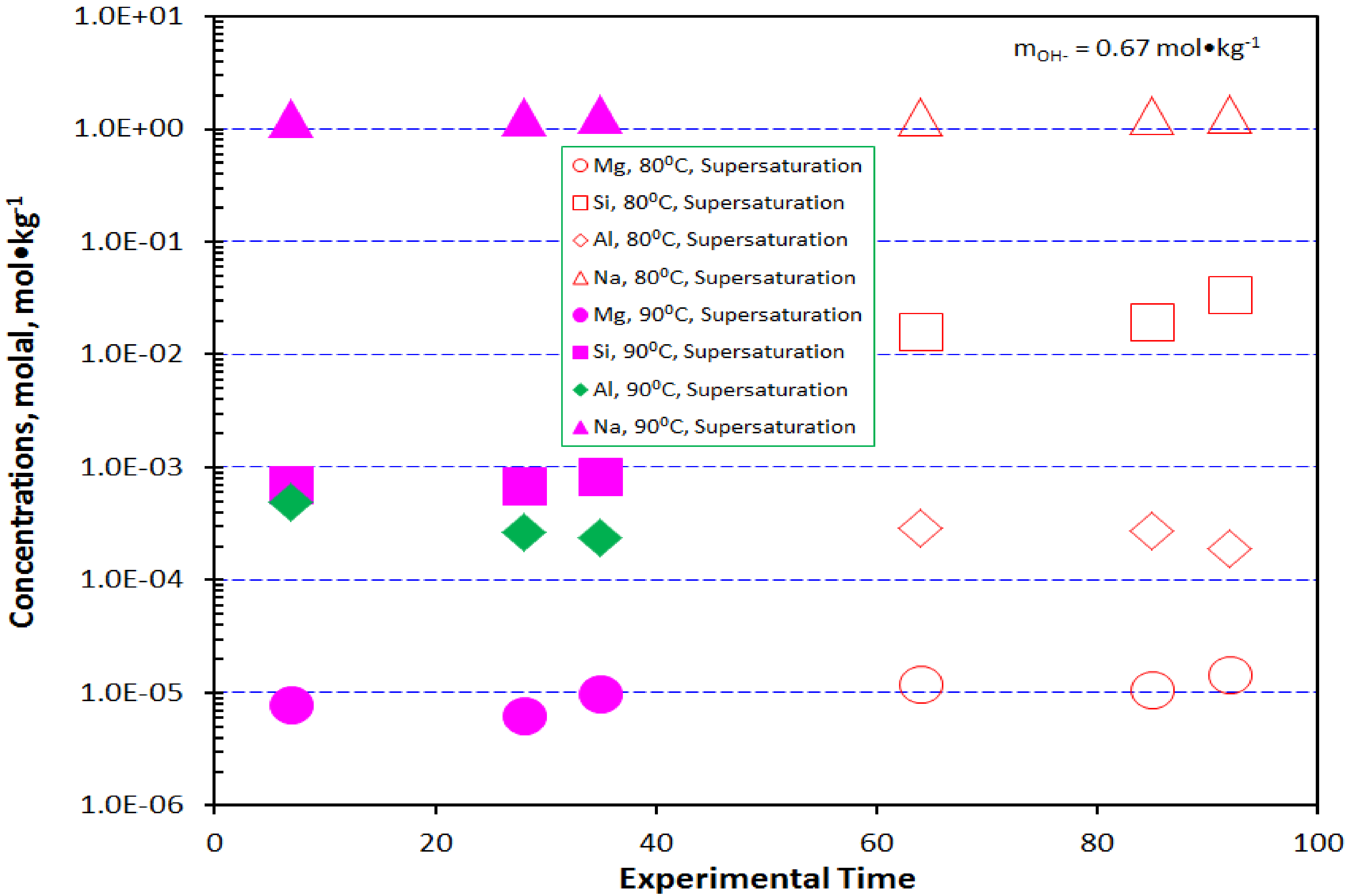




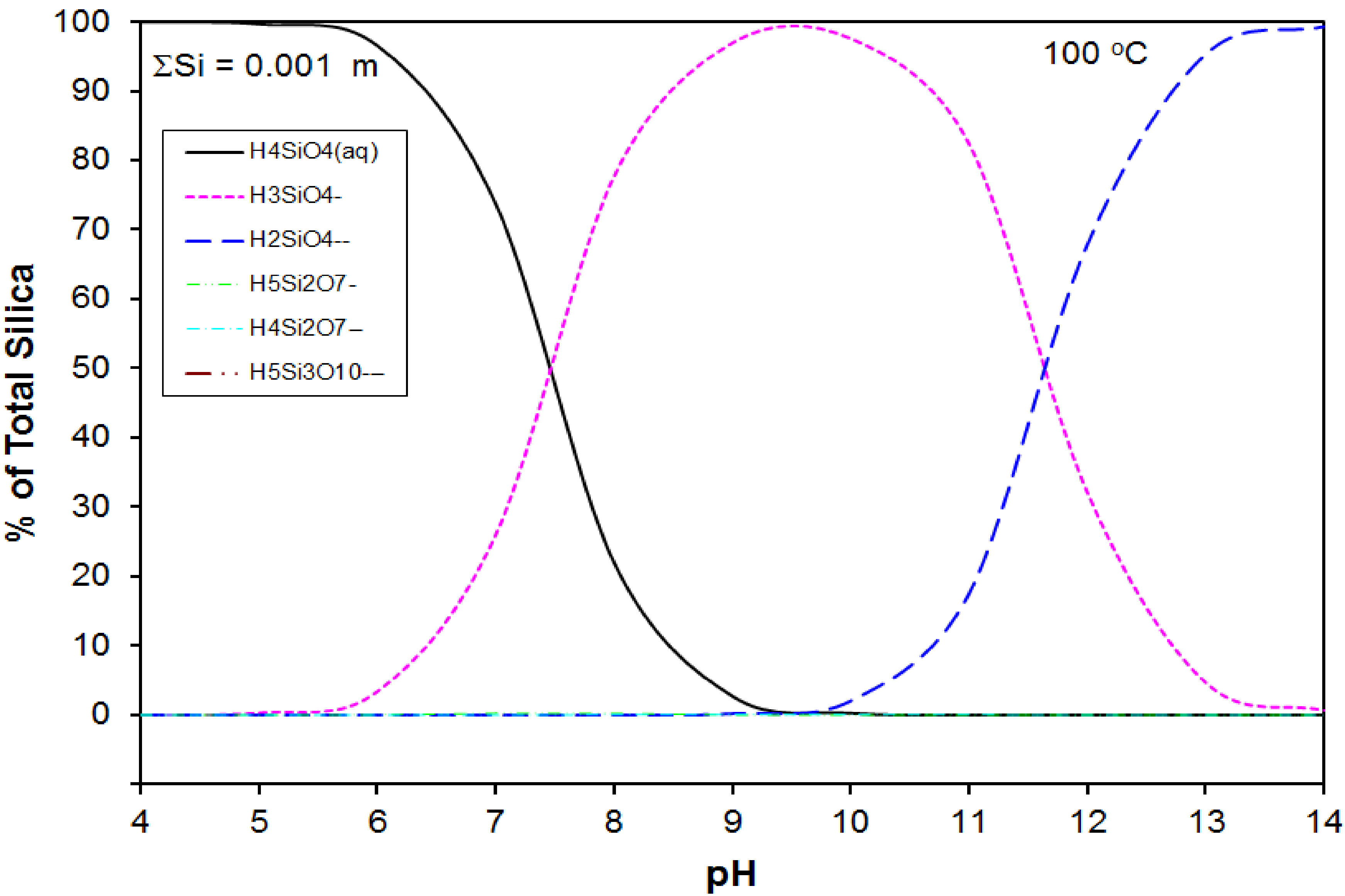




Experimental Results: Solution Chemistry (Preliminary)



Experimental Results: Calculation of Equilibrium Quotients, speciation of silica (from Xiong, 2013)



Experimental Results: Equilibrium Quotients

$$Na_{0.3}Mg_{3.85}Al_2Si_2O_{10}(OH)_2{\bullet}4H_2O + 2H_2O(l) = 0.3Na^{+} + 3.85Mg^{2+} + 2Al(OH)_4^{-} + 2H_2SiO_4^{-2} + 2OH^{-}$$

log Q = -29.75 $\pm$ 0.75 (2σ) for data at 80^{o}C

Work in Progress

- In the near future, the following will be reported
  - Experimental results from undersaturation experiments
  - Extrapolation of equilibrium quotients to infinite dilution using the Pitzer and Specific Ion Interaction Theory (SIT) models