Used Fuel Disposition Campaign

Thermodynamic database development: Al-silicate system at elevated temperatures

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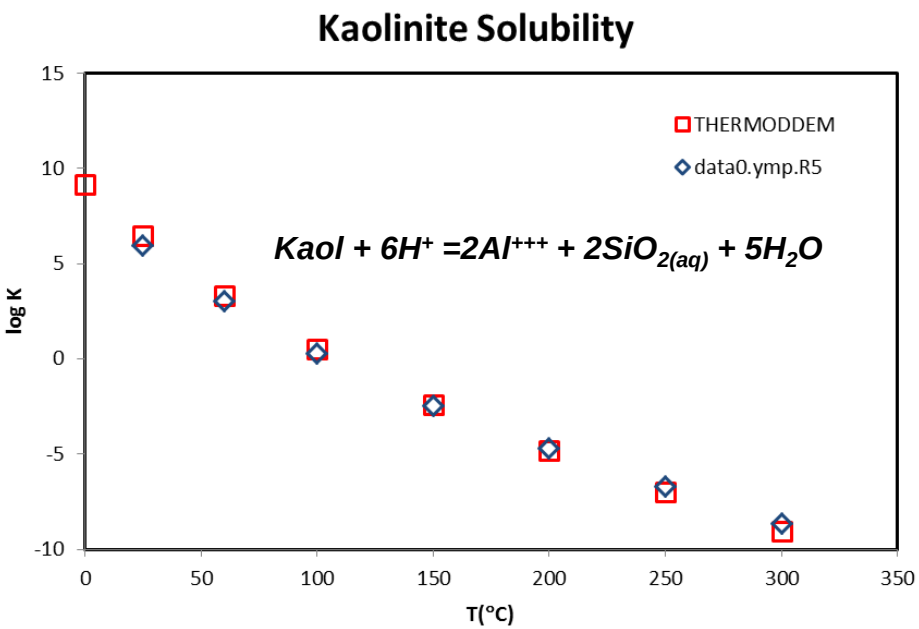
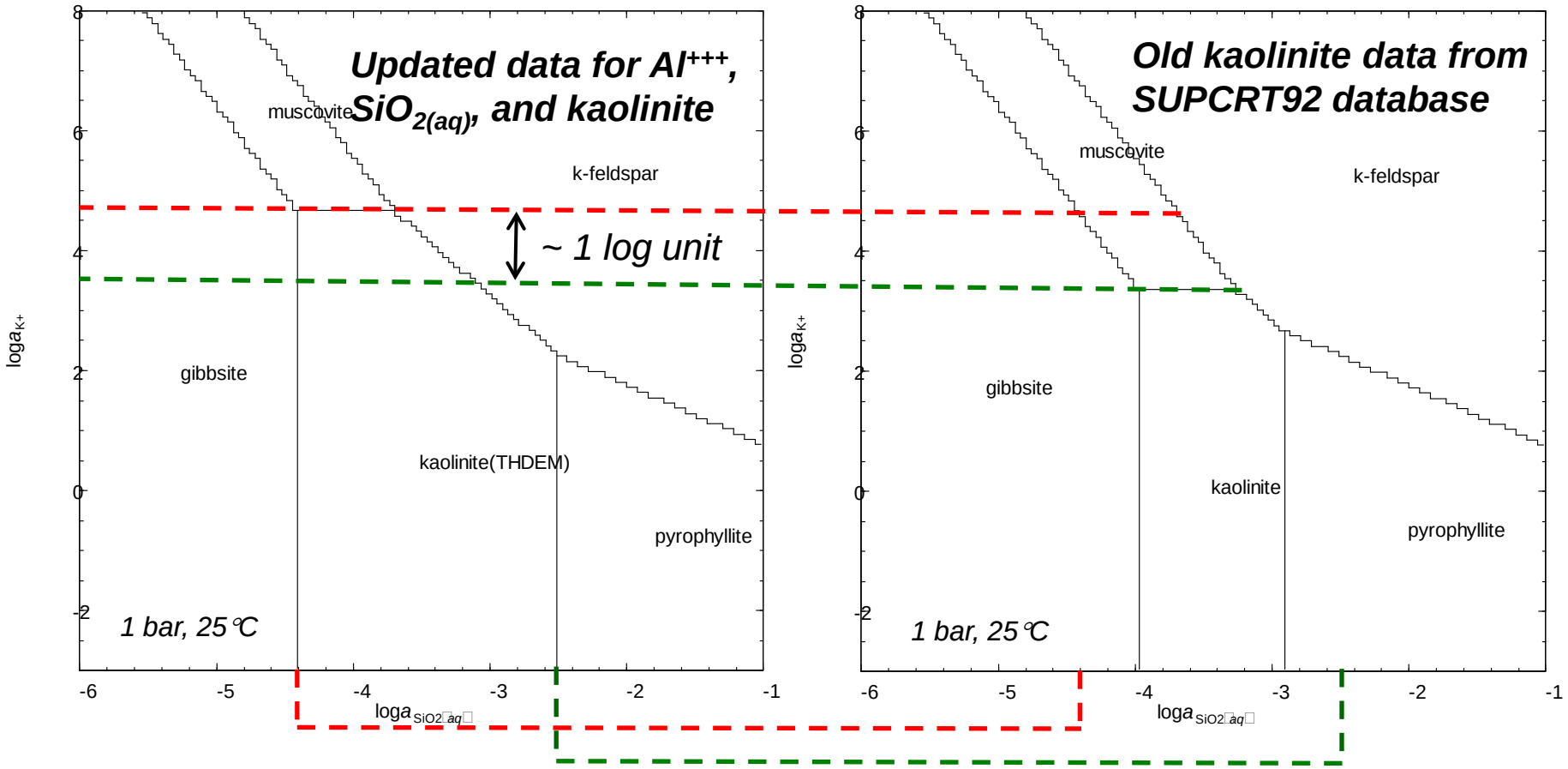
Thermodynamic Database Development: Al-silicate Systems

- **Importance of keeping (internal) consistency**
  - Agreement with benchmarks and experimental studies
  - Consistency with key reference thermodynamic data
  - Maintain consistency with aqueous species thermodynamic data
- **Relevance to barrier materials**
  - **Buffer materials:** Clays, zeolites, phyllosilicates
  - **Seals:** Cementitious phases
  - Their interactions and stability relations

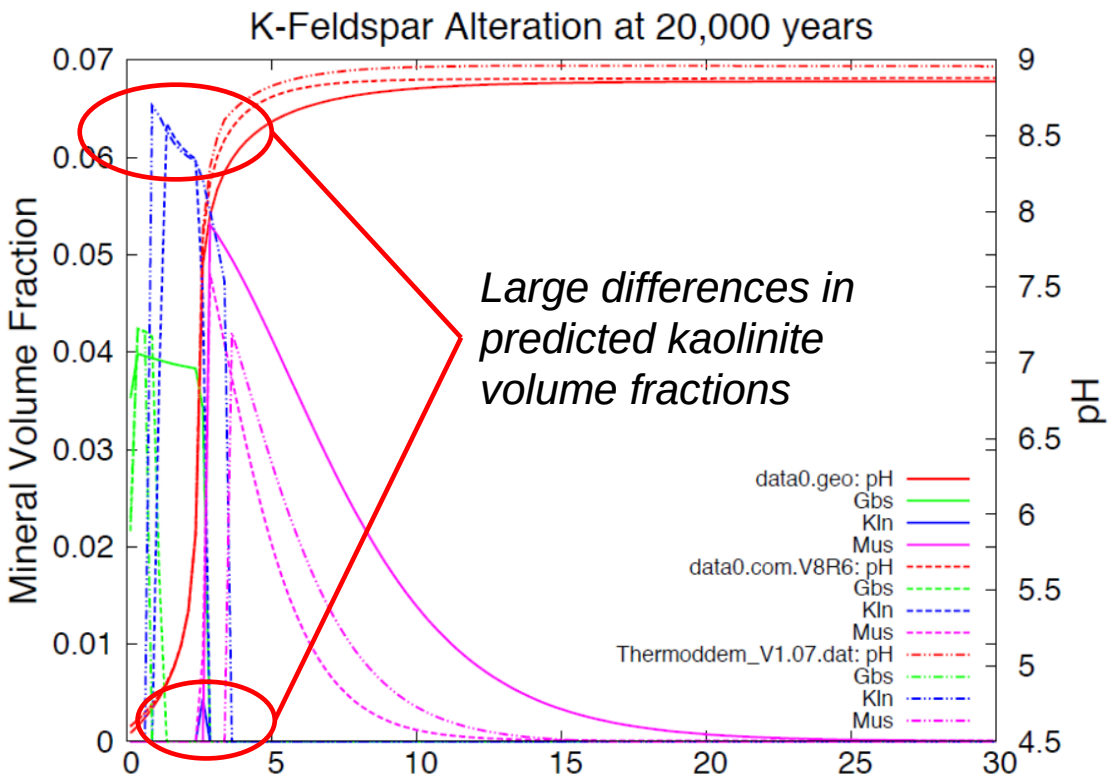


Potential Database Inconsistencies: Old vs. New: Why is this Important?

Database inconsistencies lead to shifts in kaolinite stability field



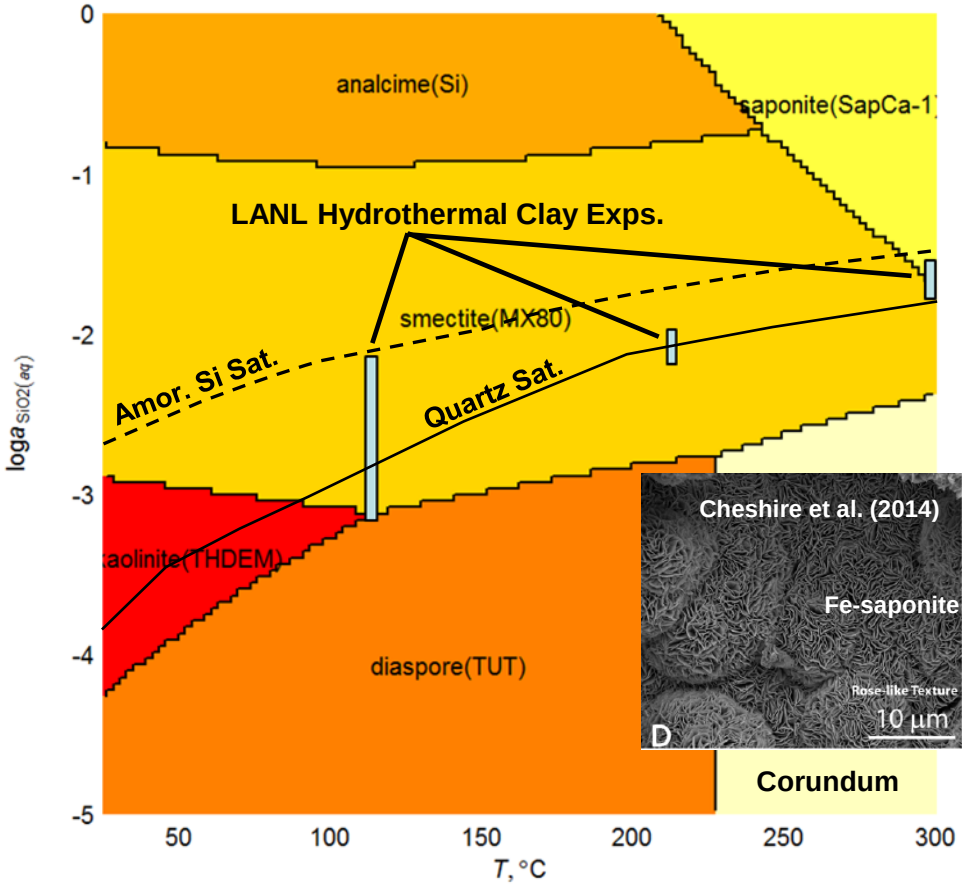
Database Inconsistencies: Effects on Reactive Transport Modeling



- **Reactive transport modeling:**
  - PFLOTRAN code problem for K-feldspar weathering to for a bauxite deposit
  - Differences between thermodynamic databases can affect predictions in mineral volume fractions

Code results courtesy of Dr. Peter Lichtner

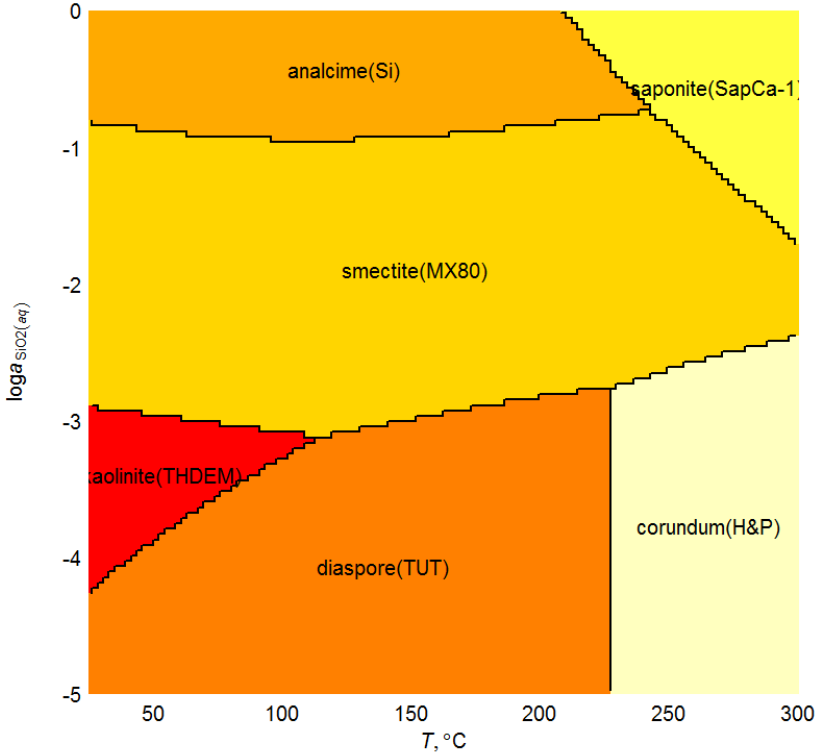
Application to Mineral-Fluid Equilibria (Clay system)



- **Construction of activity phase diagram using CHNOSZ**
- **Most recent clay thermodynamic data (Gailhanou et al., 2012, 2013; Blanc et al., 2006)**
- **Consistent with aqueous Al data from Tagirov & Schott (2001)**
- **Activity phase diagram:**
  - Fixed aqueous species activities based on speciation computed at high temperatures
  - Analysis of multiphase equilibrium topology with variable solution chemistry
  - Comparisons with experimental data
- **Serve as a tool for evaluation of thermal limits**
  - "sacrificial" domain in the clay buffer
  - Interpretation of experimental results

Ongoing Progress FY14

- **Selection of CHNOSZ software tool for thermodynamic data evaluation**
  - Open-source (developed in R language)
  - Computational and graphical capabilities
  - HKF EoS for aqueous species
  - EoS for water (SUPCRT92 and IAPWS-95)
  - Accepts standard thermodynamic parameters as inputs ($\Delta_f G°$, $\Delta_f H°$, S°, Cp coefficient data)
  - OBIGT thermodynamic database (organics)
- **Current Progress**
  - Evaluated and expanded thermodynamic data:
    - ***Solids: clays, analcime, Al hydroxides, Al silicates, Al_2O_3 (corundum)***
    - ***Aqueous "anchor" species : Al (Tagirov & Schott, 2001), $SiO_{2(aq)}$ (Rimstidt paradigm) – Consistent with recent work on thermodynamic database consistency (Tutolo et al. 2014)***
  - Evaluated consistency in key thermodynamic data
  - Comparisons with past and ongoing thermodynamic database development efforts: Thermochimie(ANDRA), Thermoddem (BRGM), Holland & Powell (2011), YMP

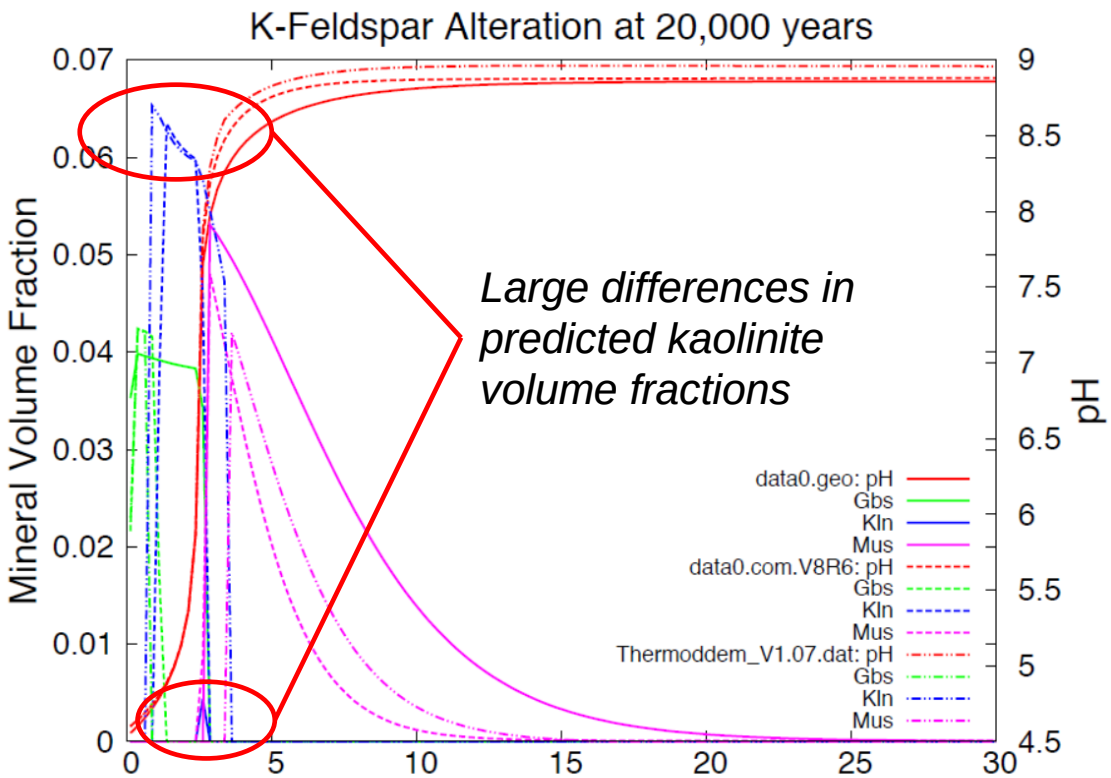


FY15 Outlook

- **Effects of redox conditions on clay phase stability**
  - Smectite(MX80) and illite(IMt-2) have Fe in their bulk composition
  - Need to evaluate compositional sensitivities (e.g., Mg, Fe, Ca) relative to idealized clay stoichiometries
- **Analysis and updates of thermodynamic data for phyllosilicates and other minerals (mentored by Tom Wolery)**
  - "deconstructing" extrapolation methodologies to high pressures and temperatures
    - *Revisit Helgeson et al. 1978 work with recent data updates*
  - Ensure high levels of data consistency
- **Make ties to the NEA thermodynamic database development and needs:**
  - Strong alignment with updates to NEA TDB ancillary data (not updated since 1992)
  - Relevant to cementitious materials database (e.g., seals interactions)
- **Development consistent with NEA TDB guidelines**
  - Uncertainty quantification
  - Benchmarking (example from the THEREDA effort)
  - Integration with other international thermodynamic database efforts (Thermochimie, Thermoddem)
  - Consistent with the UFD Data Management Plan and activities (e.g., Traceability, Transparency and Reproducibility (T^2R)

Backup Slides

Database Inconsistencies: Effects on Reactive Transport Modeling



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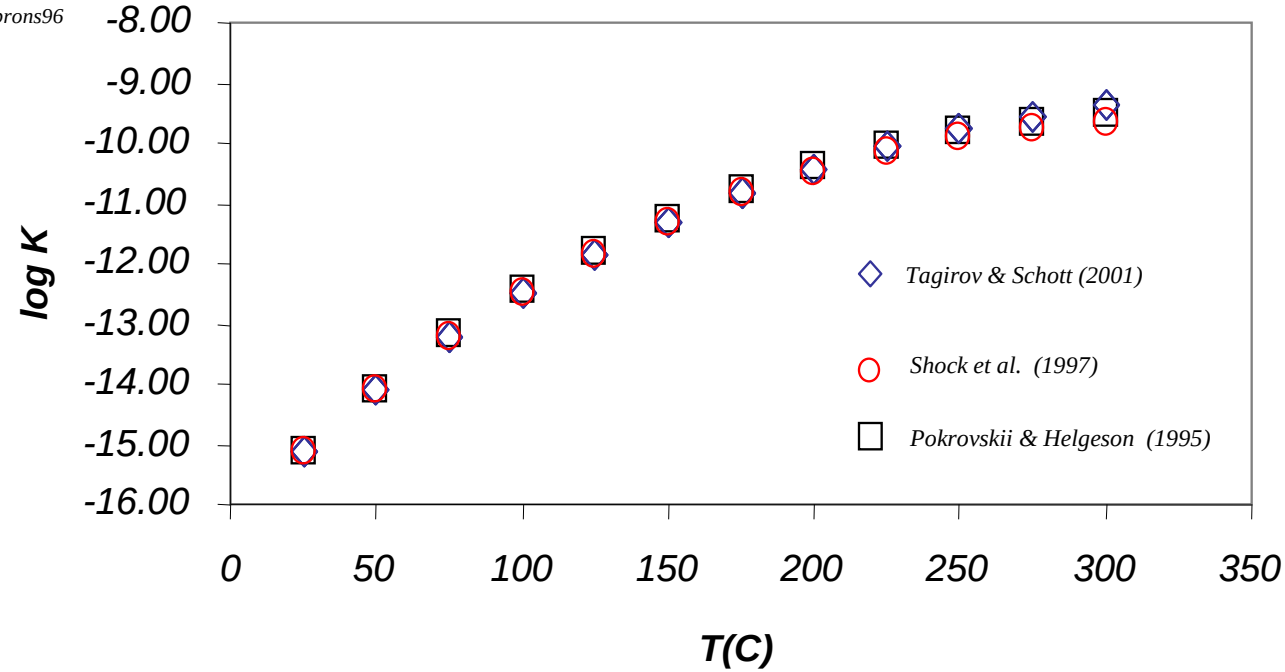
Al Database Comparison Gibbsite Solubility Along LVP

Gibbsite(Al(OH)3(cr) thermodynamic obtained from SUPCRT92 dprons96.dat database which is equivalent to that tabulated by Pokrovskii & Helgeson (1994).
H2O and H+ thermo data are also from SUPCRT92 dprons96 database.

Al(OH)3(cr) + H2O = Al(OH)4(-) + H+ (Tagirov & Schott 2001 notation.)
Al(OH)3(cr) = AlO2(-) + H+ + H2O in Pokrovskii & Helgeson (1995) and Shock et al. (1997) notation.



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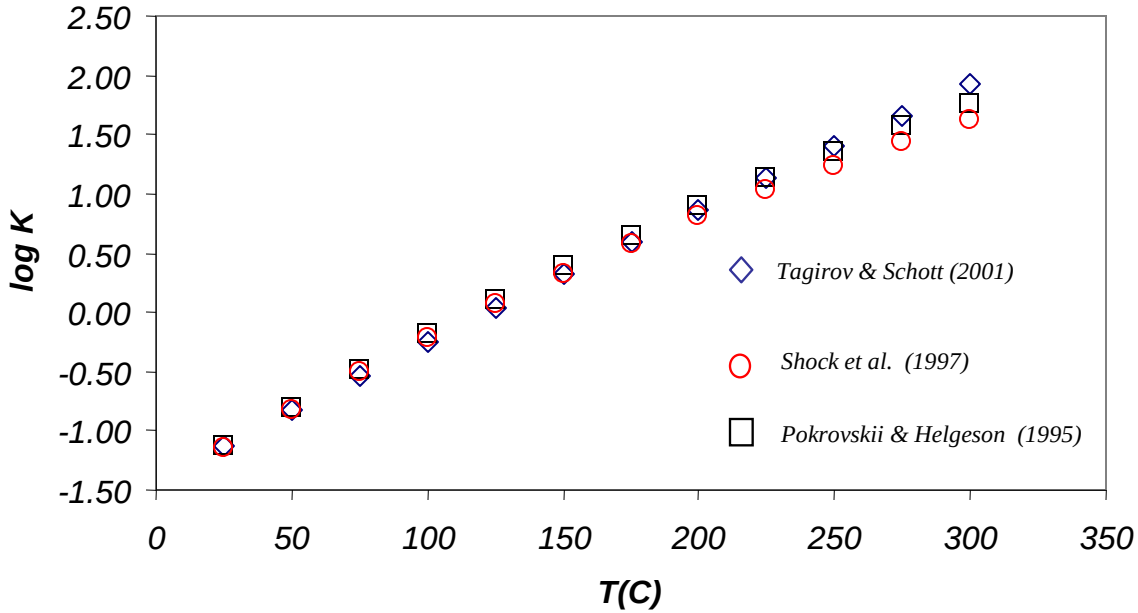

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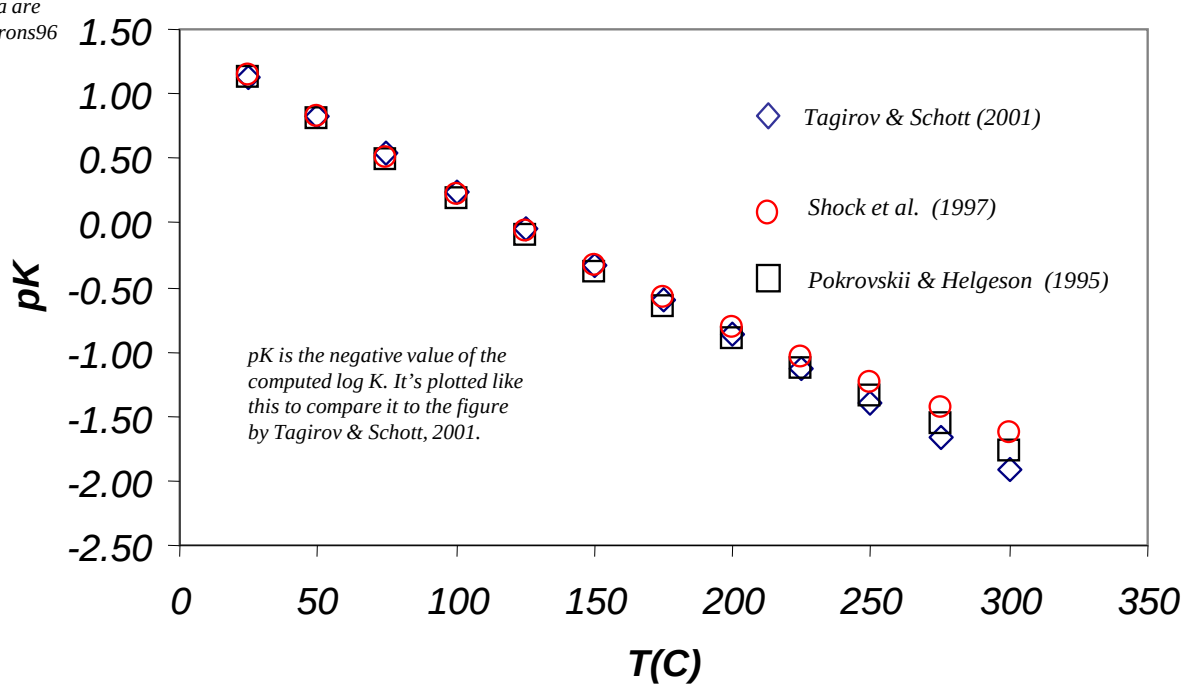

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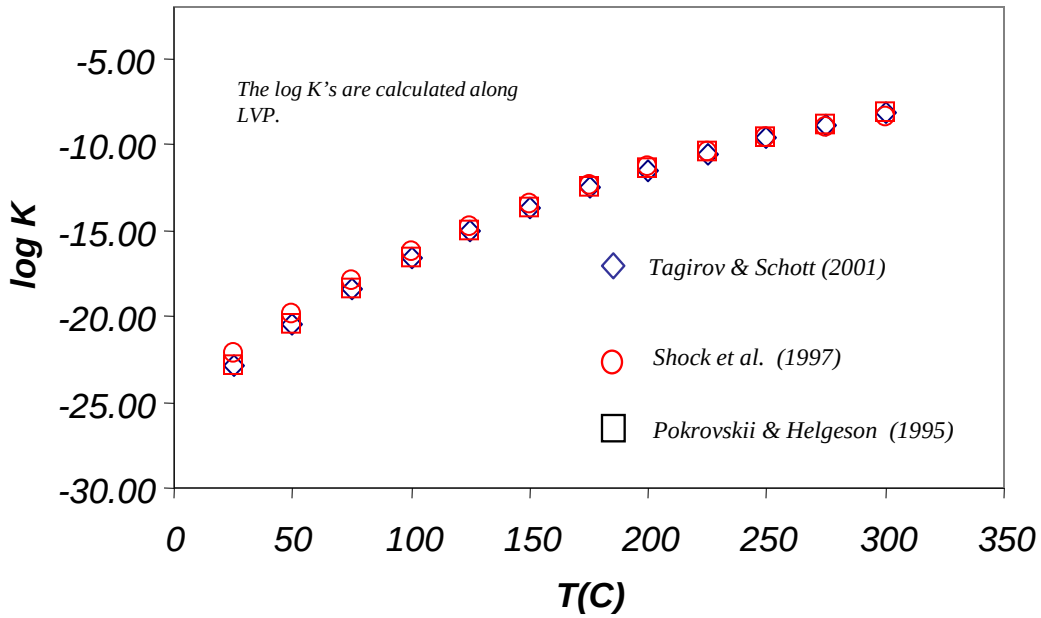
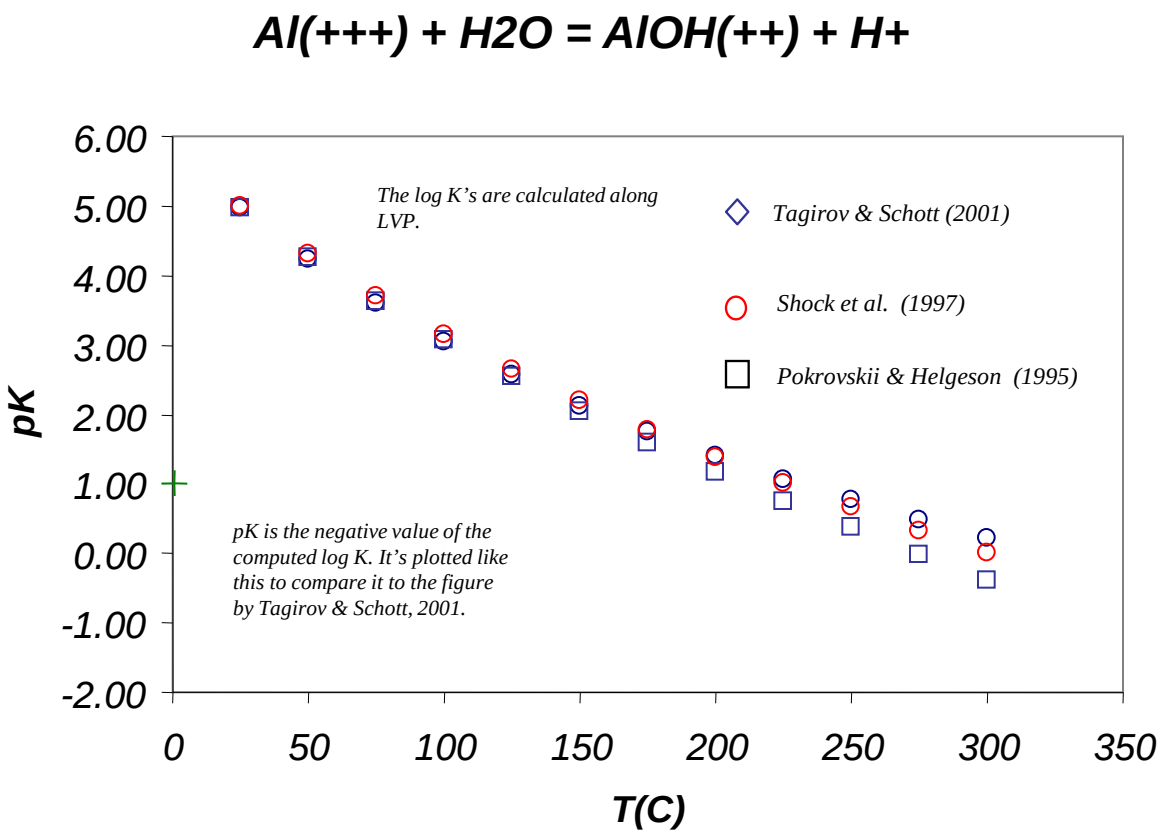
AlO_2^- and $Al(OH)_4^-$

Al(+++) + 4 H2O = Al(OH)4(-) + 4 H+ (Tagirov & Schott 2001 notation.)
Al(+++) + 2 H2O = AlO2(-) + 4 H+ in Pokrovskii & Helgeson (1995) and Shock et al. (1997) notation.



$Al^{+++} + H_2O = Al(OH)^{++} + H^+$


Al(+++) + H2O = AlOH(++) + H+
6.00
5.00
4.00
3.00
2.00
1.00
0.00
-1.00
-2.00
pK
0
50
100
150
200
250
300
350
T(C)
The log K's are calculated along LVP.
Tagirov & Schott (2001)
Shock et al. (1997)
Pokrovskii & Helgeson (1995)
pK is the negative value of the computed log K. It's plotted like this to compare it to the figure by Tagirov & Schott, 2001.

Quick Remarks

- In general, log K's seem to overlap closely and consistently (within the apparent uncertainty of the reported solubility data) at a temperature range of 25 to 150 °C. Sometimes the close overlap can extend to even higher T's for gibbsite solubility (see figures 1 - 3).
- Overall, the log K's seems to spread at high T's (> 200-250 ° C).
- There is a strong overlap between Tagirov & Schott (2001) and Pokrovskii & Helgeson (1995) in speciation reactions for the equivalent species AlO_2^- and $Al(OH)_4$- (see figure 4). However, there is some spread in the data (~0.6 log units) for AlO_2^- by Shock et al. (1997) at low T's (we already discusses this).
- Note: The gibbsite thermo data in the YMP0 database is from Helgeson et al, 1978. The most recent update by Pokrovskii & Helgeson (1995), which is in the dprons96 SUPCRT92 database, should be considered for solubility calculations using recent Al data. Visually, the log K's for the reaction Gibbsite + 3 H+ = Al3+ + 3H2O look different between YMP0 database and that calculated by Pokrovskii & Helgeson (1995).