SAND2014-4632P

Used Fuel Disposition Campaign

Thermodynamic database development: Al-silicate system at elevated temperatures

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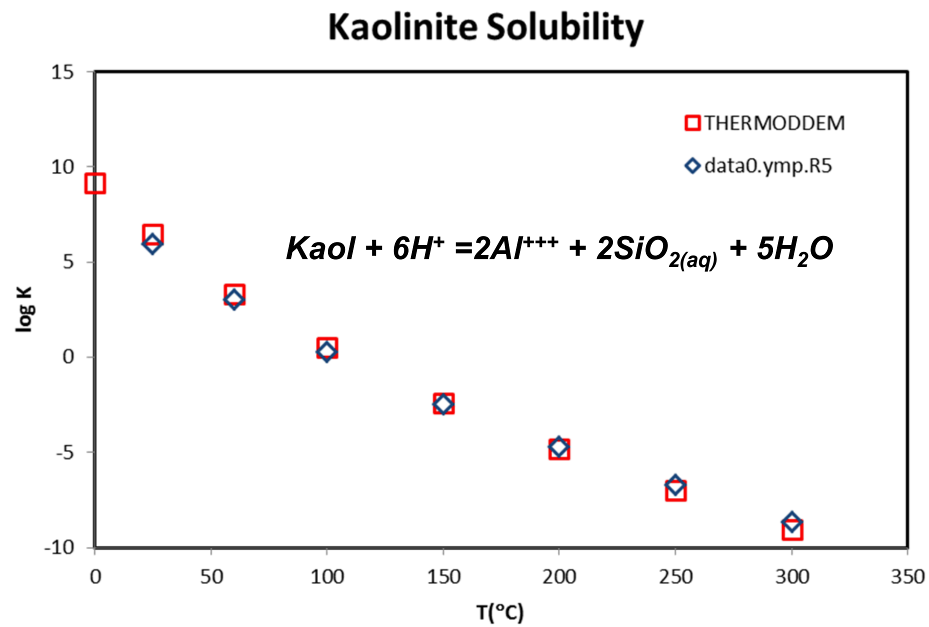
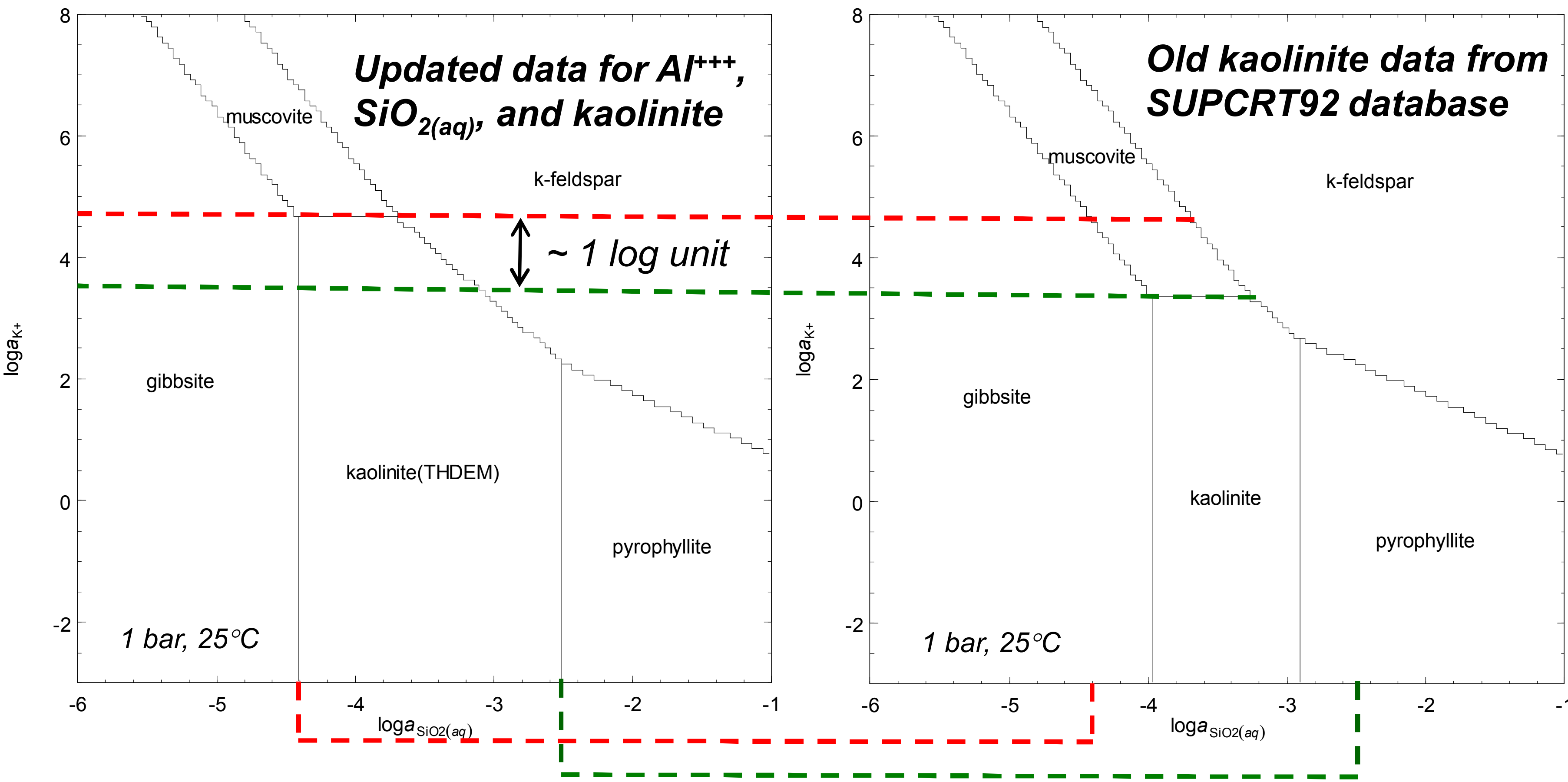
Thermodynamic Database Development: Al-silicate Systems

- **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

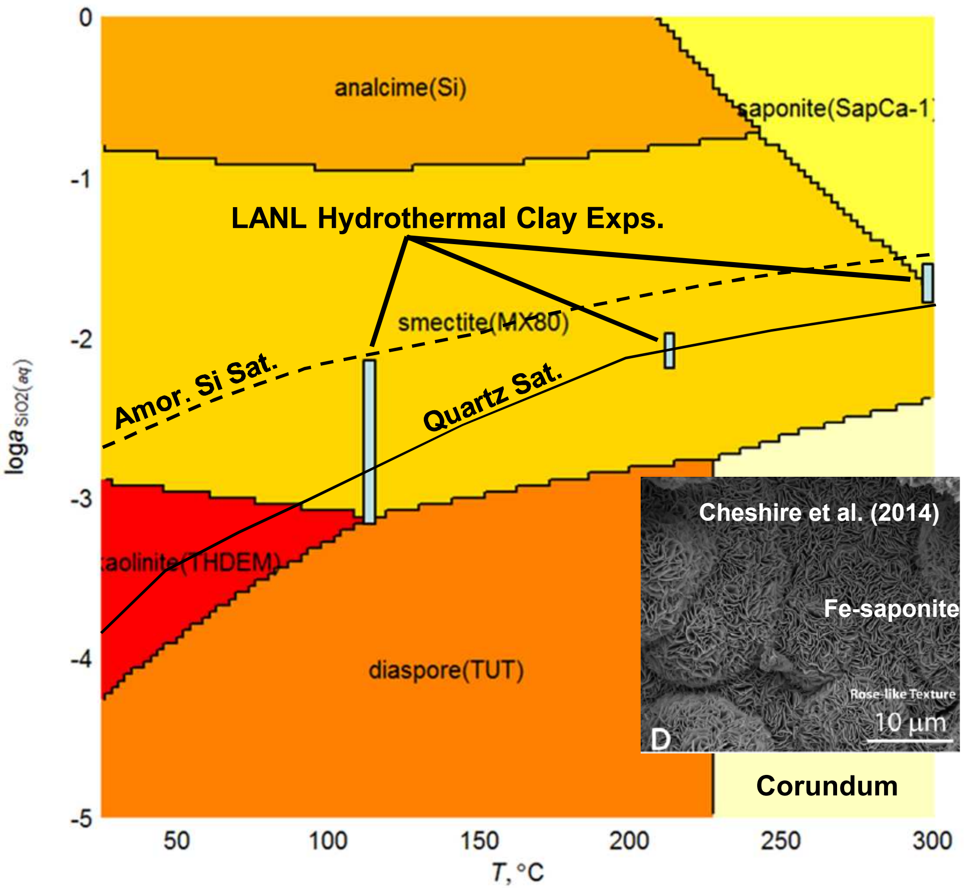


Potential Database Inconsistencies: Old vs. New: Why is this Important?

Database inconsistencies lead to shifts in kaolinite stability field



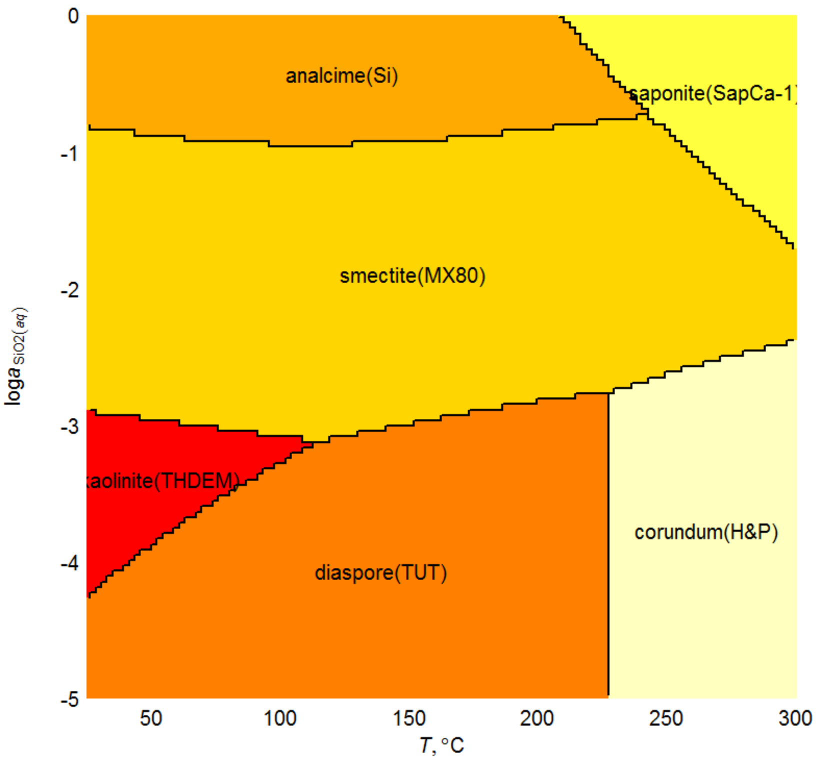
Application to Mineral-Fluid Equilibria (Clay system)



- **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



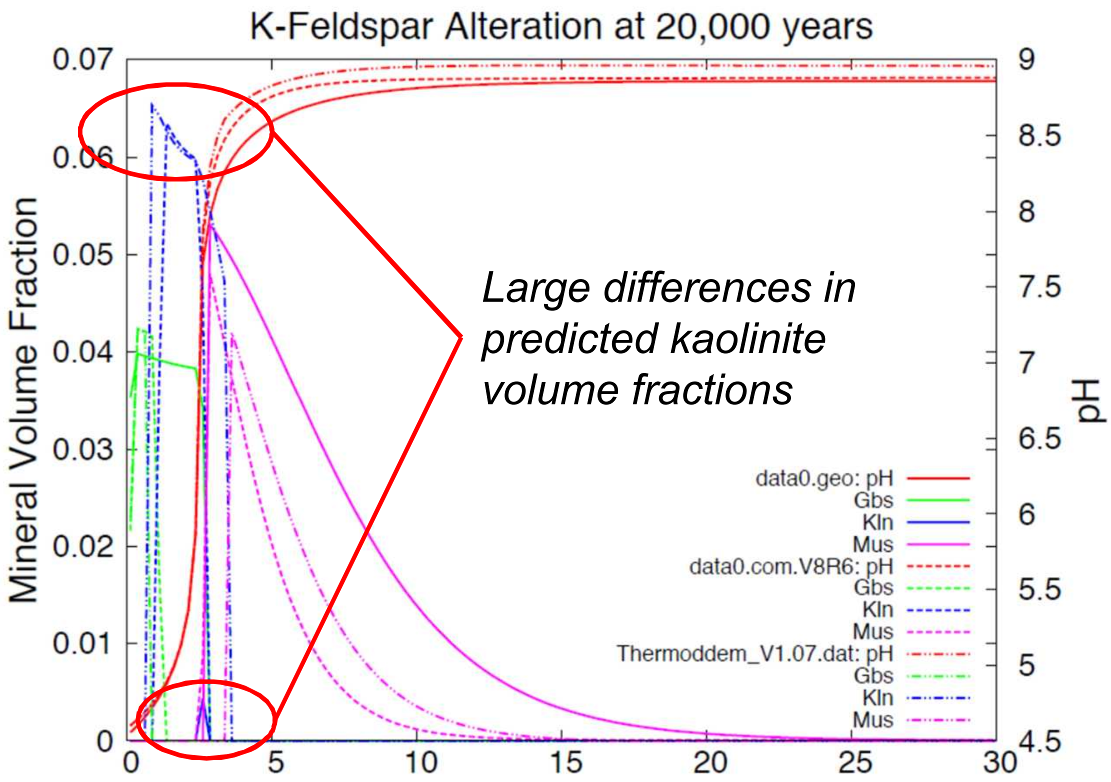
FY15 Outlook

- **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

Used Fuel Disposition

Database Inconsistencies: Effects on Reactive Transport Modeling



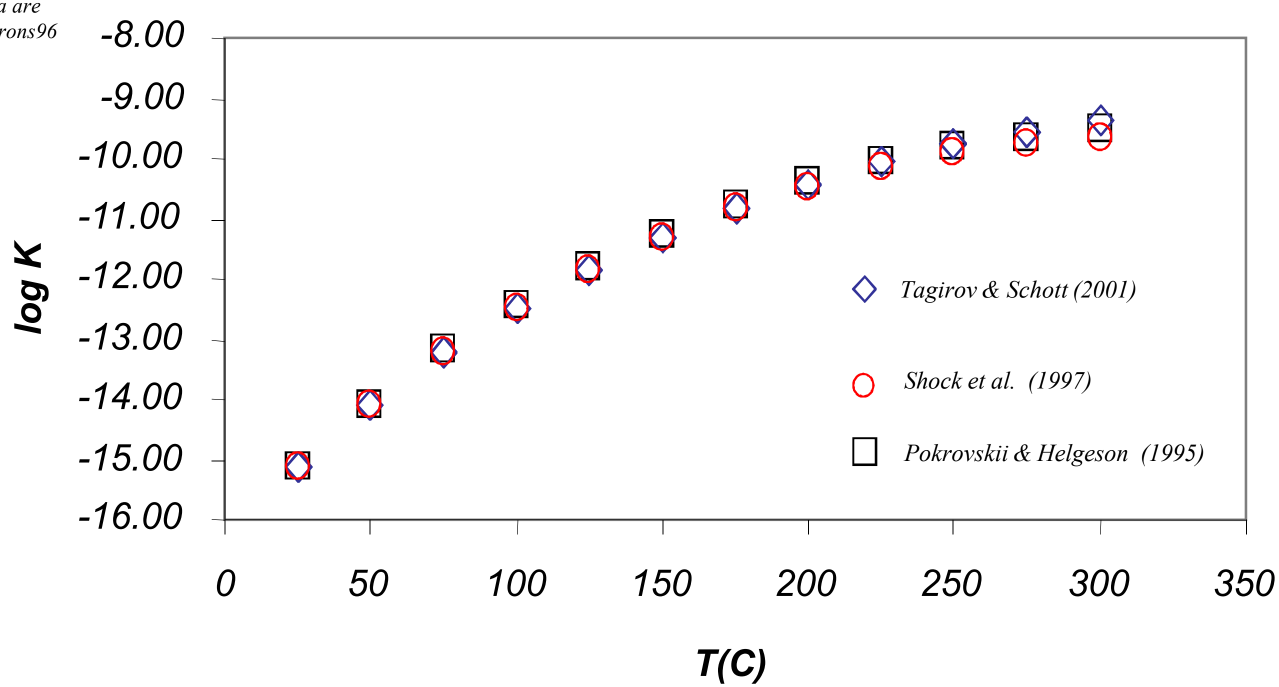
- **Reactive transport modeling:**
  - PFLOTRAN code problem for K-feldspar weathering to for a bauxite deposit
  - Differences between thermodynamic databases can affect predictions in mineral volume fractions

Code results courtesy of Dr. Peter Lichtner

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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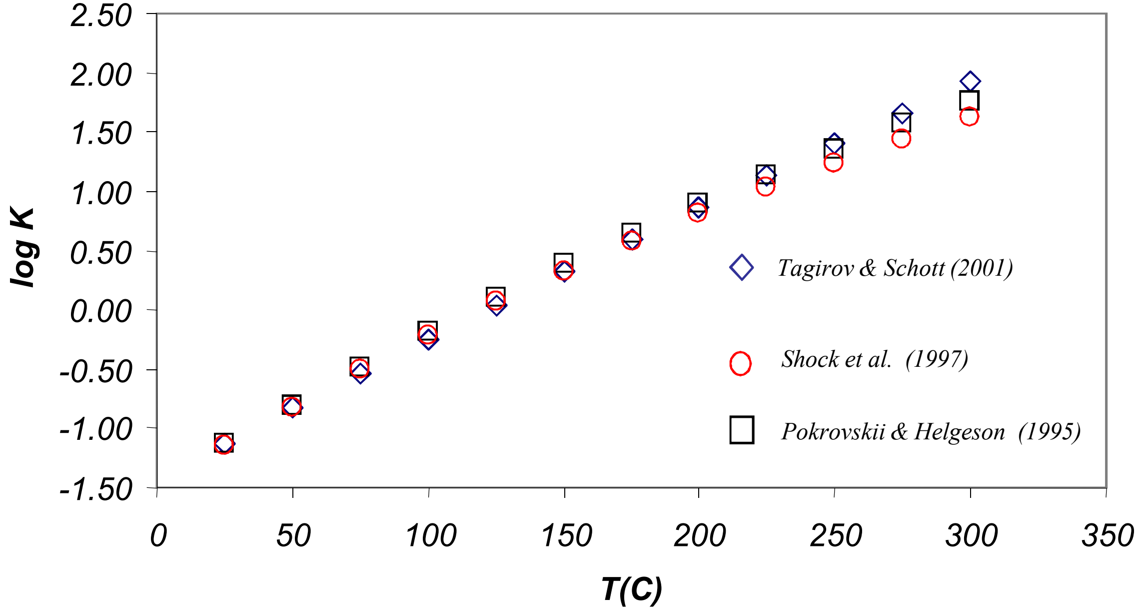

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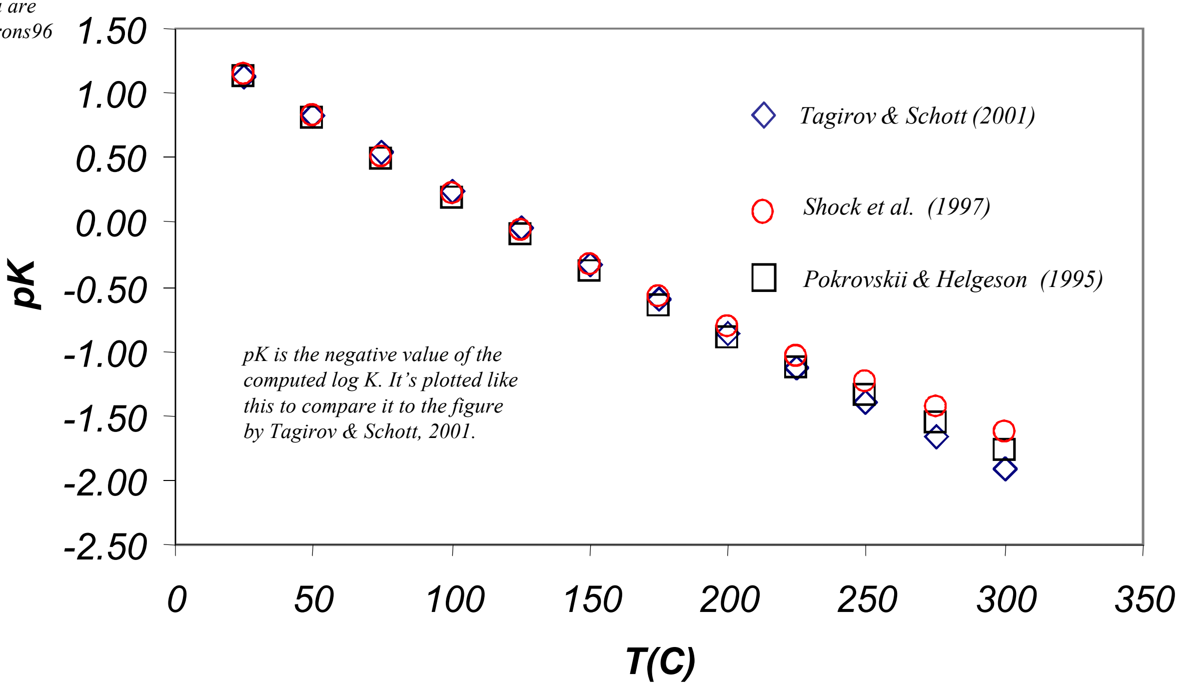
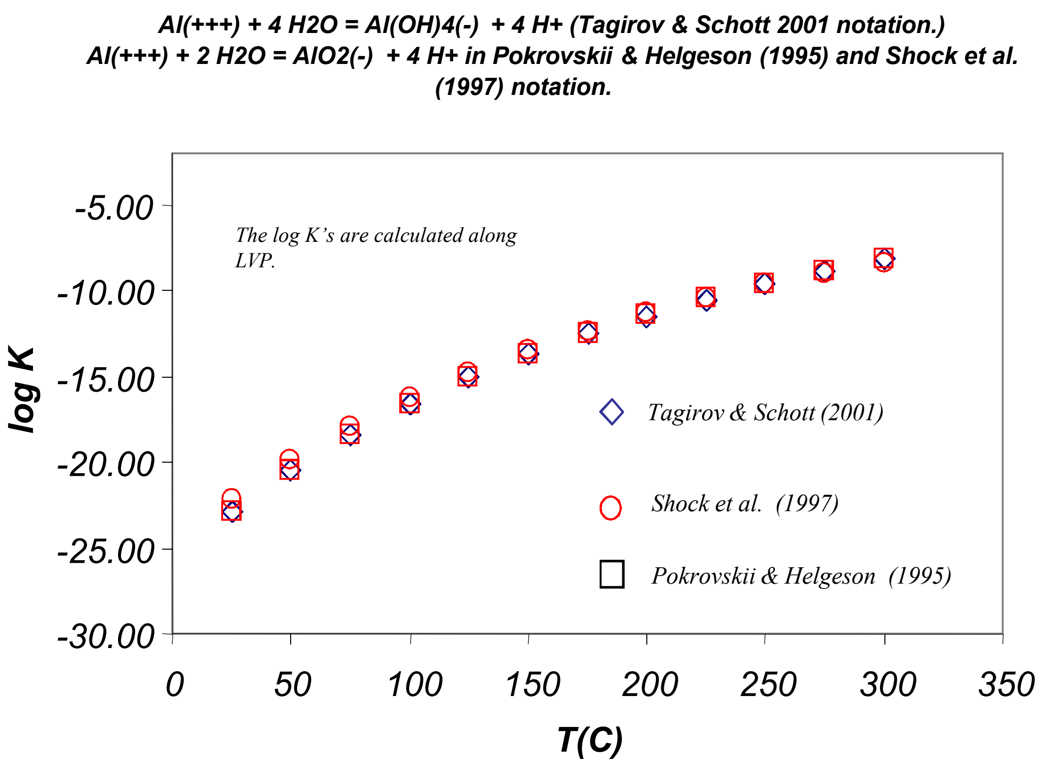


AlO_2^- and $Al(OH)_4^-$



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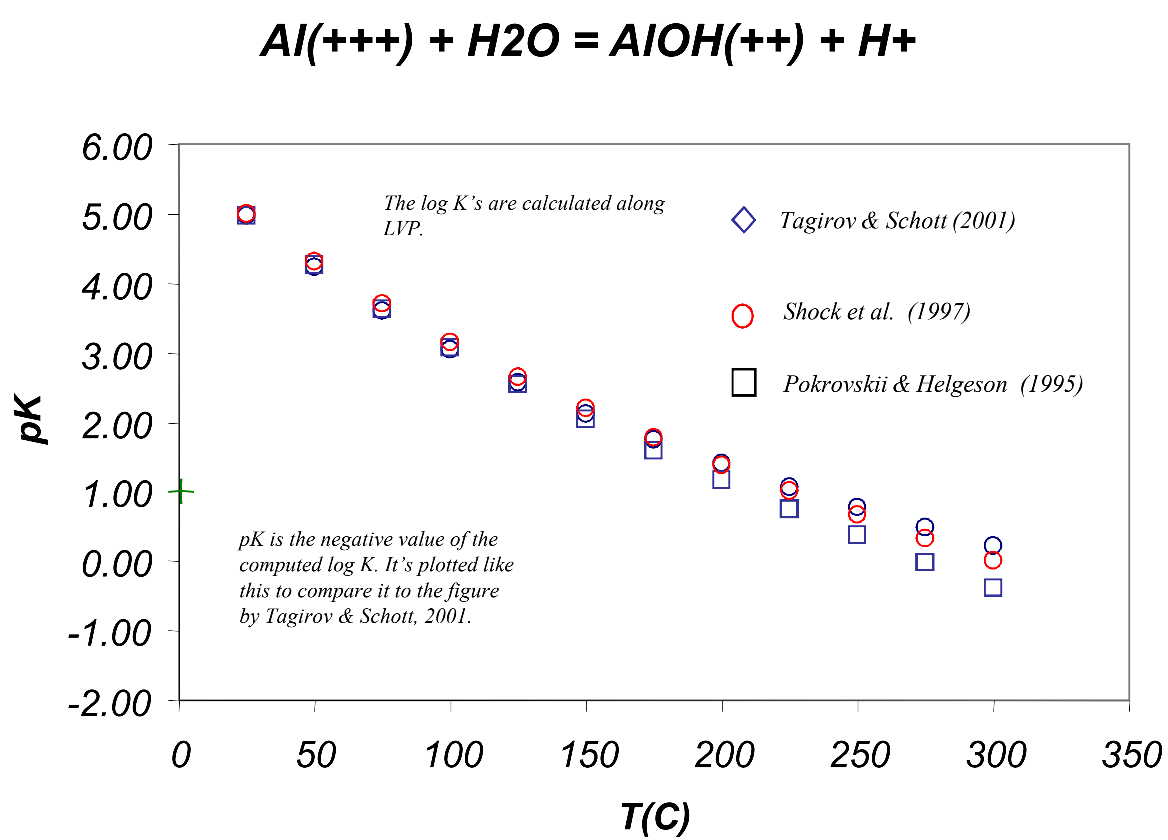
$Al^{+++} + H_2O = Al(OH)^{++} + H^+$


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).