Thermochemistry of Olivine

Gustavo Costa and Nathan Jacobson
NASA Glenn Research Center
Cleveland, OH
gustavo.costa@nasa.gov

Outline of Presentation

- Objectives
  - Measuring partial thermodynamic quantities by Knudsen Effusion Spectrometry (KEMS)
  - Component (MgO, SiO_2, FeO) thermodynamic activities in Olivine
- Thermochemistry of Olivine

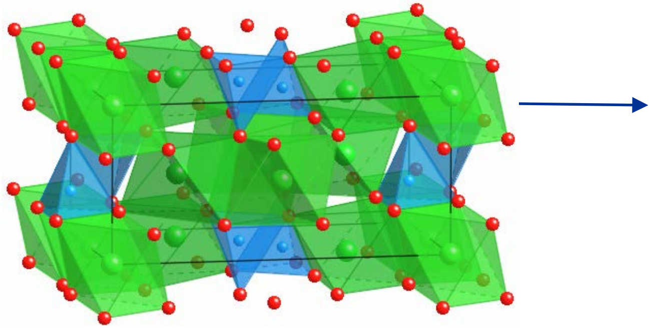
  Results for Olivine and Magnesia (reference material)
- Summary

Our Objectives

- Knudsen Effusion Mass Spectrometry of possible mineral assemblages to study the atmosphere of rocky, hot exoplanets
  - Olivine - Mg(g), Fe(g), SiO(g), O_2(g), O(g)
  - Silica - SiO(g), O_2(g), O(g)
  - Magnesia - MgO(g), O_2(g), O(g)
  - Magnetite and wüstite –FeO(g), O_2(g)

- Thermodynamic data
  - van't Hoff plot—ln(P) vs 1/T—gives ΔH and ΔS
  - Thermodynamic activities of SiO_2, FeO and MgO gives ΔG of olivine

Olivine: $(Fe_xMg_{1-x})_2SiO_4$, Orthorhombic symmetry (*Pbnm*)



- Red – O
- Blue – A sites, Si
- Green – B sites, Mg or Fe

Partial Thermodynamics Quantities: Activity and Vapor Pressure Measurement

Activity Pressure

M (s) = M (g)

Au(ℓ) = Au(g)

$\Delta_v H^o$ = -R*(-41.162) = 342.20 kJ/mol

Tables = 346.3 kJ/mol

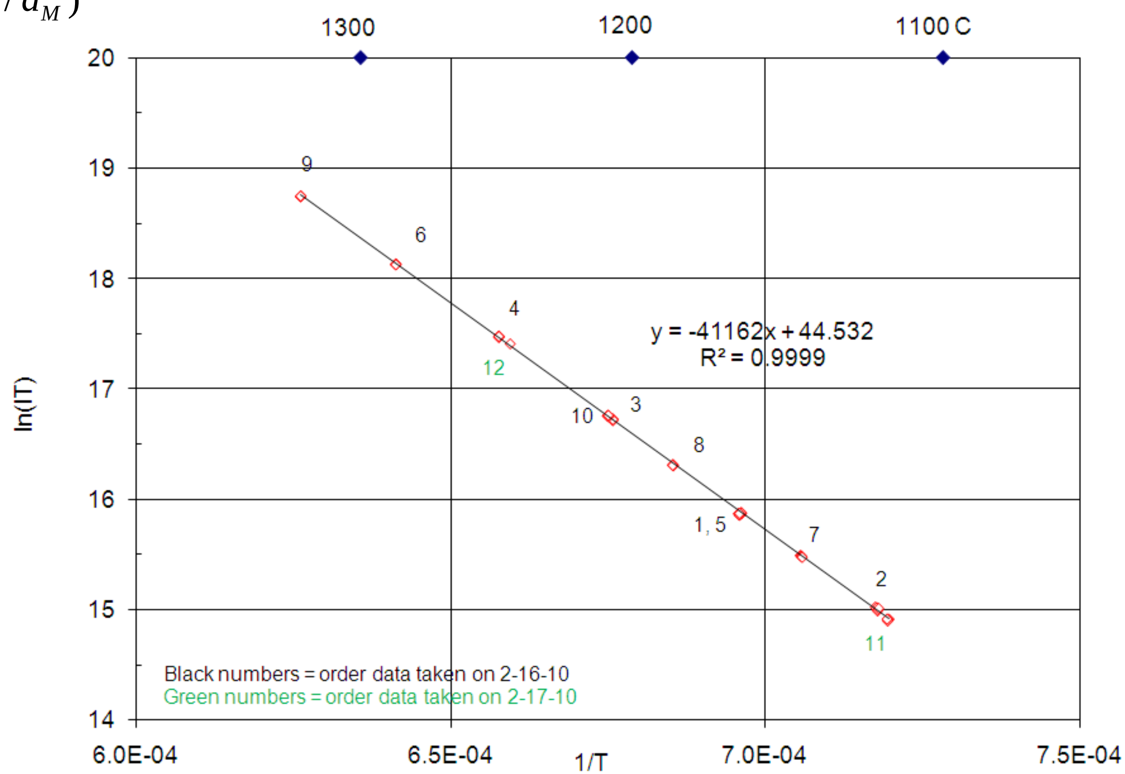
$$\Delta_v G = \Delta_v H - T\Delta_v S = -RT \ln K_p = -RT \ln(P_M / a_M)$$

$$a = \gamma \cdot C$$

$$\gamma = \text{activity coeficient; C = concentration}$$

$$\ln P_M = \frac{-\Delta_v H}{R}\left(\frac{1}{T}\right) + \frac{\Delta_v S}{R}$$

$\ln P_M$ vs 1/T is a van't Hoff plot with slope $= \frac{-\Delta_v H}{R}$



Mass Spectrometer $P_M = \frac{kIT}{\sigma}$

P_M = partial pressure of M;

k = instrument constant; I = ion intenisty;

T = Absolute temperature;

σ = ionization cross section

Thermodynamic Activities

- Important solution parameters
- Quantify how vapor pressure is reduced due to solution formation
- Example: Olivine—can treat as solution of FeO, MgO, SiO_2
- Use data to calculate thermodynamic activity of each component
- Measure thermodynamic parameters for olivine solutions
  - e.g. ln a(FeO) vs 1/T slope is partial molar enthalpy
  - Input to codes to model:
    - Atmospheres of hot, rocky exoplanets
    - Vapor over lava

Solutions: $A_{1-\alpha}B_{1-\beta}C_{1-\gamma}$
Same Phase; Variable Stoichiometry

$$\mathrm{FeO(s)} = \mathrm{Fe(g)} + 1/2\,\mathrm{O_2(g)}$$

$$\mathrm{K_p} = \frac{P^o_{Fe}[P^o_{O_2}]^{1/2}}{a_{FeO}} = \frac{P^o_{Fe}[P^o_{O_2}]^{1/2}}{1}$$

$$\mathrm{FeO(solution,\, a<1)} = \mathrm{Fe(g)} + 1/2\,\mathrm{O_2(g)}$$

$$\mathrm{K_p} = \frac{P_{Fe}[P_{O_2}]^{1/2}}{a_{FeO}}$$

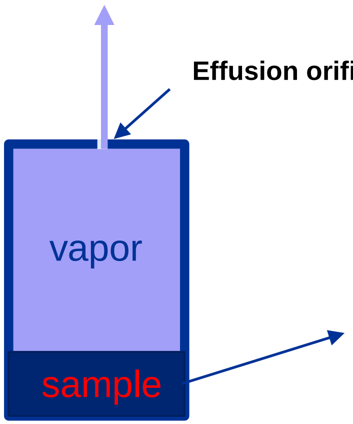
$$a_{FeO} = \frac{P_{Fe}[P_{O_2}]^{1/2}}{P^o_{Fe}[P^o_{O_2}]^{1/2}}$$

Thermodynamic Measurements

- Integral thermodynamic quantities:
  - Calorimetry (UC Davis)

- Partial thermodynamic quantities:
  - Oxidation-reduction equilibrium using gas mixtures
  - EMF methods
  - Mass Spectrometry (NASA Glenn)

Mass spectrometer: Intensity $\rightarrow$ Pressure $\rightarrow$ Activity

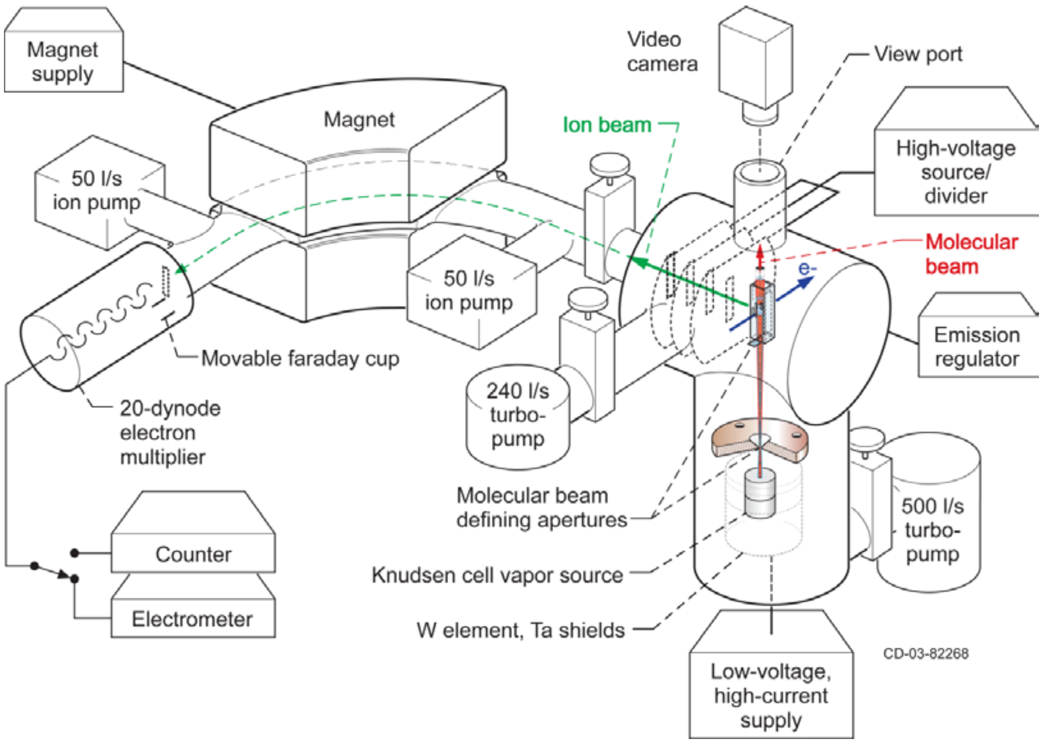


Exact approach depends on the system

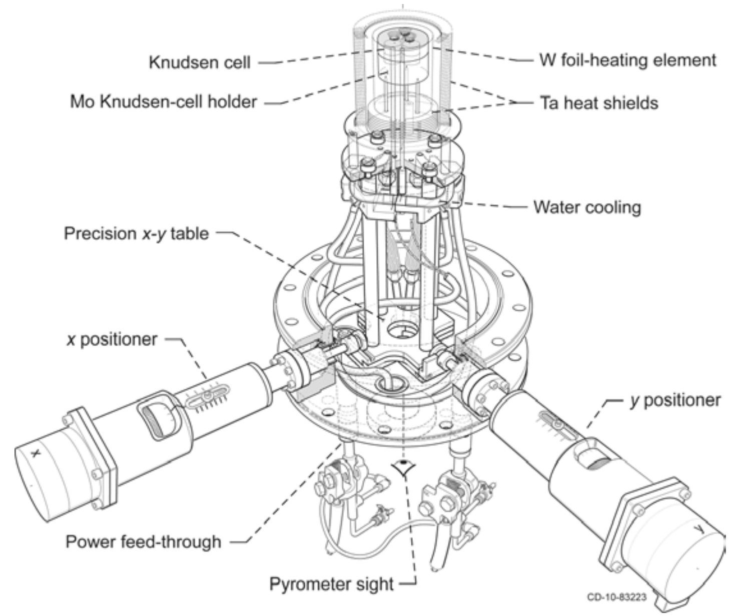
Olivine – Single cell configuration is used to attain higher temperatures

*A. I Zaitsev and B. M. Mogutnov, J Mater Chem 5, 1063 (1995)

Knudsen Effusion Mass Spectrometry (KEMS)

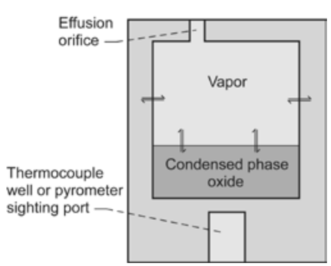


Use Multi-Cell Flange for a(SiO_2)



Design of E. Copland 2002

- 90° magnetic sector; non-magnetic ion source ion counting detector ⇒ no mass discrimination
- Cross axis electron impact ionizer
- Resistance heated cell; multiple Knudsen cell system
- Measurements to 2000°C, Pressure to 1 x 10^{-10} bar



$$p_i = k\, I_i^+ T / S_i$$

p_i = pressure of component i

k = instrument constant

T = Temperature (K)

S_i = ionization cross section

Olivine and Rare – Earth Silicates

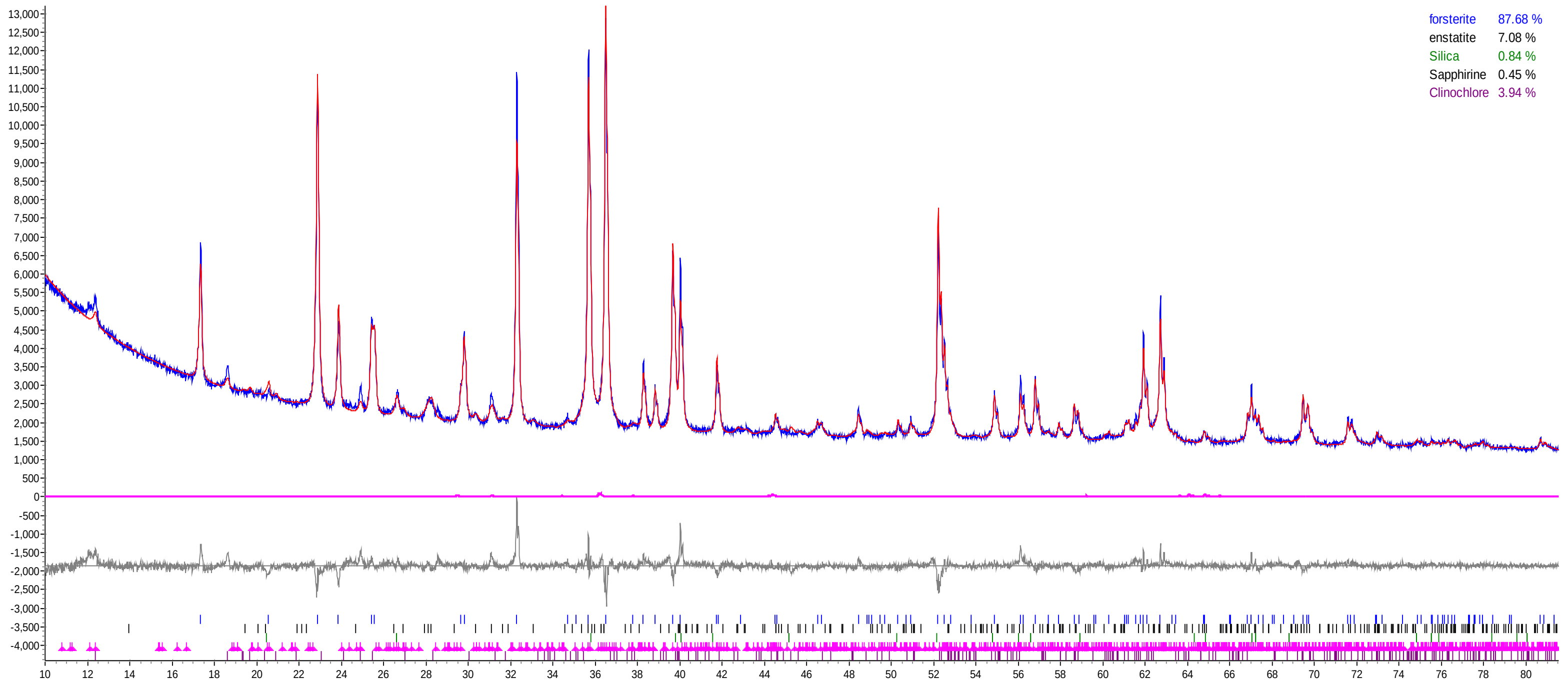
↑

Intensity → Pressure → Activity

Olivine - Results

Olivine – Starting Material and Characterization

93% forsterite and 7% fayalite, $Fo_{93}Fa_7$ - $(Fe_{0.7}Mg_{0.93})_2SiO_4$



XRD pattern and Rietveld refinement of the as received olivine samples.

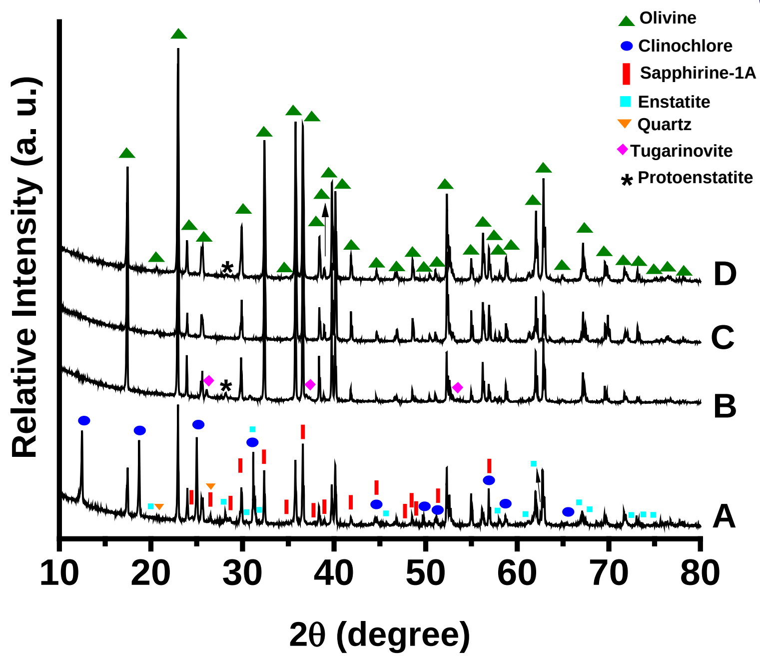
Phase content
- Forsterite – 87.7 ± 0.3%
- Enstatite – 7.1 ± 0.2%
- Silica – 0.84 ± 0.6%
- Sapphirine – 0.5 ± 0.1%
- Clinochlore – 3.9 ± 0.2%

ICP-OES analysis of the as received olivine samples.

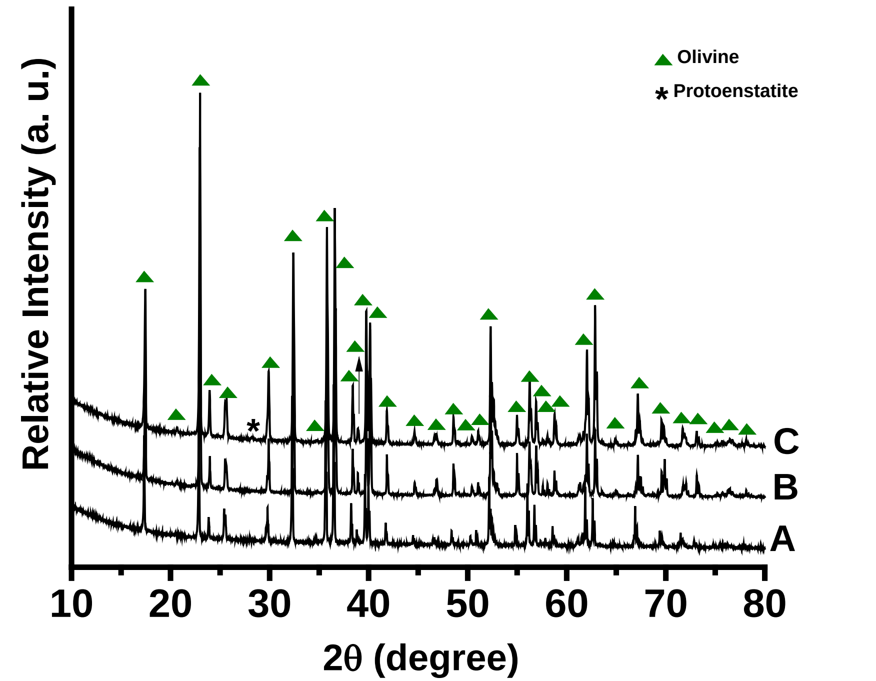
Element	*Wt (%)
Al	0.0120(6)
Ca	0.035(2)
Co	0.0120(6)
Cr	0.052(3)
Fe	5.01(3)
Mg	30(2)
Mn	0.075(4)
Na	0.0080(4)
Ni	0.27(1)
Sc	0.0040(2)
Si	20(1)

*Uncertainties of the analyses are given in parentheses.

Olivine – Impurities and Container Issues



XRD patterns of the olivine samples : (**A**) as received , (**B**) after KEMS up to 2084 K in a Mo Knudsen cell (**C**) after KEMS up to 1850 K in a Mo Knudsen cell (**D**) after KEMS up 2079 K in an Ir Knudsen cell.



XRD patterns of the olivine samples : (**A**) green sand from Hawaii, (**B**) after KEMS up to 1850 K in a Mo Knudsen cell (**C**) after KEMS up 2079 K in an Ir Knudsen cell.

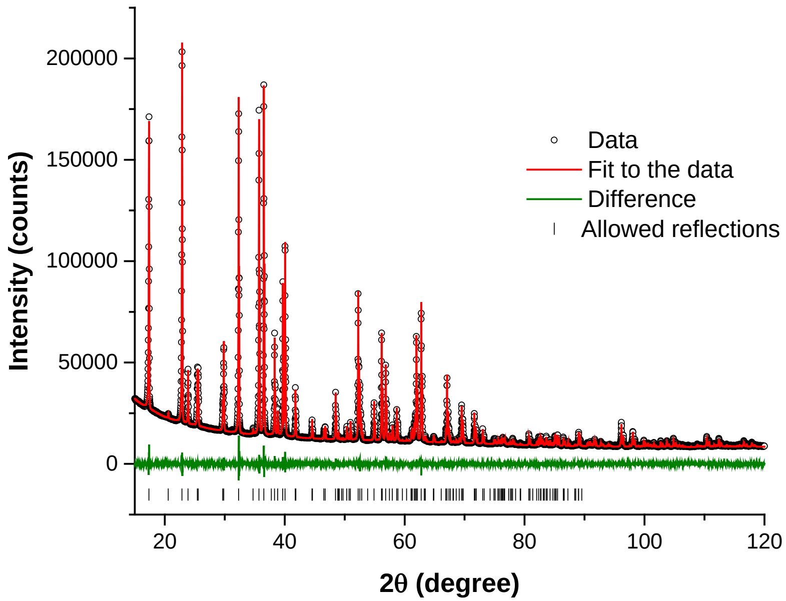
Chemical composition of the olivine powder samples $Fo_{93}Fa_7$ before and after KEMS up to 2084 K.

Element	Wt (%)		
	Sample as received[a]	After KEMS in a Mo cell	After KEMS in a Ir cell
Al	0.0120(6)	0.016(6)	0.2(1)
Ca	0.035(2)	0.009(2)	0.04(2)
Co	0.0120(6)	0.003(2)	0.004(3)
Cr	0.052(3)	0.035(4)	0.06(1)
Fe	**5.01(3)**	0.006(3)	**0.93(3)**
Mg	30(2)	35.0(1)	34(1)
Mn	0.075(4)	0.003(1)	0.031(3)
Na	0.0080(4)	-	-
Ni	0.27(1)	0.005(3)	0.006(3)
Sc	0.0040(2)	-	-
Si	20(1)	19.3(1)	21.8(8)
Mo	0	0.04(2)	0
Ir	0	0	0.06(3)

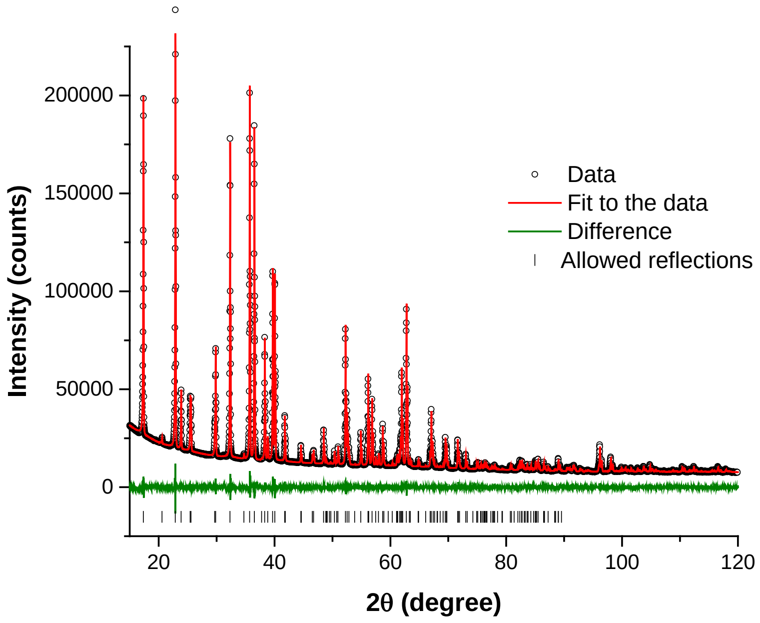
Side view (cross-section) of the Mo Knudsen cell containing the olivine sample heat treated up to 2084 K.

XRD Patterns (Rietveld Refinement) and Chemical Analysis

Sample heat treated in vacuum at 1580 °C for 10 h before KEMS



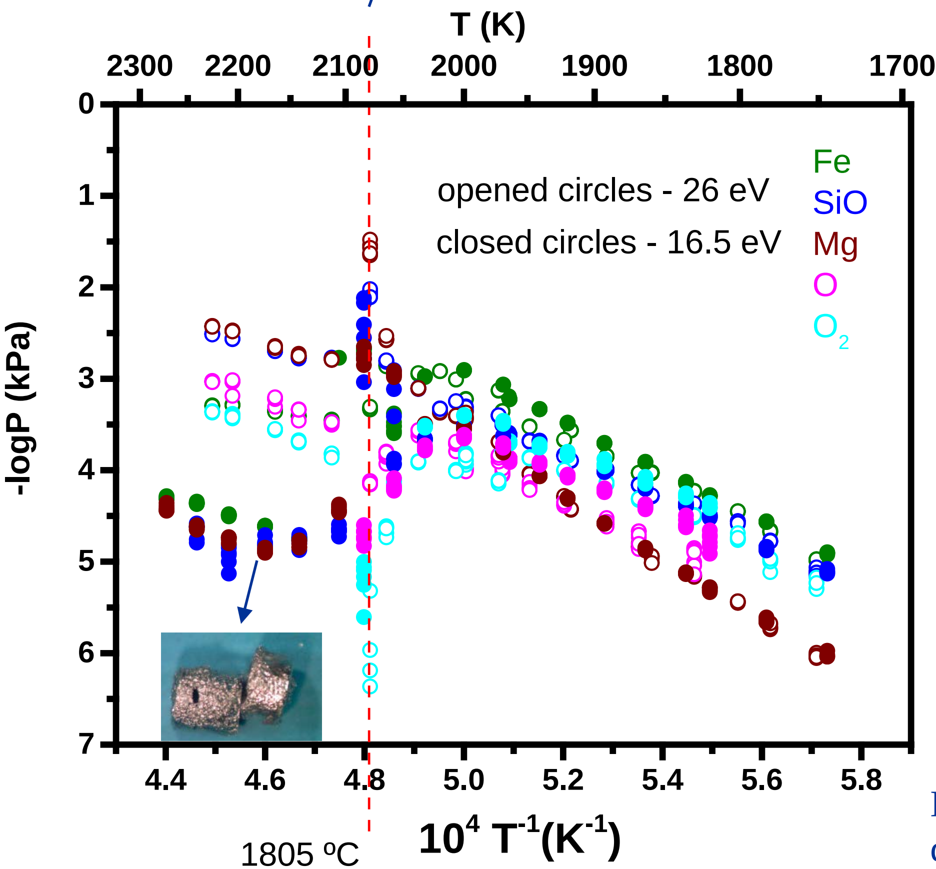
Sample after KEMS (below the melting point)

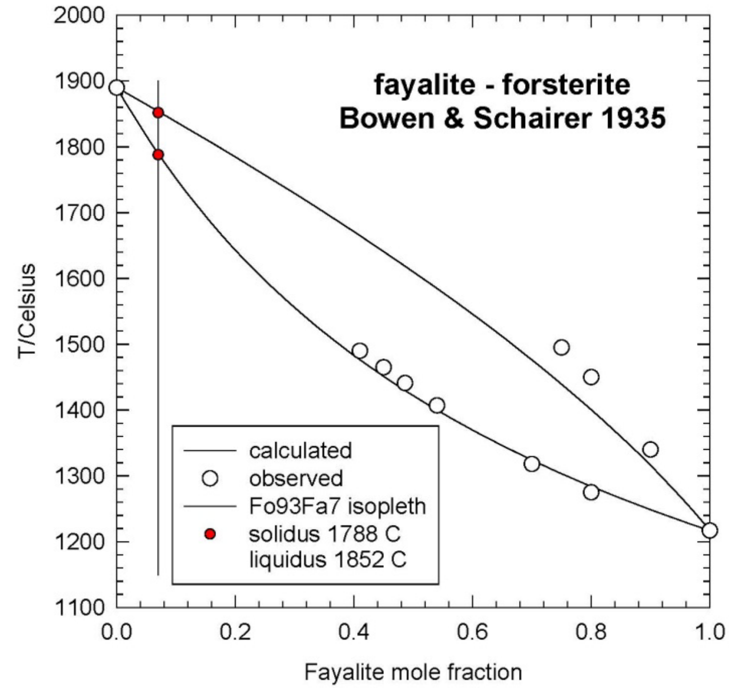


Element	Wt (%)		
	Sample as received[a]	Before KEMS "Heat treated"	After KEMS in a Ir cell
Al	0.0120(6)	0.018(9)	0.021(1)
Ca	0.035(2)	0.027(1)	0.028(1)
Co	0.0120(6)	0.0120(8)	0.005(3)
Cr	0.052(3)	0.015(1)	0.012(6)
Fe	**5.01(3)**	**3.6(2)**	**2.94(1)**
Mg	30(2)	30(2)	32(2)
Mn	0.075(4)	0.073(4)	0.068(3)
Na	0.0080(4)	0	0
Ni	0.27(1)	0.10(1)	0.020(1)
Sc	0.0040(2)	0	0
Si	20(1)	17(1)	17(1)

Complete van't Hoff Plot

Interesting discontinuity at melting





Fegley and Osborne, "Practical Chemical Thermodynamics For Geoscientists, Elsevier 2013, Fig. 12-11.

Measurements show good agreement with the phase diagram calculated by Bowen and Shairer.

Temperature dependence of ion intensity ratios of Mg^+, Fe^+, SiO^+, O^+ and O_2^+ in the olivine sample.

N. L. Bowen and J. F. Schairer, Am. J. Sci. 29, 151-171 (1935).

At 16.5 eV - low energy minimize O_2 dissociation!

Issues with KEMS Thermodynamic Measurements of Olivine

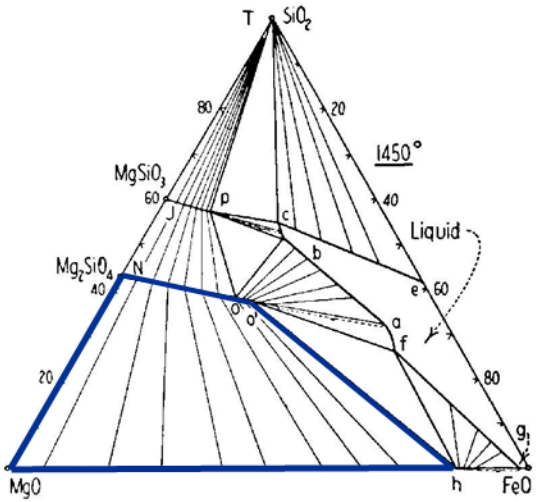
- Find high melting, 'inert' container material
  - Silicates are very reactive
  - No inert materials at high temperatures!
    - Mo very reactive
    - Pt melts
    - Ir—less reactive, but still issues with some forms of Ir above mp of olivine

- Measuring O_2, O
  - Separate from background—good pumping, use shutter
  - Low ionizing electron energy

  Want $O_2 + e^- = O_2^+ + 2e^-$ Avoid $O_2 + e^- = O + O^+ + 2e^-$
  - Trade-off—low ionizing electron energy gives

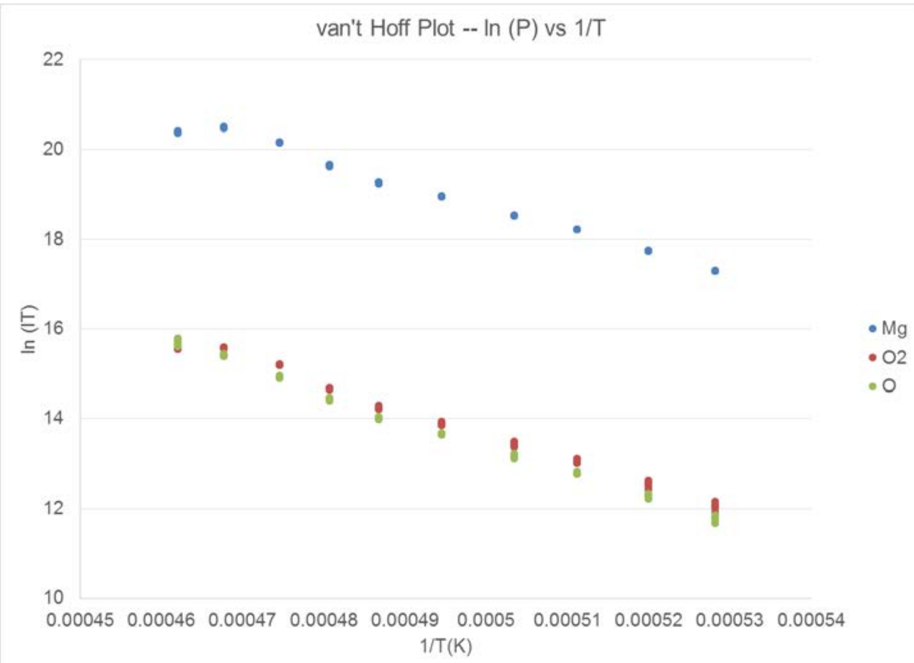
  weaker signals

- Need thermodynamically defined system
  - MgO + Olivine or SiO_2 + Olivine or FeO + Olivine
  - How to measure FeO as a reference?

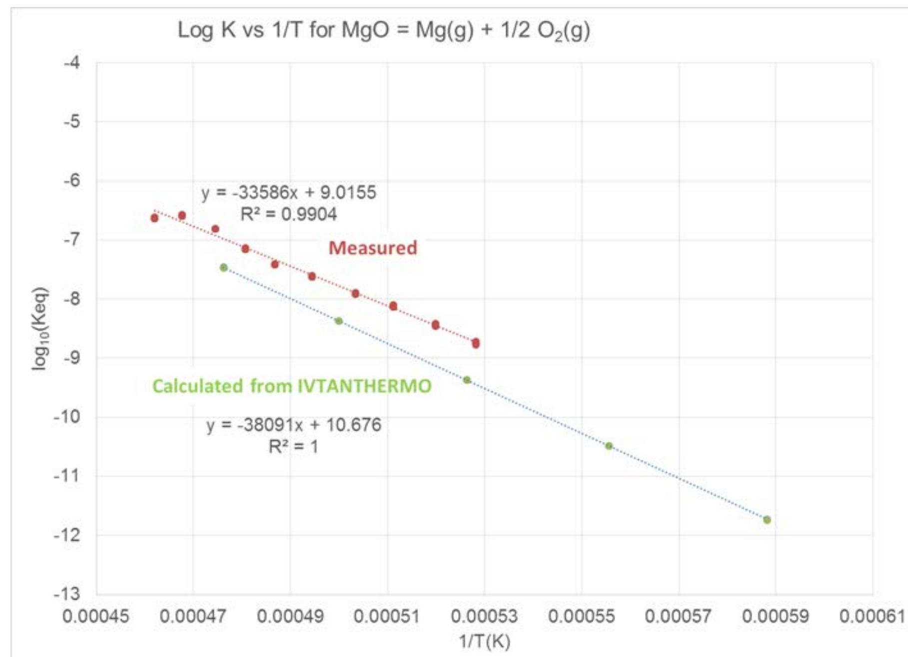


Initial Data – MgO as a Reference Material

Raw Data

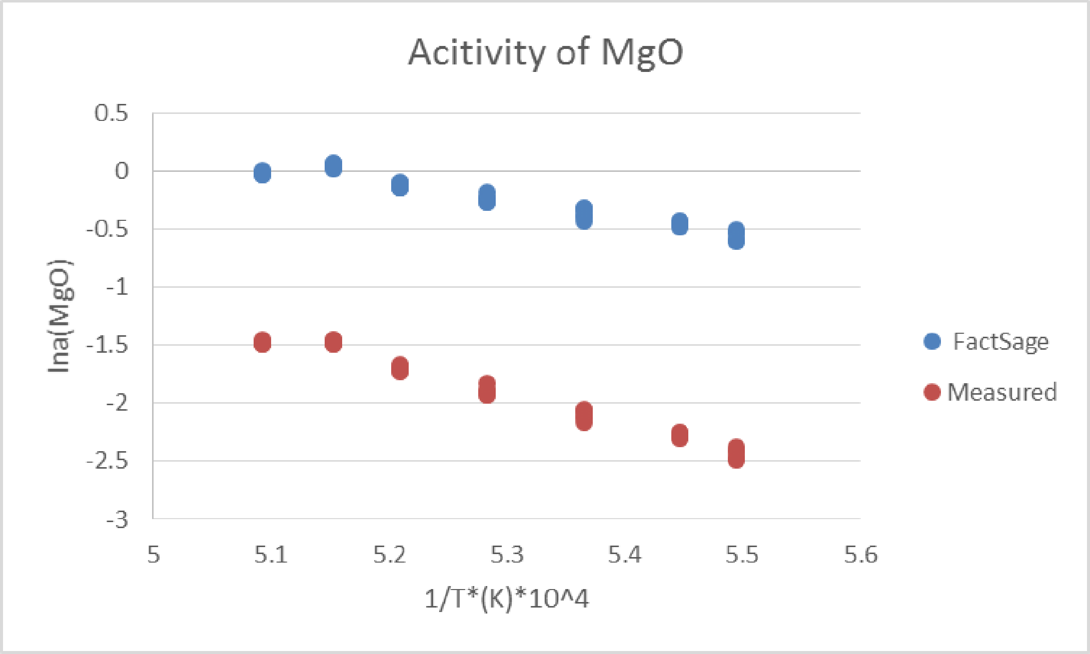


Keq from the partial pressures of Mg(g) and O_2 (g)



Plan to get data for SiO_2, FeO reference material data

Thermodynamic Activities in Olivine - $(Fe_xMg_{1-x})_2SiO_4$
This Olivine Appears to have Excess SiO_2



$MO_{(solution,\ a<1)} = M_{(g)} + 1/2O_{2(g)}$

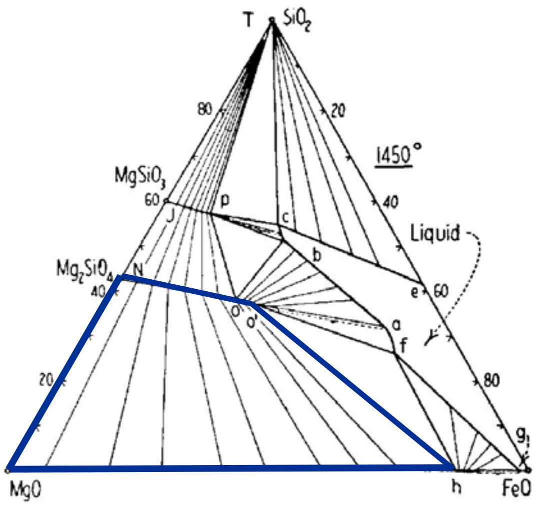
$$K_p = \frac{P_M[P_{O_2}]^{1/2}}{a_{FeO}}$$

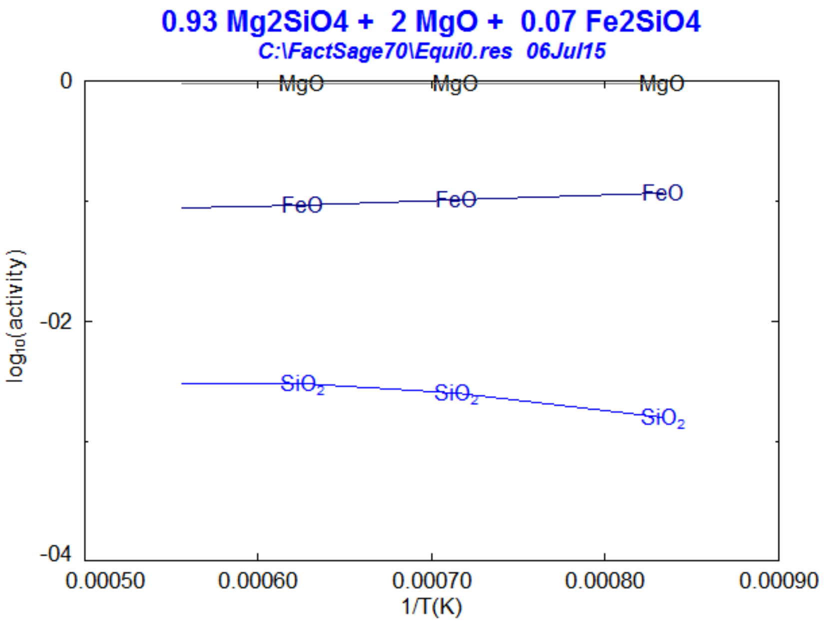
Fe, Mg or Si

$$a_{MO} = \frac{P_M[P_{O_2}]^{1/2}}{P_M^o[P_{O_2}^o]^{1/2}}$$

From FactSage or measured by KEMS

Computational Modeling of Olivine: Use FactSage Code with Sublattice model for Olivine





Two phase region

- Use excess MgO—set a(MgO) = 1
- Measure a(SiO_2), a(FeO)
  - Need to determine how to measure a(FeO)—reference as (Fe/FeO) or (FeO/Fe_3O_4)?

Summary

Previous Results presented on August 2014

- Secondary phases of the olivine sample were removed at temperatures > 1060 °C.
- Mo and Re cell reacts with olivine sample. Ir must be used
- The main vapor species of the olivine sample are Fe^+, SiO^+, O_2^+, O^+ and Mg^+ following this order of vaporization.
- The melting point of the olivine sample was determined by the ion intensity discontinuity to be 1805 °C.
- Temperature dependence of partial pressures of the species were determined.

New Results

- Temperature dependence of the activity of MgO was determined.
- Method developed for O_2, O measurements
- Extending methods to obtain consistent solution thermodynamic data for olivine

Next Steps

- KEMS measurements of SiO_2, Fe_2O_3-FeO or FeO/Fe and MgO-Olivine