

Synchrotron X-ray Diffraction Studies of Metal-Oxide Pairs

Greg Shofner
University of Maryland

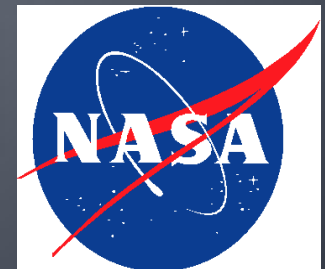
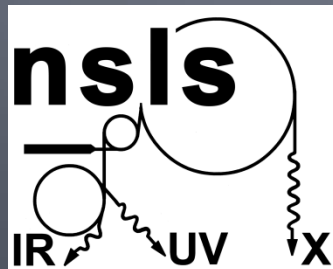
Andrew Campbell – Univ. Maryland

Lisa Danielson – NASA-JSC

Kevin Righter– NASA-JSC

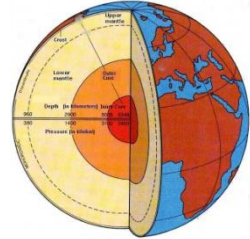
Yanbin Wang – GSECARS, APS

Jingzhu Hu - X17C, NSLS



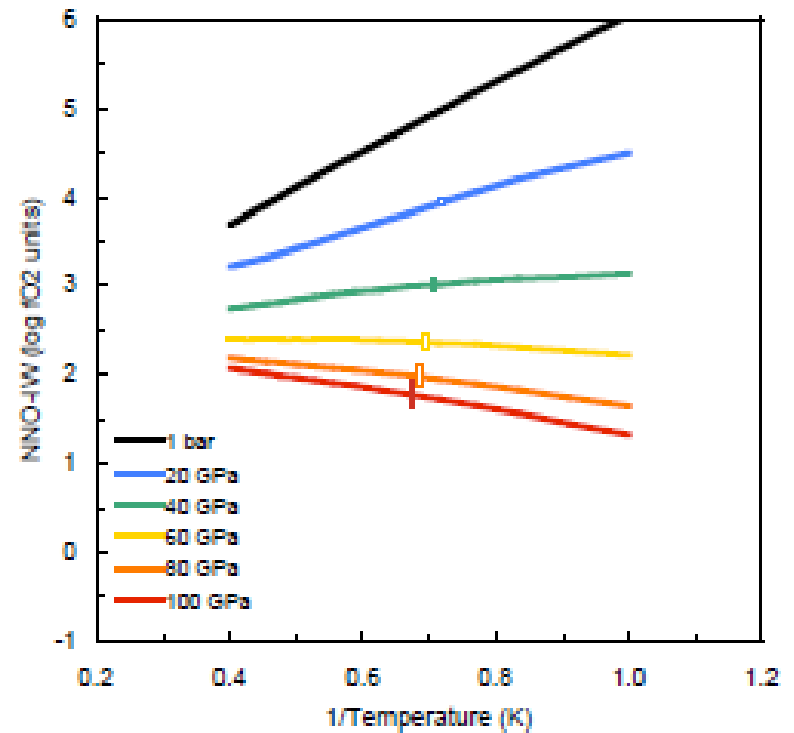
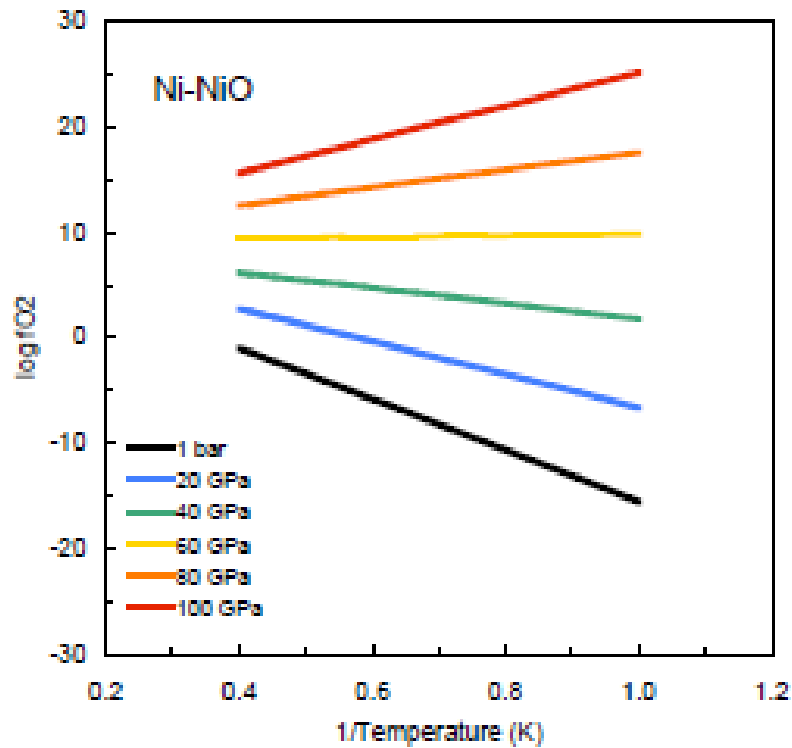
Background

- Why study metal-oxide pairs?
 - Both phases under same experimental conditions
 - Increased precision for equilibrium calculations (e.g. fO_2)
- Oxygen fugacity (fO_2) an important thermodynamic parameter
 - Multivalent phase equilibria
 - Partitioning of redox-sensitive elements
- fO_2 buffers
 - Control and measure fO_2 in high-P,T experiments
 - Basis for understanding partitioning in natural systems
- How do buffers change with increasing pressure?



Previous Work

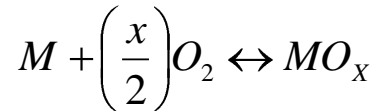
Ni-NiO Buffer



from Campbell et al. (Submitted)

Constructing fO_2 Buffers

Thermodynamics of a metal-oxide reaction:



$$G_{MO_x} = G_M + \frac{x}{2}G_{O_2}$$

$$G_{MO_x} = G_M + \frac{x}{2}RT \ln fO_2$$

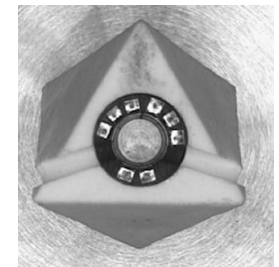
Along any isotherm, at some pressure P:

$$G_{MO_x} - G_M = \Delta G = \frac{x}{2}RT \ln fO_2 = \Delta G_0 + \int_{P=1bar}^P \Delta V dP \quad \leftarrow \text{Need } \Delta V$$

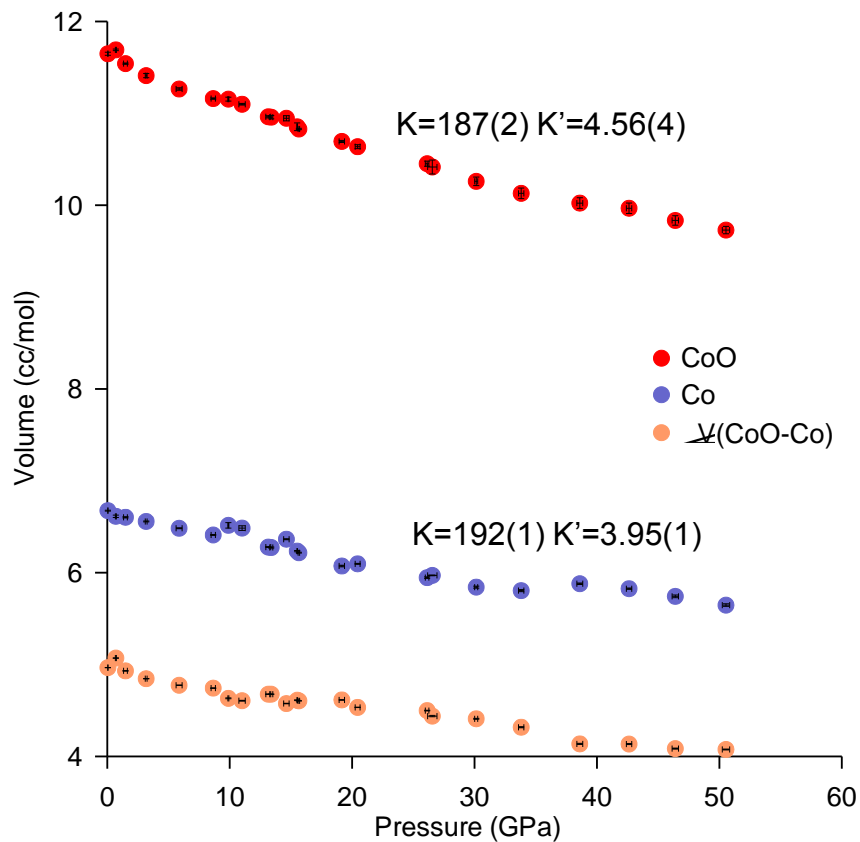
$$\log fO_2 = \log fO_2(1bar) + \left(\frac{0.8686}{RT}\right) \int \Delta V dP \quad \leftarrow \text{Need } \Delta V$$

Experiments

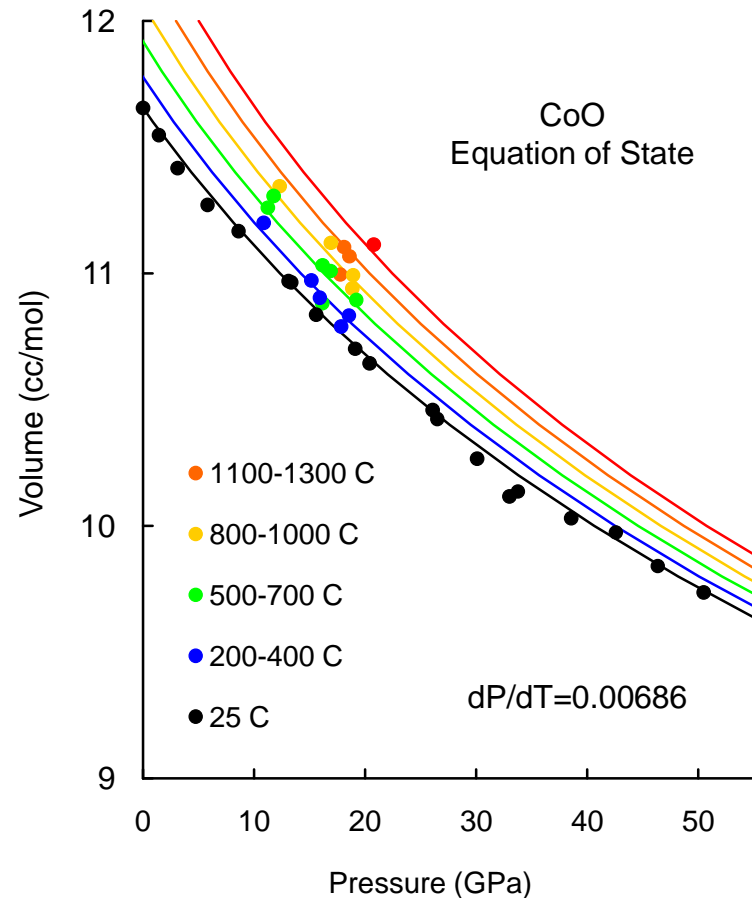
- Synchrotron XRD (Co and Cr)
 - Unit-cell volumes of individual phases
 - determine EOS
 - ΔV between metal and oxide phases
 - construct fO_2 buffers
- DAC experiments at X17C, NSLS
 - High-P, room-T; Pt pressure calibrant
 - Argon, silicone oil pressure media
- MAP experiments at 13-ID-D, APS
 - High-P,T; NaCl and MgO pressure calibrants
 - COMPRES 10/5 assembly (ASU)
- MAP and DAC data have overlapping pressure ranges



Co, CoO Equations of State

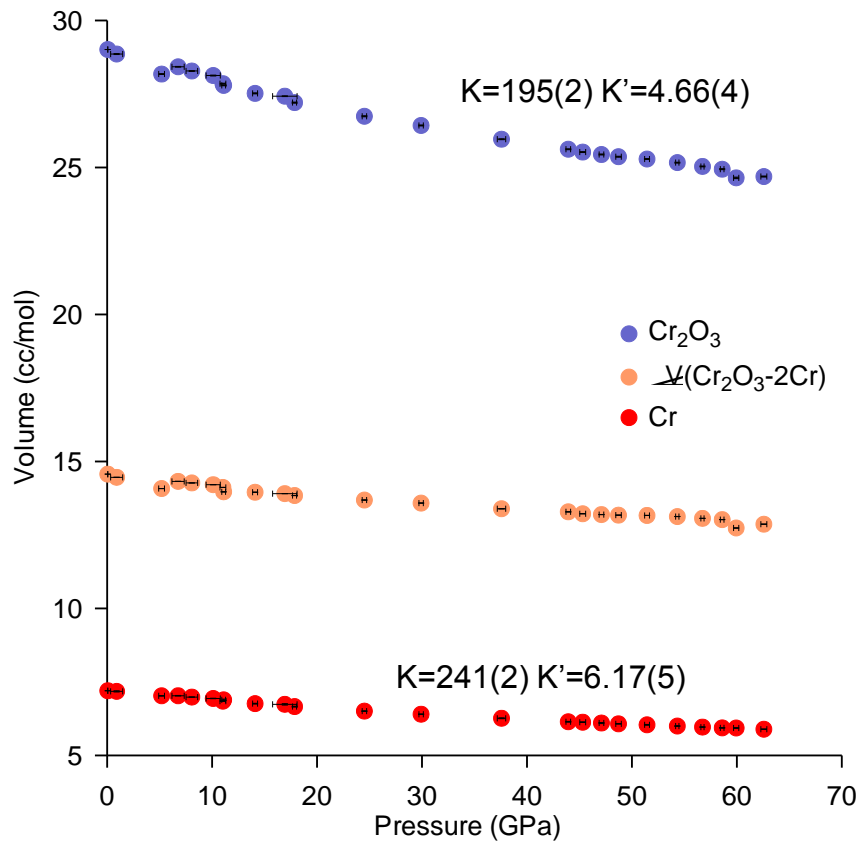


Birch-Murnaghan 3rd order

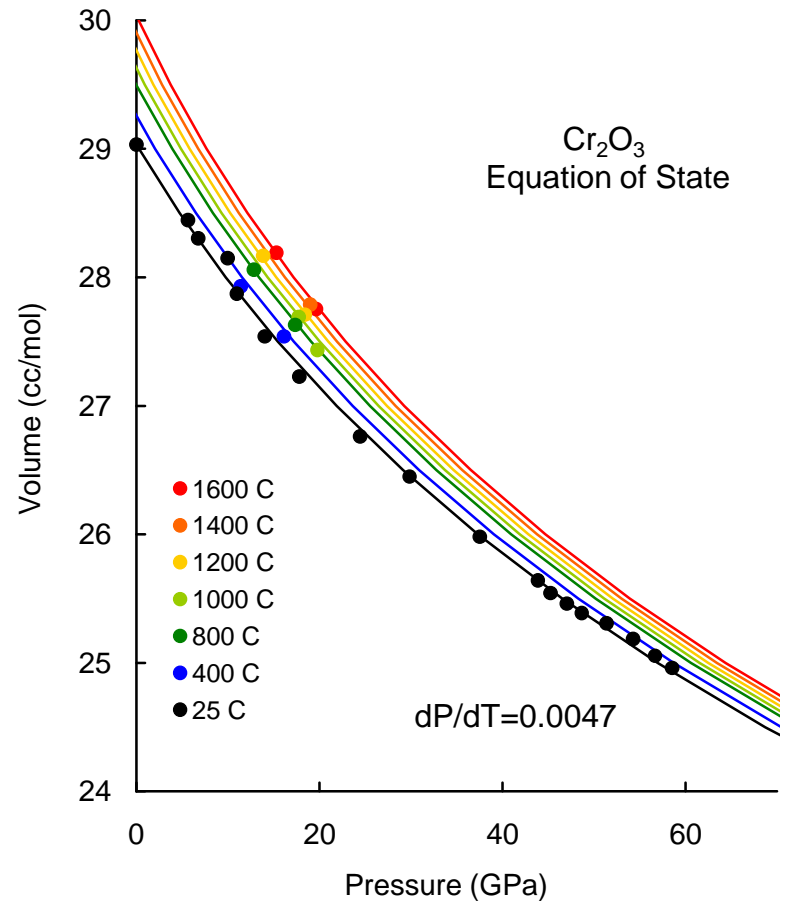


Mie-Grüneisen

Cr-Cr₂O₃ Equations of State

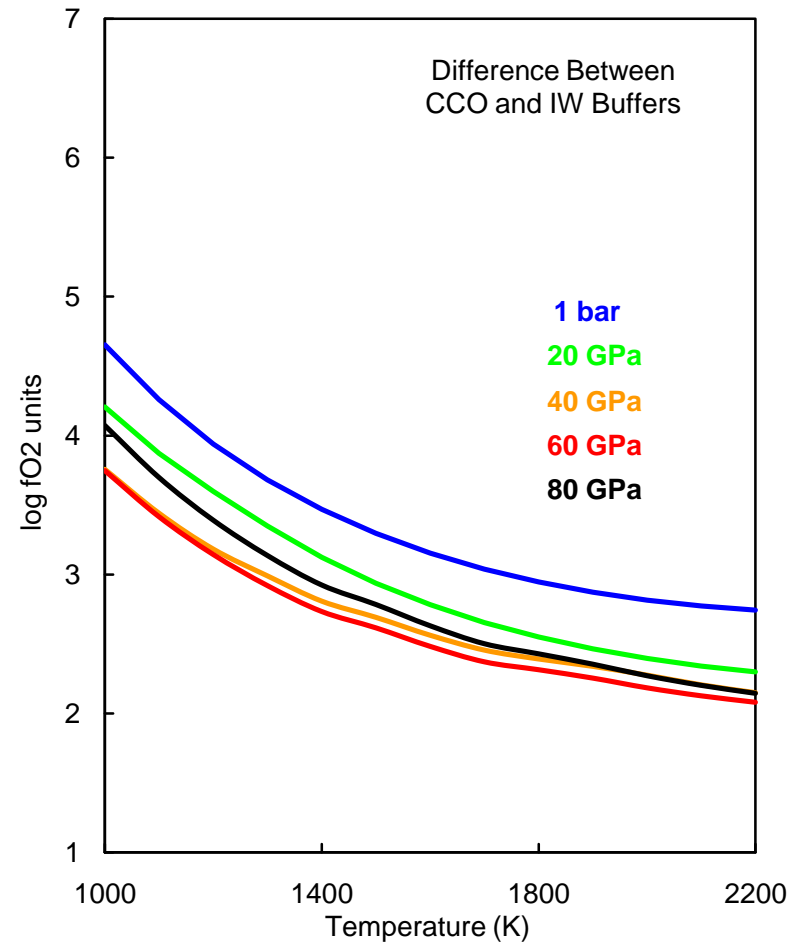
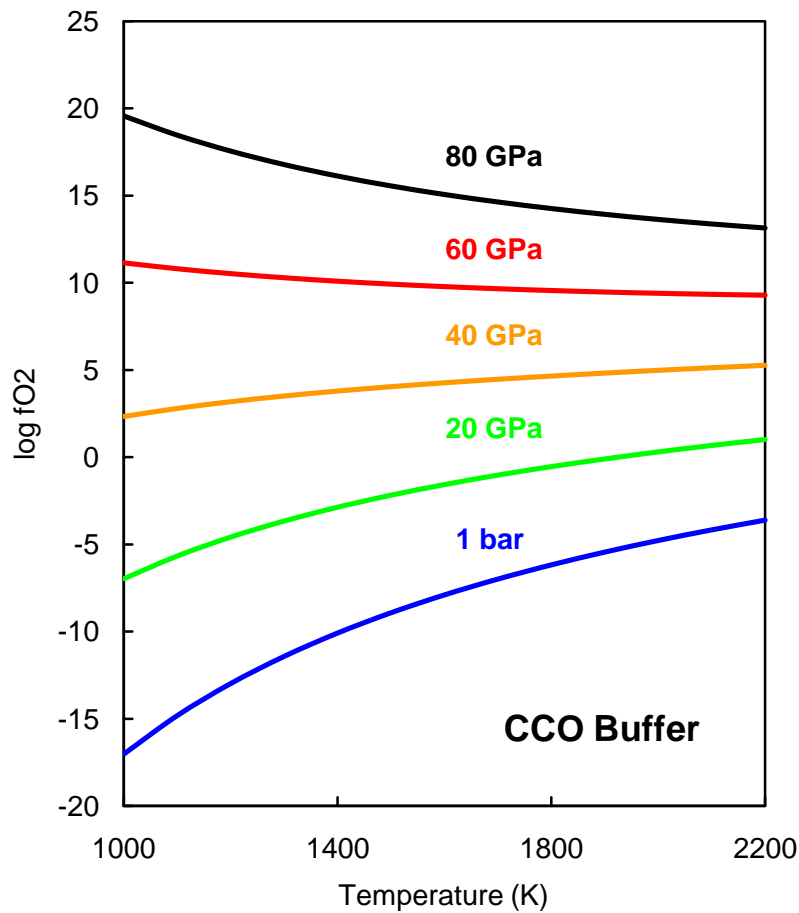


Birch-Murnaghan 3rd order



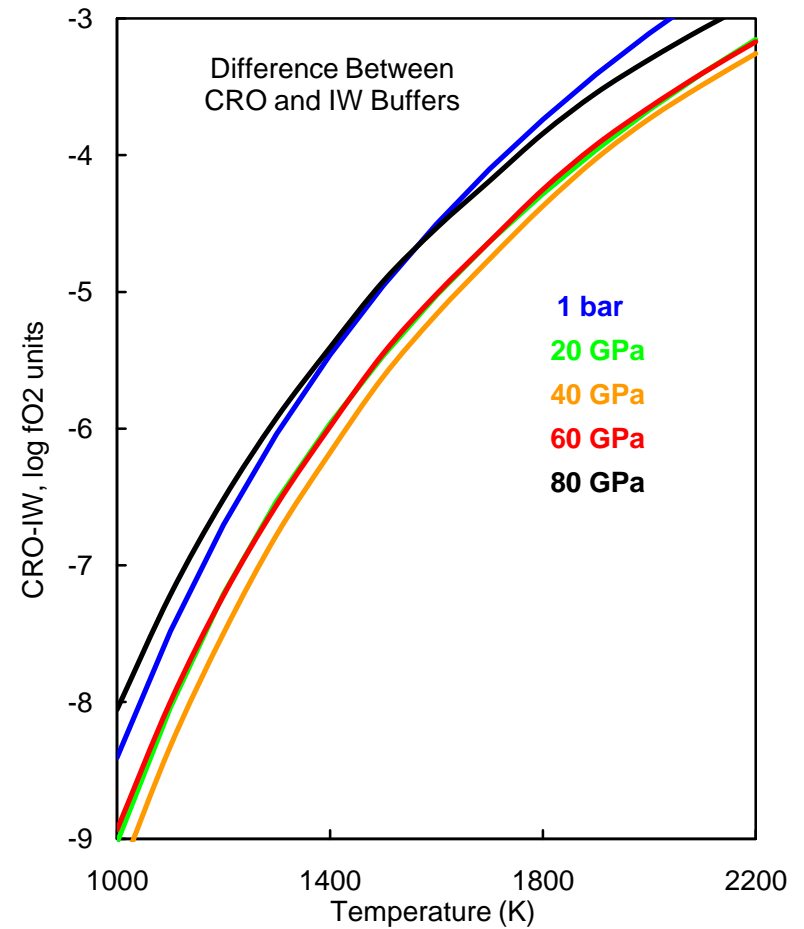
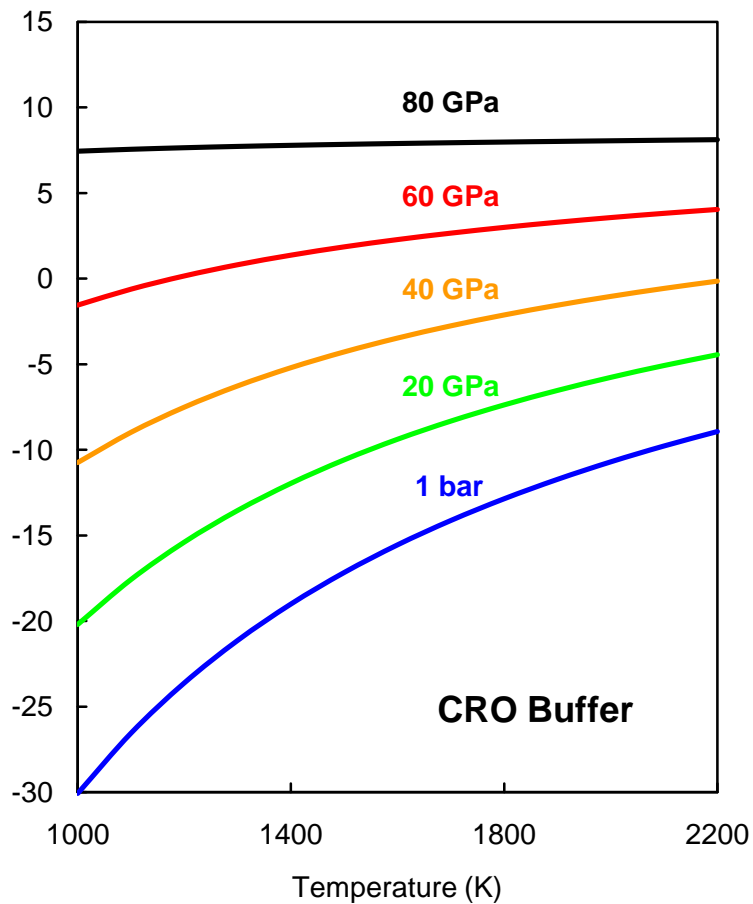
Mie-Grüneisen

Co-CoO Buffer



$$\log f_{O_2} = \log f_{O_2}(1bar) + \left(\frac{0.8686}{RT} \right) \int \Delta V dP$$

Cr-Cr₂O₃ Buffer



$$\log fO_2 = \log fO_2(1bar) + \left(\frac{0.8686}{RT} \right) \int \Delta V dP$$

Conclusion

- Unlike the NNO buffer (>4 log units), the CCO and CRO buffers do not change greatly relative to the IW buffer (<1 log unit) at high pressures

Acknowledgements

- Andrew Campbell (dissertation advisor)
- Lisa Danielson
- Kevin Righter
- Jingzhu Hu (X17C, NSLS)
- Yanbin Wang (13-ID-GSECARS, APS)

Constructing fO_2 Buffers

- The pressure effect on fO_2 is related to change in ΔG with pressure.

$$\frac{x}{2} RT \ln fO_2 = \Delta G$$

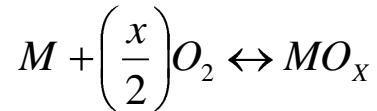
$$dG = -SdT + VdP$$

$$\partial G / \partial P |_T = V$$

$$\partial(\ln fO_2) / \partial P |_T = \left(\frac{2}{xRT} \right) \Delta V \quad (1)$$

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Need ΔV

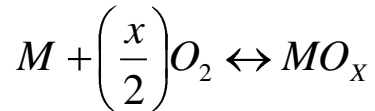
Constructing fO_2 Buffers

- How to get ΔV ?
 - Use BM EOS determined for each metal and oxide in this study to calculate V at selected P along selected isotherms. (e.g. $P = 5, 10, 15, \dots$ $T = 1000, 1200, 1400K, \dots$)
 - Must do this iteratively using least squares minimization (no establish relationship between ΔV - P - T such that an equation can be fit)
- Calculating high- P, T fO_2
 - Integrate (1) from previous slide along at specific pressures along isotherms using ΔV s from above process

$$\log fO_2 = \log fO_2(1bar) + \left(\frac{0.8686}{RT} \right) \int \Delta V dP$$

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Need ΔV