



W-WO₂ and W-WO₃ Oxygen Fugacity Relationship at High Temperature and Pressure

TJ Deane

Advisor: Dr. Andrew Campbell

Introduction

Understanding different thermodynamic properties of materials is important for a variety of reasons. Tungsten is a moderately siderophile element considered to be found in both the core and silicate portions of the Earth.

Understanding how tungsten behaves under high temperature and pressure conditions can help to lead to a better understanding of how and under what conditions the core formed.

Fully understanding the tungsten oxide buffer system is essential for scientists who would use tungsten oxide as a means of controlling oxygen fugacity within their experiments.

Current research suggests that at high pressures W⁴⁺ becomes more stable than W⁶⁺ in silicate melts coexisting with metal. [3].

Gibbs free energy : $dG = -SdT + VdP$
- for fixed T : $dG = VdP$

Relating Gibbs free energy and oxygen fugacity:

$$G_{(O_2)} = RT \ln f_{O_2}$$

Understanding that for the tungsten – tungsten oxide system

$$x/2G_{(O_2)} = G_{(WO_x)} - G_{(W)}$$

Therefore, along an isotherm

$$RT \ln f_{O_2(P,T)} = RT \ln f_{O_2(1 \text{ bar}, T)} + \int \Delta V dP$$

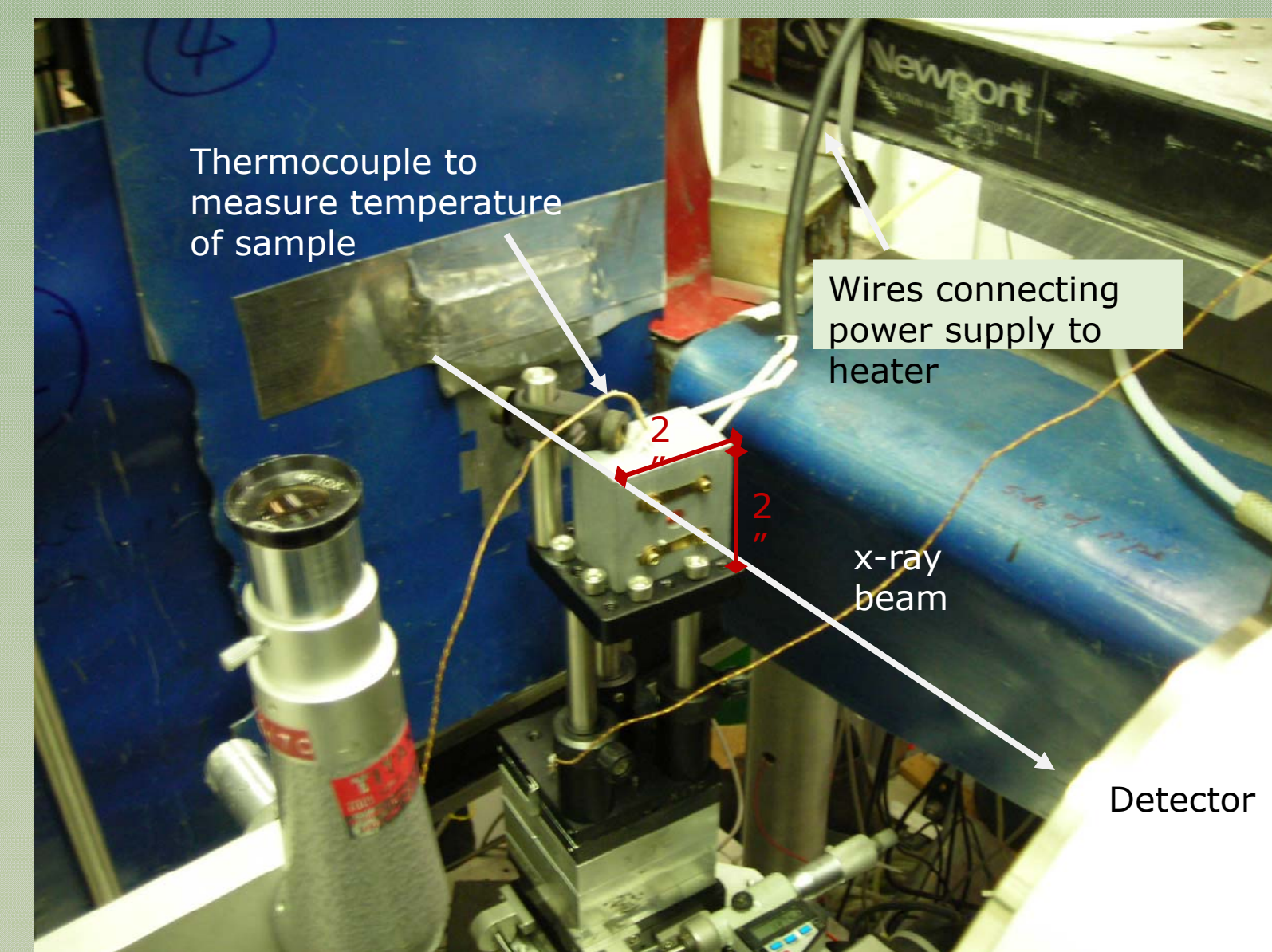
- where the oxygen fugacity at 1bar is known, leaving the only unknown term to be $\int \Delta V dP$. [2].

This relationship between volume and pressure at a given temperature is known as an equation of state.

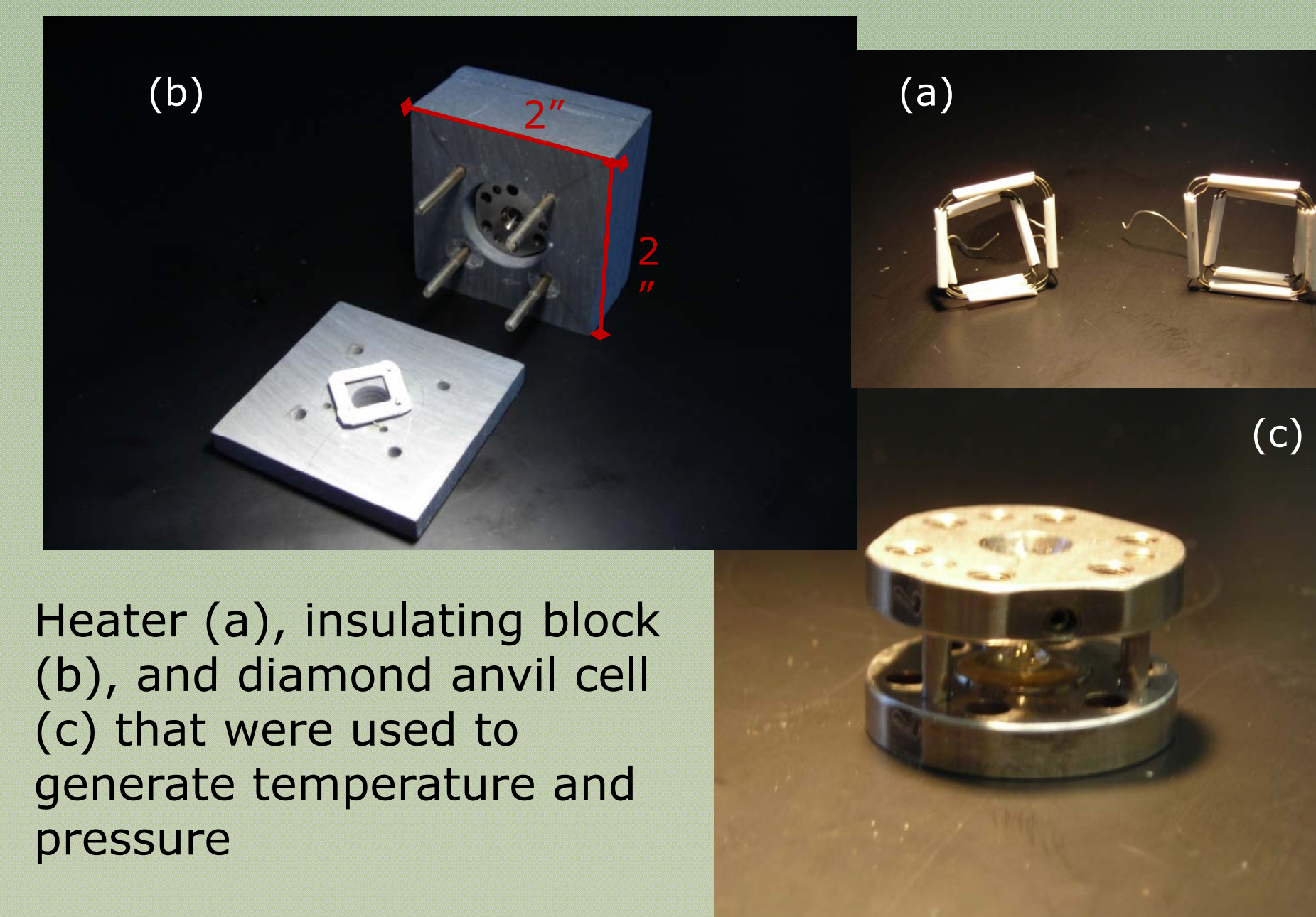
Hypothesis

As pressure is increased, I hypothesized that the WO₂ and the WO₃ buffer curves will increase at similar rates with respect to one another, thus maintaining a consistent log(*f*O₂) distance between them.

Experiment

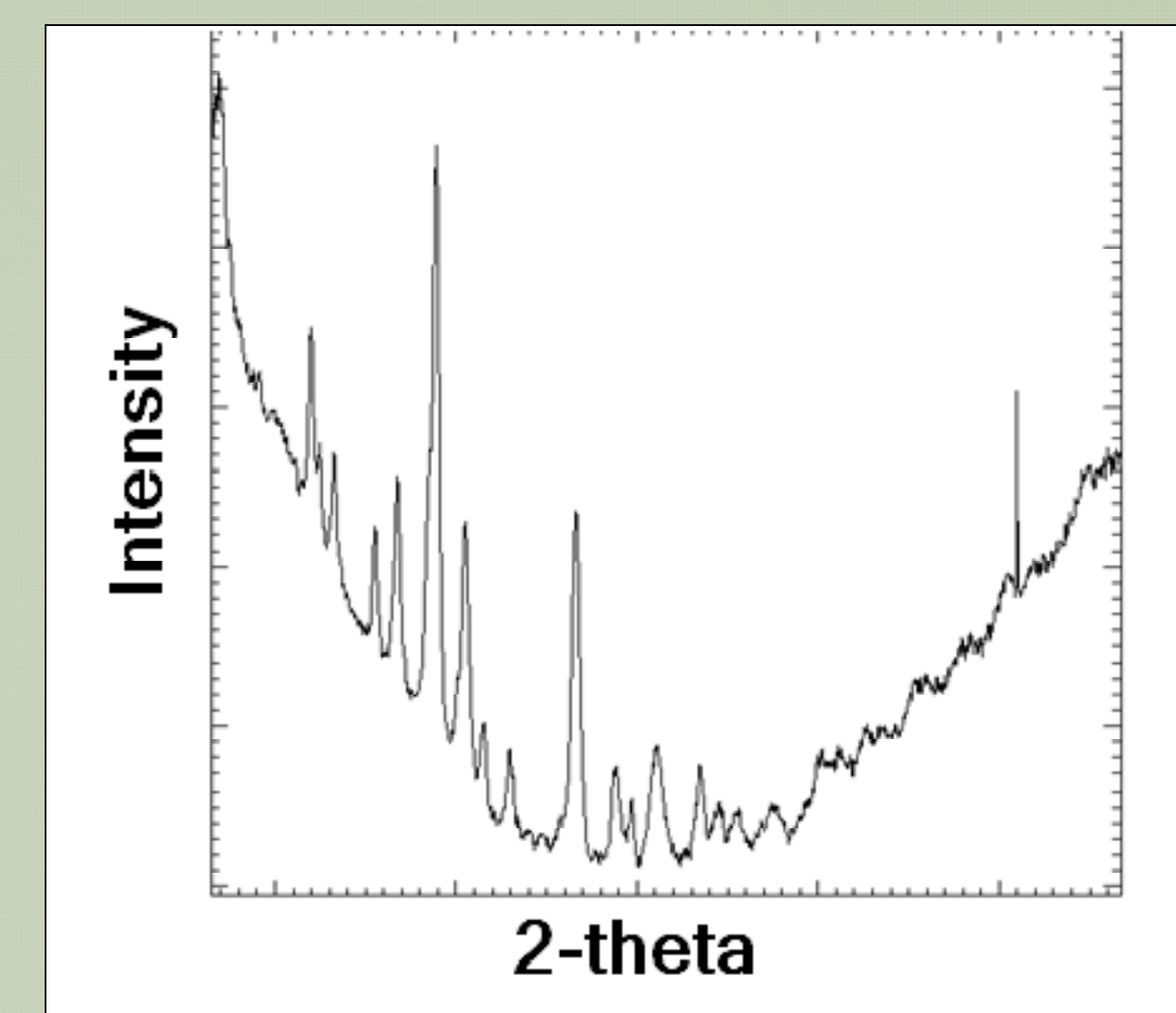
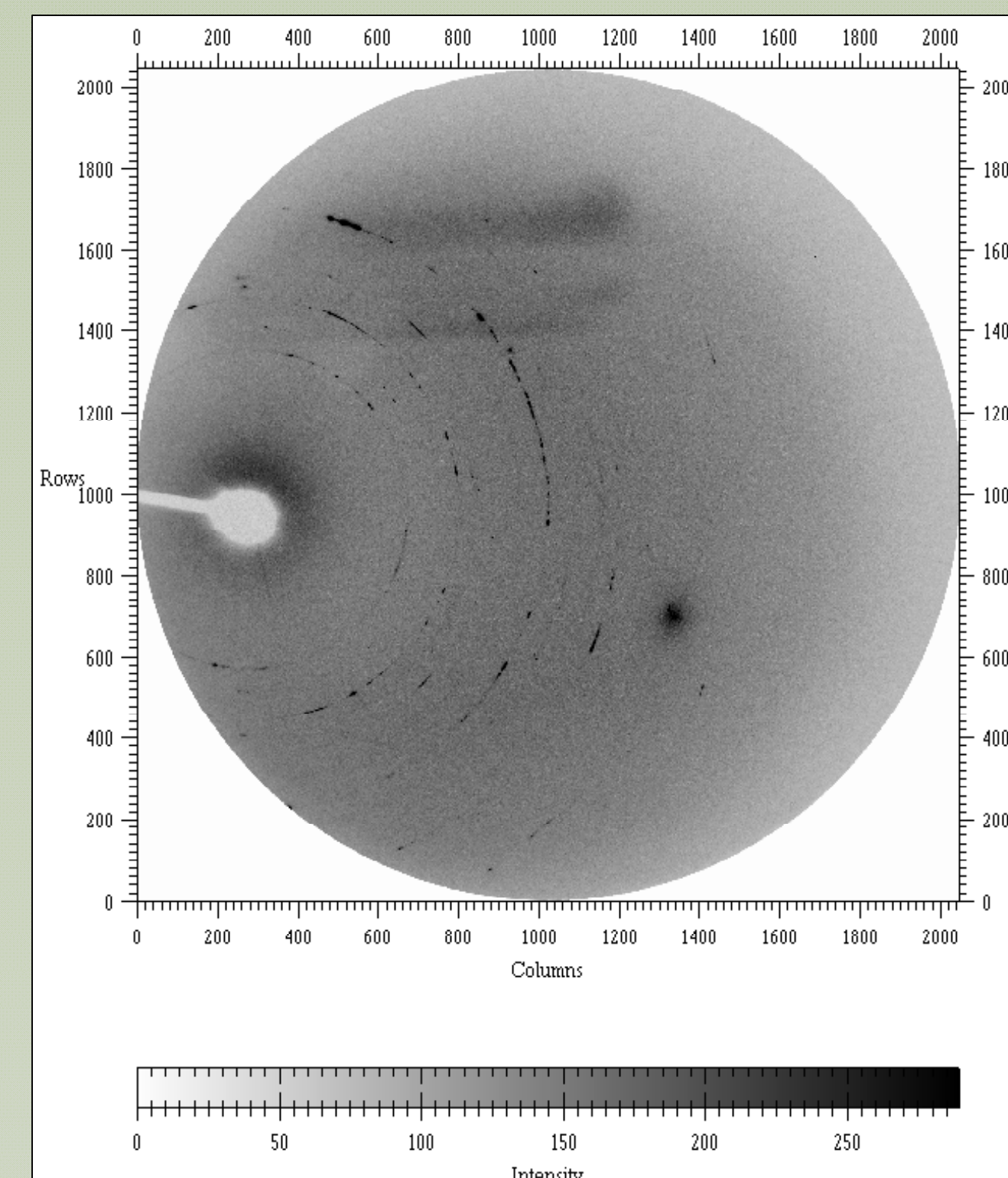


Sample along the x-ray beam line during trip to NSLS in Brookhaven New York, July 2009



Heater (a), insulating block (b), and diamond anvil cell (c) that were used to generate temperature and pressure

X-ray diffraction experiments were conducted at the National Synchrotron Light Source (NSLS) in Brookhaven New York. A high powered x-ray was directed at the sample which was held within a diamond anvil cell to generate high pressures and surrounded by individually constructed heaters to generate high temperatures. Multiple diffraction patterns were taken at varying P-T conditions and analyzed to determine the molar volumes of each of the phases present.



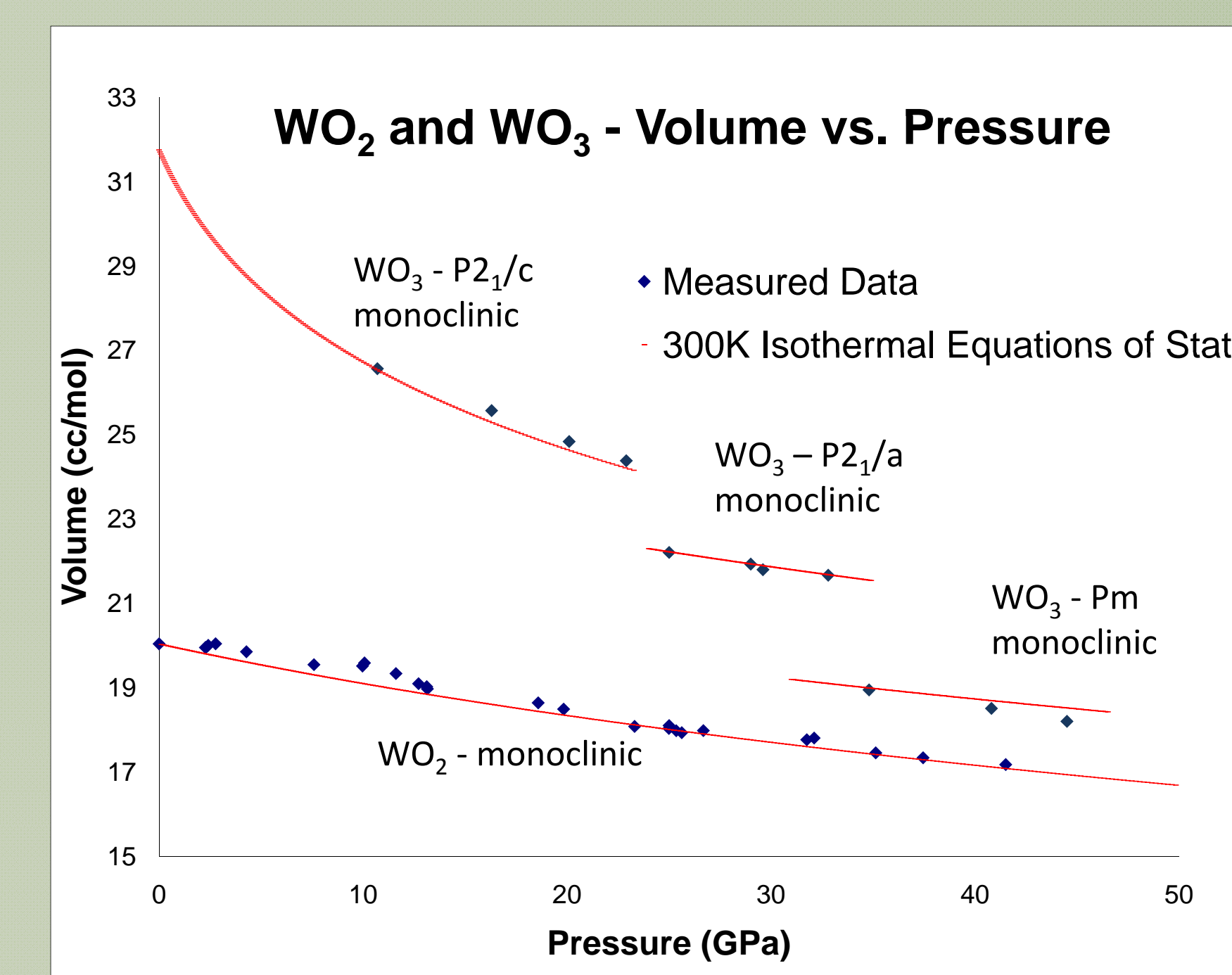
A computer program called Fit2D reads the diffraction patterns output by the detector and turns them into plots of 2-theta angle vs. peak intensity. We assign each peak a phase and a set of Miller indices which determine the molar volume of a particular phase for that diffraction pattern.

Results

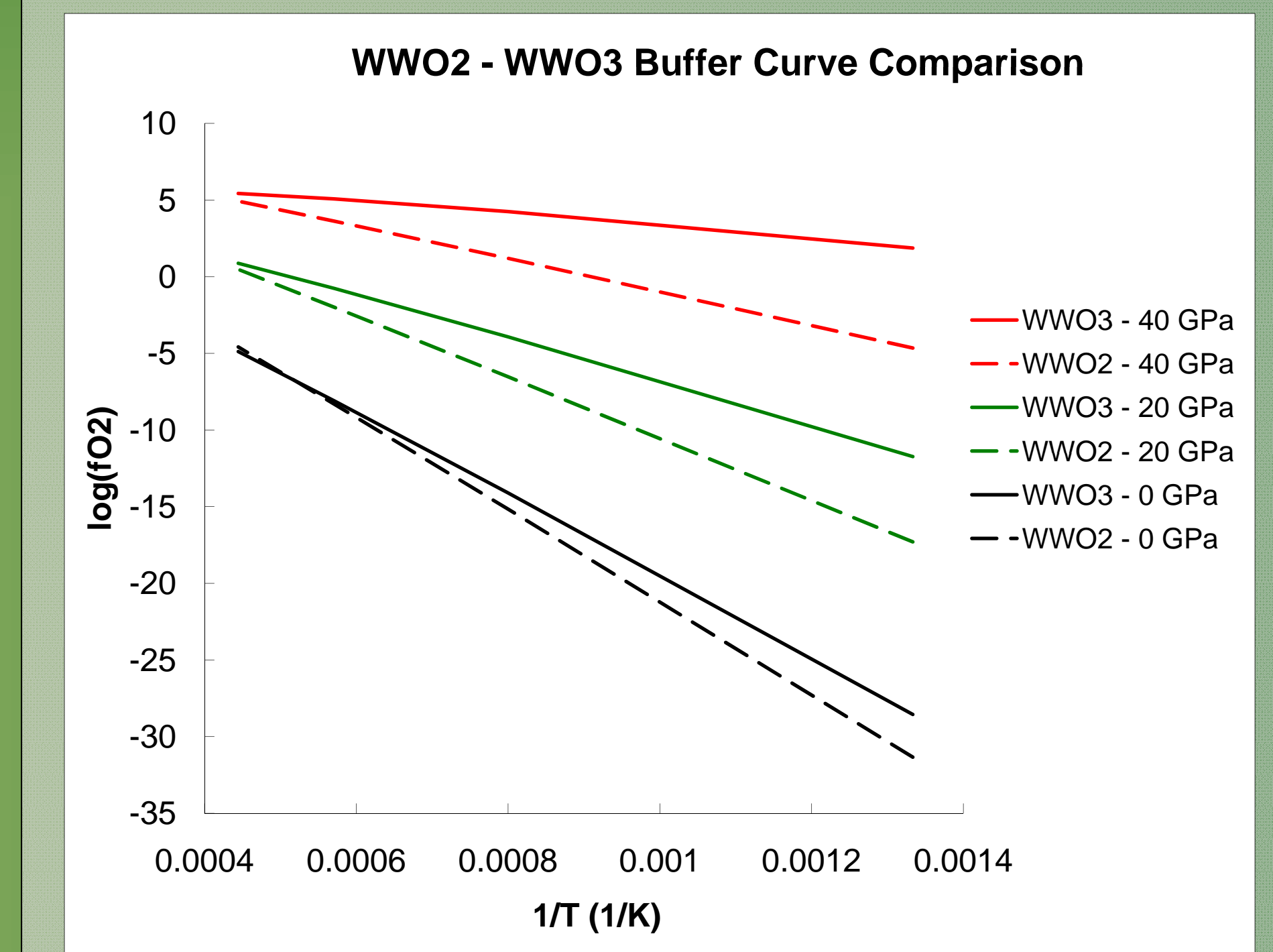
The WO₂ data was collected at various temperatures (300-750 K) and pressures (0-45 GPa) with NaCl being the pressure calibrant [5]. The WO₃ data was 300 K isothermal compression data. The published 300 K isothermal equations of state for each of the WO₃ phases ([1], [4], [7]) needed to be corrected, but results match well with the data collected. The resulting buffer curves showed trends that were expected prior

to the experiment. As the pressure is increased, the buffer curves move "up" the graph for both phases tested. Of the various WO₃ phases, the monoclinic P2₁/c WO₃ phase was used for *f*O₂ buffer calculations because thermal data were available for it and it covered the widest pressure range. for the other phases. We calculate the *f*O₂ buffer curves by inputting pressure, temperature and molar volume into the Birch Murhaghan equation of state:

$$P(V) = 3K_0/2 [(V_0/V)^{7/3} - (V_0/V)^{5/3}] \{1 + 3/4(K_0' - 4) [(V_0/V)^{2/3} - 1]\} \quad [2]$$



Conclusion



By calculating the difference in oxygen fugacity between WO₃ and WO₂ we find that the Δ*f*O₂ is always positive, indicating the *f*O₂ of WO₃ is continually higher than that of WO₂ for this pressure – temperature regime. This indicates that WO₂ has a lower Gibbs free energy in this regime, making it the more stable phase. This Δ*f*O₂ is increasingly more positive as the pressure is increased, meaning WO₂ is becoming more and more stable at increasing pressure, supporting the results found with [3], while disproving my hypothesis.

References

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