

Pressure-Volume-Temperature Studies of Metal-Oxide Pairs

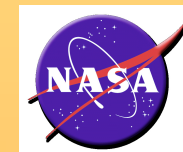
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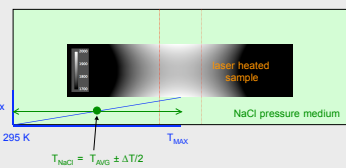


Introduction

As high-pressure, high-temperature petrology and geochemistry advance (e.g., [1]), equations of state (EOS) are needed for more than comparisons to seismological data; they are essential to a thermodynamic framework to describe reactions in the mantle and core. Here we illustrate this by determining the chemical potential of oxygen in metal-oxide equilibria at high pressures. Oxygen fugacity (f_{O_2}) is an important factor in many high-P,T geochemistry experiments, especially those determining phase relations or trace element partitioning (e.g., [2]). In those experiments, f_{O_2} is frequently set by, or determined in relation to, a metal-oxide f_{O_2} buffer (e.g., Fe-FeO (IW), Ni-NiO (NNO), Re-ReO₂ (RRO)). To compare the experimental results to one another, it is important to know how these buffers change with pressure. Extension of the 1-bar f_{O_2} buffers to high pressure, high-temperature conditions depends on the ΔV between phases. Here we report P- ΔV -T measurements on metal-oxide pairs, and from these calculate the effects of high pressure on their associated oxygen fugacity buffers.

Experimental

Mixtures of Ni-NiO, Fe-Fe_{1-x}O and Re-ReO₂ were studied by high-P,T X-ray diffraction at GSECARS, Advanced Photon Source. Multi-anvil press samples were mixed with NaCl and loaded into a boron nitride capsule in a beamline version of a 14/8 assembly developed by the COMPRES multi-anvil assembly initiative [3]. Diamond anvil cell samples were compressed into a thin (5-10 μ m) flake and loaded between layers of NaCl. NaCl was the pressure calibrant [4,5] both in MAP and DAC experiments. Corrections (< 100 K) were made to the laser heating temperatures according to modelling of the gradients [6]. In the experimental geometry (figure below), the NaCl is at a different mean temperature than the sample. Error (2 σ) in thermal pressure is propagated from the thermal gradient from the sample surface to the anvil.

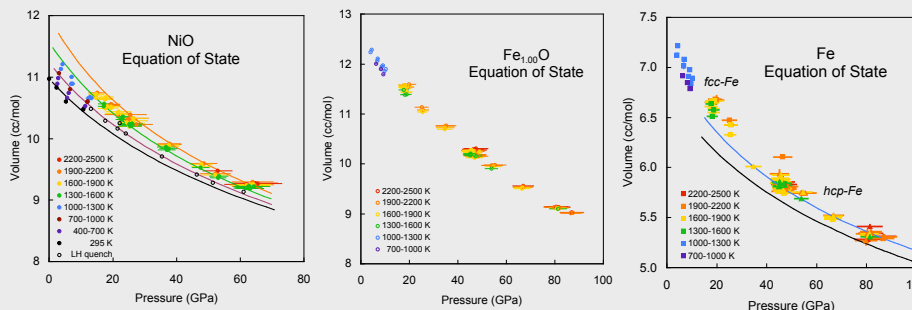


EOS Data

The high temperature data show good agreement between the MAP (<15 GPa) and DAC (>15 GPa) results. However, the data from quenched laser-heated spots systematically overestimate the pressure (e.g., NiO below); rapid quench (>10⁴ K/s) apparently induces residual strains.

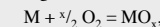
These data were obtained from stoichiometric FeO, taking advantage of high-P,T equilibration between the wüstite starting material and coexisting Fe.

P-V-T data for Fe (fcc=squares, hcp=triangles) are compared below to literature data (black line, 300 K [7]; blue line, 1150 K from [8]). The 1150 K curve lies at slightly higher pressures than our data suggest, partly because the Pt scale used by [8] overestimates pressure relative to the NaCl scale we used [5].



fO₂ Buffers at High Pressure

For the general metal-oxide reaction



the f_{O_2} is related to the Gibbs energies (G) by

$$x/2 RT \ln f_{O_2} = G(MO_x) - G(M).$$

The pressure effect on this buffer is in the G terms. Along each isotherm, $d(\Delta G) = \Delta V dP$. Using the ΔV -P-T relations from this study, the effects of pressure on the Fe-FeO and, Ni-NiO oxygen fugacity buffers are shown in the figure above. Similar effects are observed on the Re-ReO₂ oxygen fugacity buffer.

The difference between f_{O_2} buffers is an important factor for making comparisons between high pressure experiments that used different buffers. The difference between the NNO and IW buffers and the RRO and IW buffers are shown at 1 bar [9,10] and at high pressures [this work] in the figure below. The effect of pressure is to tend to reduce the siderophilicity of Ni and Re.

P- ΔV -T Data

The cell volumes of the oxides and the coexisting metal were measured simultaneously, permitting ΔV to be calculated under identical P,T conditions. This minimizes systematic biases and improves precision in ΔV over independently determined equations of state for the two phases.

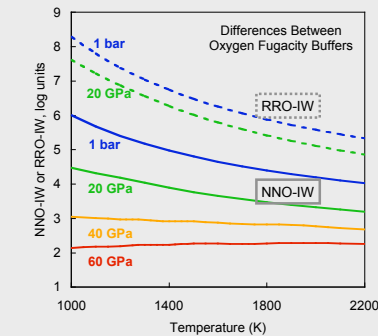
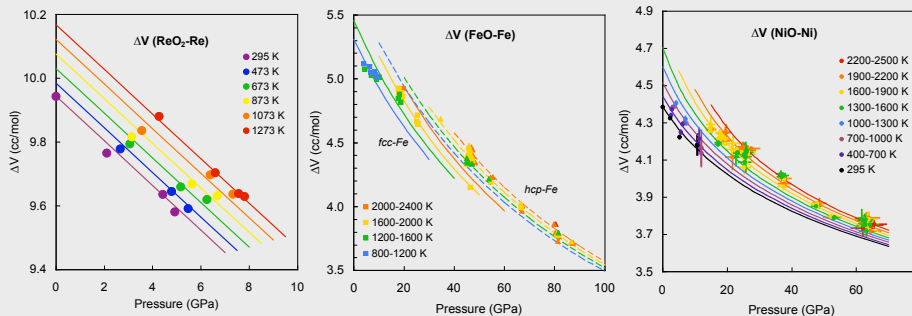
The data for each oxide-metal pair were fitted to one of the two forms:

$$\Delta V = \Delta V_0 + aP + b\Delta T$$

or

$$\Delta V = \Delta V_0 [1 + (P - b\Delta T)/a]^{1/n}$$

r.m.s. deviations to the fit were < 0.03 cc/mol



References

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