FIREFOX – AN OXYGEN FUGACITY SENSOR FOR VENUS. Noam R. Izenberg, Johns Hopkins University Applied Physics Laboratory, 11100 Johns Hopkins Road, Laurel, MD 20723, USA. Noam.izenberg@jhuapl.edu

Introduction: Understanding the composition of the atmosphere at the surface of Venus is critical to knowing the stable mineralogy of the rocks there. Oxygen fugacity is a key telltale in this story. "FirefOx" is a simple, low power and cost oxygen fugacity sensor derived from common industrial and off-the-shelf ceramic oxygen sensors, with the express purpose of determining the partial pressure of oxygen in the lowest scale heights of the Venus atmosphere, and especially the lowest hundreds of meters, and the surface atmosphere interface, where the atmosphere and surface move to thermodynamic equilibrium.

FirefOx is a Metal/Metal Oxide oxygen fugacity sensors to be mounted on the outside of a Venus descent probe, with electronics to be housed inside a thermally controlled environment. The primary sensor capability is the detection of the partial pressure of oxygen gas (fO_2) in the near-surface environment of Venus, so the sensor must operate in the 710-740K temperature range and at up to 95-bar pressure (predominantly CO_2) for sufficient time to obtain a precise, accurate measurement. The baseline sensor objective is survival for least two hours at Venus surface conditions, and production accurate measurements (fO_2 to +/- 0.3 order of magnitude within the range of 10^{-18} to 10^{-24}) and a temperature range between 710 and 740K. Mean planetary elevation has a temperature near 735 K and the operational temperature range covers a range of potential landing elevations. FirefOx requirements are low (~100-200 grams, mass, milliwatt power, several kilobytes total sicence data), while it's potential science return is high.

Importance of Oxygen Fugacity Knowledge: Oxygen is a trace gas in the lower atmosphere of Venus, controlled by the CO-CO_2 chemical equilibrium

$$2CO + O2 = 2CO_2 \qquad (1)$$

with equilibrium constant K given by

$$K = (X_{CO2}/X_{CO})^2 \bullet (1/fO_2) \qquad (2)$$

where f_{O2} is the oxygen fugacity. Substitute in thermodynamic data, rearrange, a temperature (and thus altitude) dependent function for oxygen fugacity based on CO/CO_2 rations at 22 km altitude can be produced:

$$\log_{10}fO_2 = 18.57 -29621(\pm19)/T \qquad (3)$$

assumed to be valid from the surface to 22 km altitude by [1]. Additional constraints revised the equation in [2]. Calculated oxygen fugacity as a function of temperature (and altitude) from is shown in Figure 1. At mean planetary radius and temperature of ~740 K, fO_2 is shown to be ~ $10^{-21.5}$ bars. Lower actual CO values at the surface (i.e. below the 20 ppm measured

at 22 km), oxygen fugacity would be higher. Observational and theoretical constraints suggest a CO abundance of 3-20 ppm at the surface of Venus [2], thus a plausible range of oxygen fugacity would be ~ 10^{-20} bars to ~ 10^{-24} bars.
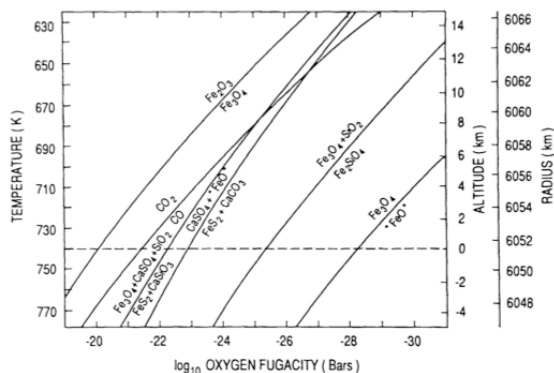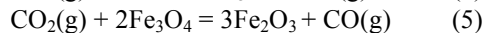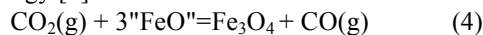

Figure 1. Iron bearing mineral assemblages possible as a function of fO2 for Venus' surface, from [1].

The pressure, temperature, and atmospheric composition above the surface materials of Venus determine the surface oxidation state and therefore its mineralogy [3]. Gas-solid reactions such as

$$CO_2(g) + 3"FeO"=Fe_3O_4 + CO(g) \qquad (4)$$
$$CO_2(g) + 2Fe_3O_4 = 3Fe_2O_3 + CO(g) \qquad (5)$$

relate iron oxidation state of surface minerals to atmospheric gases (where "FeO" represents non-stoichiometric wustite, as per [1]). Expected oxygen fugacities for Venus put the Venus surface in the magnetite (Fe_3O_4) stability field (Figure 1) over all temperatures of the Venus surface. Oxygen fugacities several orders of magnitude more reducing than predicted would be required for hematite (Fe_2O_3) stability [4]. Thus magnetite is predicted to be stable at the surface of Venus, given current atmospheric assumptions. Other mineral equilibriums are not directly dependent on oxygen fugacity, but dependent on carbon gas chemistry [1, 5], and relate sulfate/sulfide mineralogy to fO_2. Direct measurement of fO_2 would both improve understanding of the carbon gas chemistry (equations (1) and (2)) in the lower atmosphere of Venus and possible result in a revision of the values in equation (3). This might change the stability regimes presented in Figure 1, and in turn the stable mineral phases at the surface. Direct measurement of the partial pressure of oxygen would provide robust constraints on gas chemistry and surface mineral stability, and confirmation of carbon gas measurements obtained by other methods.

Use of fO2 Sensors for Future Planetary Missions: Venus is not the only possible target for oxygen

fugacity measurements. Creation and validation of the ceramic oxygen sensor at Venus surface temperature and pressure conditions provides a pathway to develop similar sensors for additional atmospheres, such as gas giants (via descent probe) and potentially active volcanic vents on Io (via dedicated probe).

Principles of Technique: The oxygen sensor is a solid-state, solid electrolyte oxygen concentration cell (henceforth called a ceramic oxygen sensor). Ceramic oxygen sensors have been used to measure oxygen fugacity in hot gases for nearly 50 years [6]. The basic principle (Figure 2) relies on a reference material of a known fO_2, a solid electrolyte, and a sample atmosphere or material. The fO_2 differential between the known and unknown materials causes a diffusion of oxygen through the electrolyte, resulting in a small, measurable voltage. A prototype schematic is shown in Figure 2.
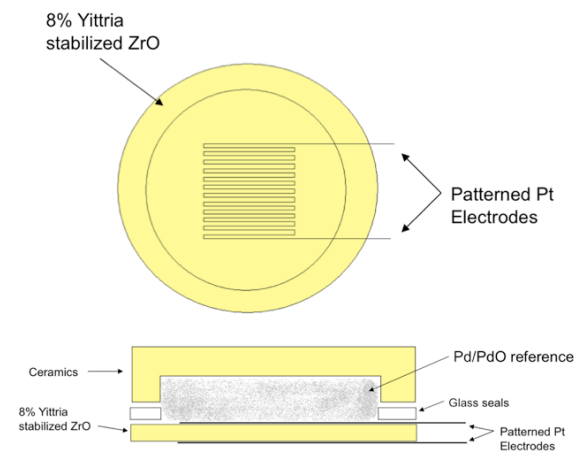

Figure 2. Prototype schematic of FirefOx sensor (David Deglau, JHUAPL)

Ceramic oxygen sensors function over wide ranges of temperature (from below 500 K to well over 1000 K) and oxygen fugacity ($fO_2 = 10^{-35}$ to 1 bars) [7]. The operational range for a solid electrolyte is in the regime where (T-fO_2) ionic conduction dominates electronic conduction. This range is known from literature data [e.g. 8-10] and overlaps the expected fO_2 values for high temperature planetary environments.

A simple COS fO_2 sensor should the Nernst equation [cf. 11-12], and is thus a primary sensor (in other words, one that should not actually need calibration, but whose output is fundamentally related to the inputs). The Nernst equation directly relates the potential generated by the diffusing oxygen atoms through the sensor to the fO_2 via a relationship similar to

$$E = RT/4F \ln(P_{O2}/P_{refO2}) \qquad (6)$$

Where E is the open circuit potential across the sensor electrolyte (directly measured by the sensor), R is the universal gas constant, T is the temperature, F is

the Faraday constant, P_{refO2} is the reference oxygen pressure on one side of the electrolyte (a known gas, or metal oxide), and P_{O2} is the unknown oxygen pressure of the outside environment [12].

Science Enabled by knowledge of fO_2: Accurate constraint of fO_2 would provide definitive constraints for near surface gas-phase equilibria and surface/atmosphere stability. Oxygen fugacity, and gas equilibrium at Venus surface is still primarily derived values from upper atmosphere measurements and thermodynamic calculations (Figure 3). [2]. Direct measurements of fO_2 would provide confirmation or falsification of these models.
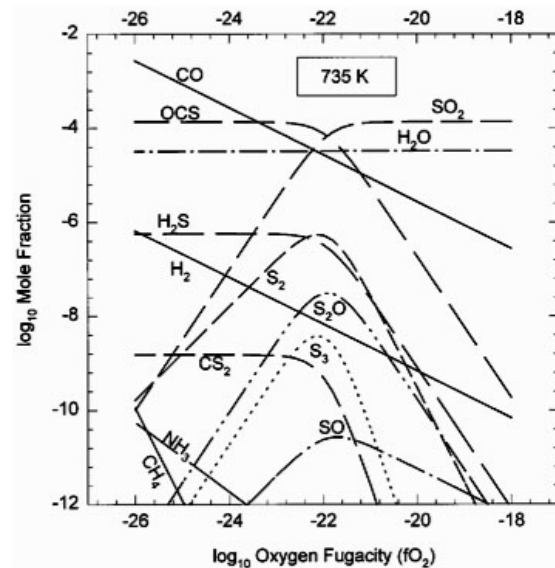

Figure 3. Atmospheric gases at surface of Venus as a function of fO_2 from [2].

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