Fire*f*Ox Design Reference Oxygen Sensor for Hot, Deep Atmospheres

Noam R. Izenberg (noam.izenberg@jhuapl.edu), Stergios J. Papadakis, David M. Deglau, and A. Shaun Francomacaro
Johns Hopkins University Applied Physics Laboratory, Laurel, Maryland, USA

JOHNS HOPKINS APPLIED PHYSICS LABORATORY

#1024

Abstract

Understanding the composition of the lowest portion of Venus' atmosphere is critical to knowing the stable mineralogy of the rocks there. Oxygen gas is a critical trace component, with fugacity (fO_2), or partial pressure, estimated in the range of 10^{-19} to 10^{-22} from early probe measurements down to 22km altitude (Pioneer Venus, Venera), chemical equilibrium measurements, and other modeling. "Fire*f*Ox" is a simple oxygen fugacity sensor 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; the surface atmosphere interface, where the atmosphere and surface materials move to thermodynamic equilibrium.

Fire*f*Ox is a ceramic sensor intended to be mounted on the outside of a descent probe, with electronics housed inside a thermally controlled environment. The sole sensor capability is the detection of fO_2 in environments such as the near-surface of Venus, at up to 95-bar pressure (predominantly CO_2. Surface temperatures at mean planetary elevation are near 735 K, thus a required operational temperature range of 710-740 K covers a range of near-surface elevations.

A design reference sensor, composed of custom, Yttria-ZrO ceramic electrolyte, with an encapsulated Pd/PdO standard and patterned Pt electrodes has demonstrated scientifically useful signal-to-noise fractional-volt level potential at temperatures between 665-738 K, relatable to fO_2 by a Nernst equation. The Fire*f*Ox sensor shows promise for direct fO_2 measurement on potential upcoming Venus in situ and other deep atmosphere probes.

fO_2 on Venus

Oxygen fugacity on Venus is controlled by the CO-CO_2 chemical equilibrium:

- $2CO + O_2 = 2CO_2$
- Eq. constant $K = (X_{CO2}/X_{CO})^2 \cdot (1/fO_2)$

At 22 km altitude [1]:

- $\log_{10} fO_2 = 18.57 - 29621(\pm 19)/T$
- At planetary radius and temperature of ~740 K, fO_2 is calculated to be ~ $10^{-21.5}$ bar [2].
- Lower CO values at the surface → higher fO_2.
- Constraints suggest CO of 3-20 ppm at surface [2], thus a plausible range of oxygen fugacity would be ~10^{-20} to ~10^{-24} bar. **Fig. 1** [1], whereas kinetic modeling and Venera 13/14 measurements go as high as 10^{-19} bar [2].

P, T, and atmospheric composition above surface materials determine surface oxidation state and therefore mineralogy [1]. Gas-solid reactions

- $CO_2(g) + 3''FeO'' = Fe_3O_4 + CO(g)$
- $CO_2(g) + 2Fe_3O_4 = 3Fe_2O_3 + CO(g)$

relate Fe oxidation of surface minerals to atmospheric gases. **Fig. 2** [1]

Accurate constraint of fO_2 would provide definitive constraints for near surface gas-phase equilibria and stable surface mineral assemblages. **Fig. 3**, **Table1**.
Direct measurements of fO_2 would provide confirmation or falsification of these models.

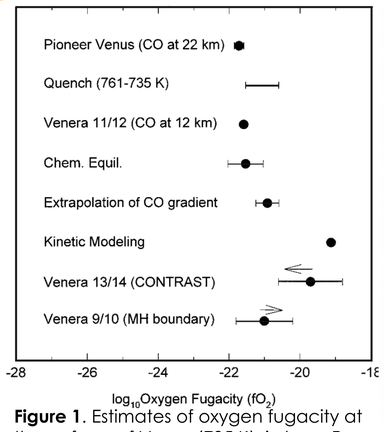


Figure 1. Estimates of oxygen fugacity at the surface of Venus (735 K), in bars. From [2].

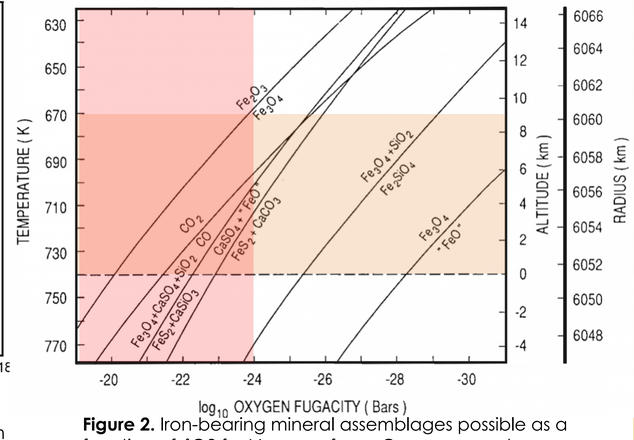


Figure 2. Iron-bearing mineral assemblages possible as a function of $fO2$ for Venus surface. Orange zone shows ranges of elevation-dependent surface temperatures. Red zone shows range of estimated fO_2 at surface. Adapted from [1].

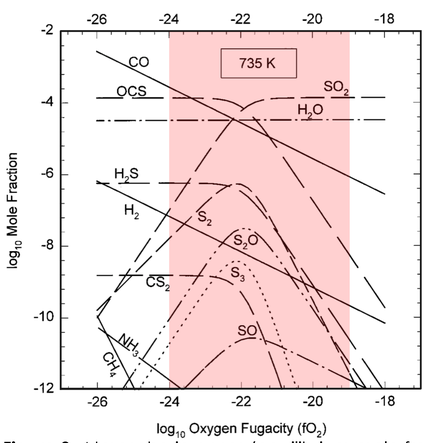


Figure 3. Atmospheric gases (equilibrium mole fraction) near surface of Venus as a function of fO_2. From [2].

Table 1. Possible stable assemblages at Venus surface

Mineral Assemblage	Equilibrium $\log_{10} fO_2$ Value
py + wo + mag + anh + qtz	-22.3 ± 0.2
py + cal + anh + wu	-23.0 ± 0.2
py + cal + anh + mag	-22.4 ± 0.2
py + dp + anh + mag + en + qtz	-21.5 ± 0.4
py + an + anh + mag + ad + qtz	-21.5 ± 0.4
py + dp + $MgSO_4$ + mag + wo + qtz	-19.2 ± 0.4

py = pyrite, wo = wollastonite, mag = magnetite, anh = anhydrite, qtz = quartz, cal = calcite, wu = wüstite, dp = diopside, en = enstatite, an = anorthite, ad = andalusite. From [1]

fO_2 Sensor Operating Principle

The fO_2 differential between a known reference and unknown materials causes a diffusion of oxygen through the electrolyte, resulting in a small, measurable voltage. **Fig. 4**

Fire*f*Ox is a primary sensor following the Nernst equation; directly relates the potential generated by the diffusing oxygen ions to $fO2$ via:

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

where
E = open circuit potential across the sensor electrolyte,
R = universal gas constant,
T = temperature,
F = Faraday's constant,
P_{refO2} = reference oxygen pressure,
P_{O2} = unknown oxygen pressure of the outside environment.

Operating range of common ceramic sensors is high for Venus temperatures. **Fig. 5**

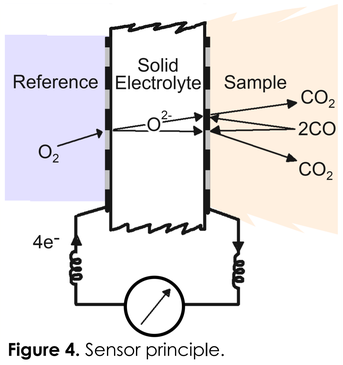


Figure 4. Sensor principle.

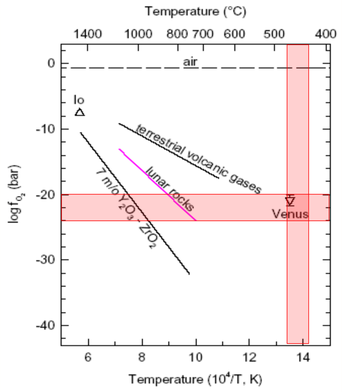


Figure 5. Operating range of ceramic sensors to be used for Fire*f*Ox sensors.

Fire*f*Ox Instrument, traceability

- Single, basic science question
- Single, moderately simple observation
- High science value answer

Type of data collected: ***Voltage (~mV)***
Data requirements: ***1 Hz, 10 bits/sec***
Pressure vessel penetration: ***2 wires/sensor***
Exterior hardware: ***"Button" sensor.***
Interior hardware: ***Wire, single chip electronics (Fig. 6)***.
Mass: ***~0.1-0.2 kg*** *max.*
Science Traceability: ***Table 2.***

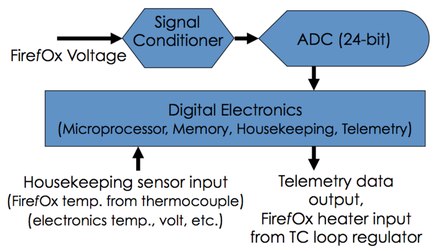


Figure 6. Preliminary electronics schematic for Fire*f*Ox sensor. Includes additional complexity of heater for sensor, not necessary for Venus environment, but possibly for other targets.

Table 2. Science Traceability

Science Question:	What is the stable mineralogy and gas chemistry at the Venus surface-atmosphere interface?
Fire*f*Ox Objective:	Determine oxygen fugacity of Venus atmosphere near surface (within 500m).
Science Mission Objective:	fO_2 measurement accuracy to +/- 0.3 order of magnitude of at 710-740 K over range of 10^{-18} to 10^{-23} bar.
Instrument Requirement:	Voltage sensitivity of approx. 0.01 mV at 735 K
Mission/ Spacecraft Requirement:	Exposure to ambient atmosphere. During descent and/or at surface. Protected electronics. Known atmosphere temperature.
Data Product:	Voltages measured during descent and near/at surface.
Analysis Product:	fO_2 profile of the lower atmosphere of Venus.
Science Results:	Stability regime for minerals and atmospheric gases near/at Venus surface.

Fire*f*Ox Investigations

Linearly scalable
- Multiple sensors for redundancy/cross-calibration
- Contact sensor to measure fO_2 of surface materials.

Flexible, low resource investigation
- EPO possibilities with student teams
- Inclusion as engineering system
- "In the noise" for most mission requirements
- Laboratory experimentation with flight sisters/spares

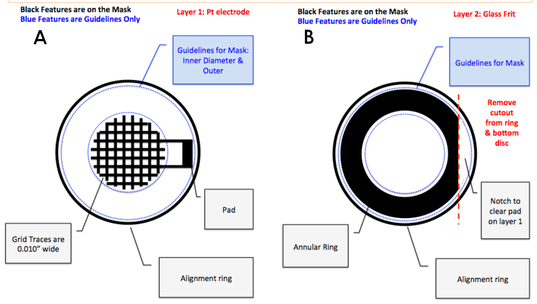
Assumes accurate T from other sources. If not the case, sensor could be augmented.

Fire*f*Ox Roadmap

- Effective sensor TRL = 6.
- Laboratory proof-of-concept at 1-atm: complete.
- Full functional test at Venus T, P, low fO_2: complete.
- Sensitivity tests: Q1-2, 2017, ongoing
- Max operational range and calibration: Q2 2017.
- Real-time Venus descent profile test: TBD.
- Full spacecraft electronic integration pathway: TBD.
- Ready to use for multiple mission applications in short order.

Reference Sensor Construction

Under Applied Physics Laboratory IRAD sensor development project (**Fig. 7**)



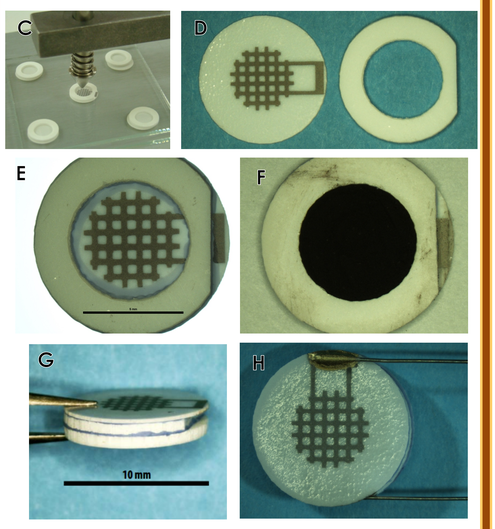


Figure 7: A, B: Design reference schematic of ceramic top (electrolyte) and ring.
C: Bonding rig, multiple sensor copies
D: Top disc and middle ring cut from ceramic tube/dowel.
E: First bond (ceramic paste).
F: PdO powder fill for standard.
G: Finished sensor "sandwich" fired at over 1100 K.
H: Lead attached (Pt/Au alloys) to finished sensor.

Reference Sensor Testing

1) Full environment pilot test at at Goddard Space Flight Center Venus Environment Test Chamber. Multiple hour test to Venus surface-like temperature (465° C) and pressure (92 bars). Gas mixture was ~95% (vol.) CO_2, ~5% N_2. Low fO_2 (<1%) but not as low as Venus levels. (**Figs. 8, 9**)
2) Multiple temperature excursion and hold tests conducted at Applied Physics Laboratory (**Fig . 10, Table 3**). Standard pressure (1-atm) of Ar gas flow (ppm-level oxygen). Equilibration behaviors, repeatability under investigation.
3) Hot-Soak test (1-Atm, Argon, Pristine sensor (ongoing)
4) Very low fO_2 test (custom gas mixture) Q2, 2017

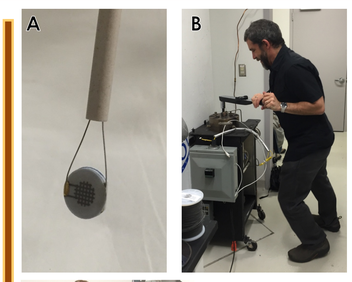


Figure 8 A-C. Testing at GSFC. **A**) Sensor mounted in chamber lid. **B**) Sealing chamber. **C**) monitoring full-function Venus condition test.

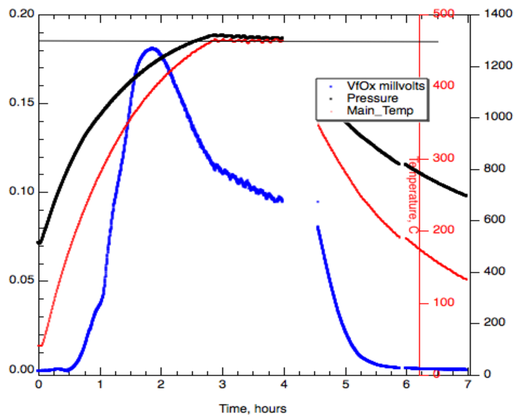


Figure 9. Goddard Venus Test Chamber. Sensor function behaved linearly with temperature above 390° C. Change in voltage at max T, P hold suggests required bake-out period.

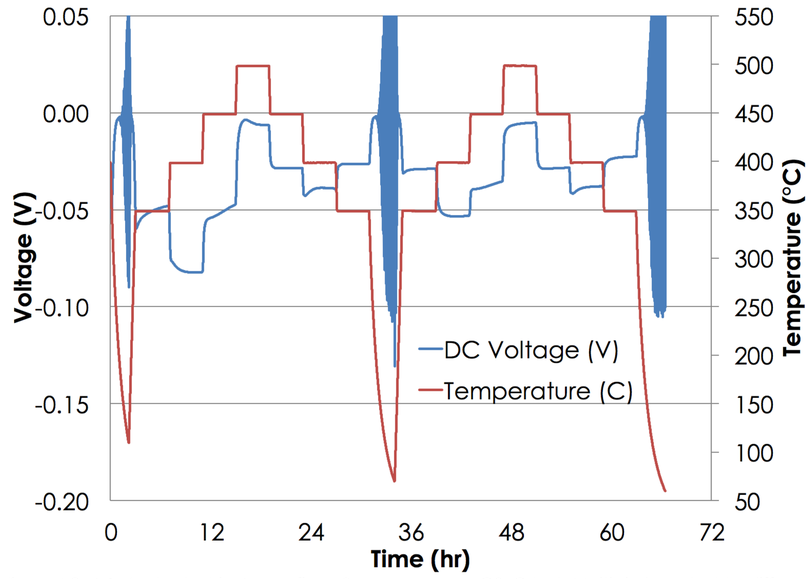


Figure 10. APL 1-atm test in Argon flow. Same sensor as GSFC test. Multiple hour test to different Temperature holds ascending to 500° C and descending in 2 cycles. fO_2 was ppm level. Sensor function behaved linearly with temperature above 390° C. Change in voltage at max T, P hold suggests required bake-out period.

Table 3. Temperature Excursion Tests

Comparison \ T(°C) ▲▼	350▲	400▲	450▲	500	450▼	400▼	350▼
Voltage, Avg(V) ($x10^{-2}$)	-4.01	-6.69	-4.48	-0.601	-2.85	-3.92	-2.50
Voltage, SD(V) ($x10^{-2}$)	1.68	1.93	2.10	1.79	1.67	2.13	2.22
Cycle Voltage Difference, Avg(V) ($x10^{-2}$)	2.19	2.85	1.41	0.14	0.015	0.063	0.320
Cycle Voltage Difference, SD(V) ($x10^{-3}$)	2.16	0.648	1.51	0.979	0.085	0.316	6.76
Difference as f(n) of signal (%)	54.52%	42.60%	31.37%	23.73%	0.54%	1.61%	12.83%

Work sponsored by APL IRAD program. [1] Fegley &Trieman, (1992) Venus & Mars: Atmospheres, Ionospheres, & Solar Wind Interactions, 7-71. [2] Fegley et al., (1997), Icarus, 125(2), 416-439.