

FirefOx: An Oxygen Fugacity Sensor for Venus

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Abstract

FirefOx is a Metal/Metal Oxide oxygen fugacity sensor to be mounted on the outside of a Venus descent probe or lander, with electronics to be housed inside a thermally controlled environment. It is a simple, low power and cost 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.

The primary sensor capability is the detection of the partial pressure of oxygen gas (f_{O_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 at least two hours at Venus surface conditions, and produce accurate measurements (f_{O_2} to $0.5 \pm 0.5 \times 10^{-24}$ within the range of 10^{-18} to 10^{-24}) at 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, milliwatt power, several kilobytes total science data), while its potential science return is high.

f_{O_2} on Venus

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

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

At 22 km altitude [1]:

- $\log_{10} f_{O_2} = 18.57 - 29621(\pm 19)/T$
- Calculated oxygen fugacity as a function of temperature (and altitude) [2].
- At planetary radius and temperature of ~740 K, f_{O_2} is calculated to be $\sim 10^{-21.5}$ bar.
- Lower CO values at the surface \rightarrow higher f_{O_2} .
- Constraints suggest CO of 3-20 ppm at surface [2], thus a plausible range of oxygen fugacity would be $\sim 10^{-20}$ to $\sim 10^{-24}$ bar. Fig. 1 [1]

P, T, and atmospheric composition above surface materials determine surface oxidation state and therefore mineralogy [3]. Gas-solid reactions

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

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

Accurate constraint of f_{O_2} would provide definitive constraints for near surface gas-phase equilibria and stable surface mineral assemblages. Fig. 3, Table 1.

Direct measurements of f_{O_2} would provide confirmation or falsification of these models.

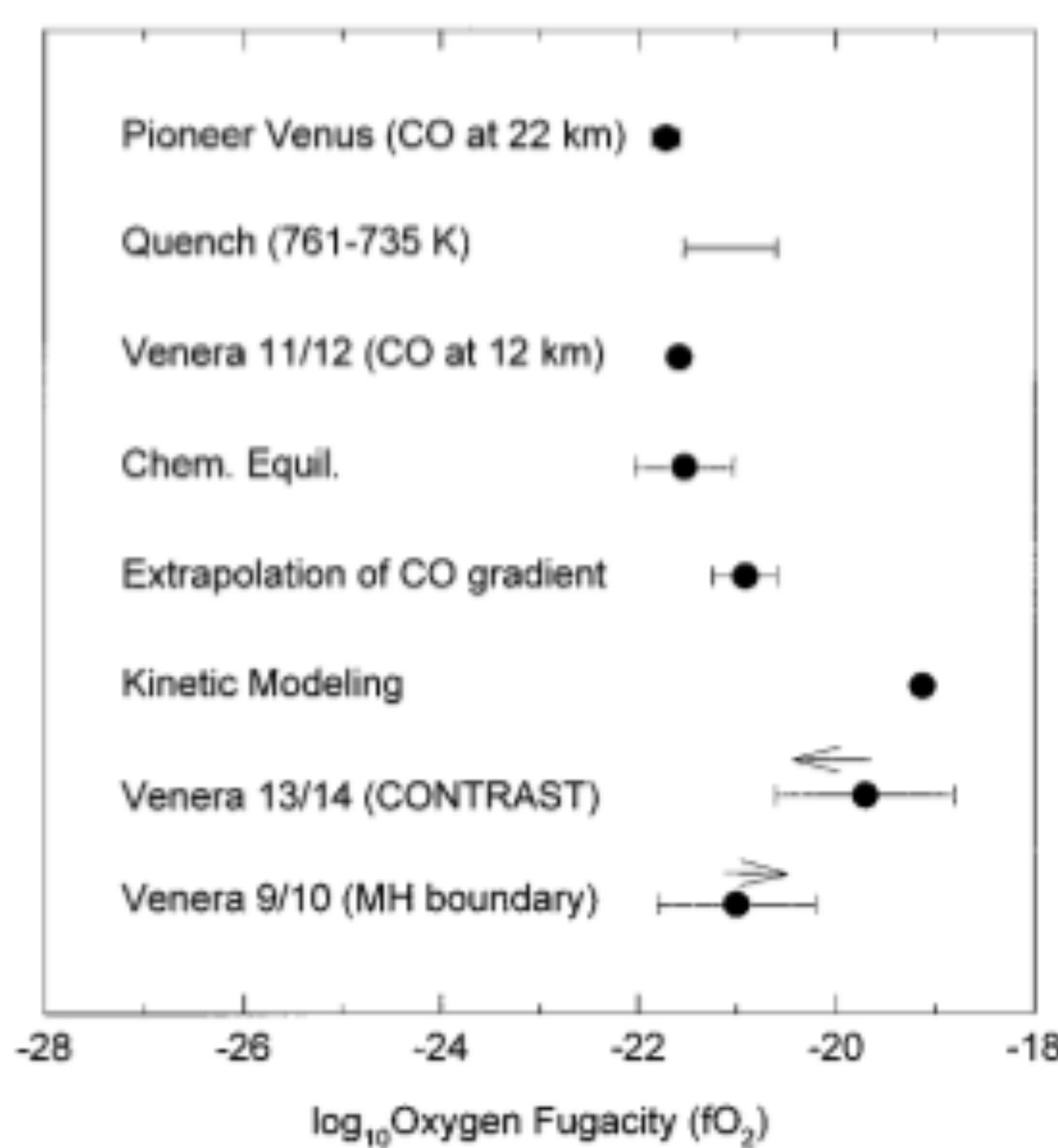


Figure 1. Estimates of oxygen fugacity at the surface of Venus (735 K), in bars. From [2].

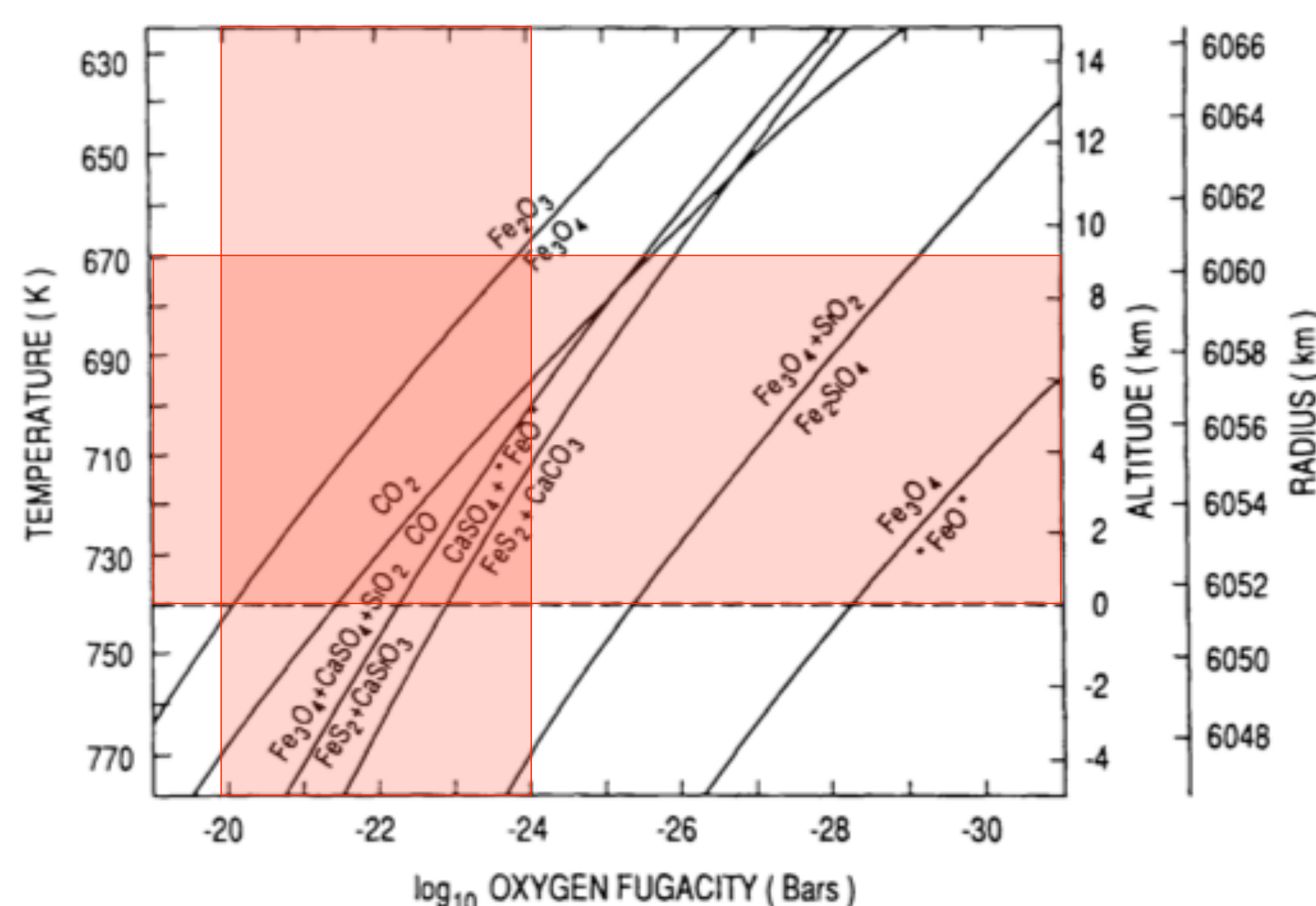


Figure 2. Iron-bearing mineral assemblages possible as a function of f_{O_2} for Venus surface. Red zones show ranges of elevation-dependent surface temperatures, and estimated f_{O_2} at surface. Adapted from [3].

Table 1. Sulfide/Sulfate Equilibria on Venus Surface

Mineral Assemblage	Equilibrium $\log_{10} f_{O_2}$ 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 + qz	-21.5 ± 0.4
py + an + anh + mag + ad + qz	-21.5 ± 0.4
py + dp + $MgSO_4$ + mag + wo + qz	-19.2 ± 0.4

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

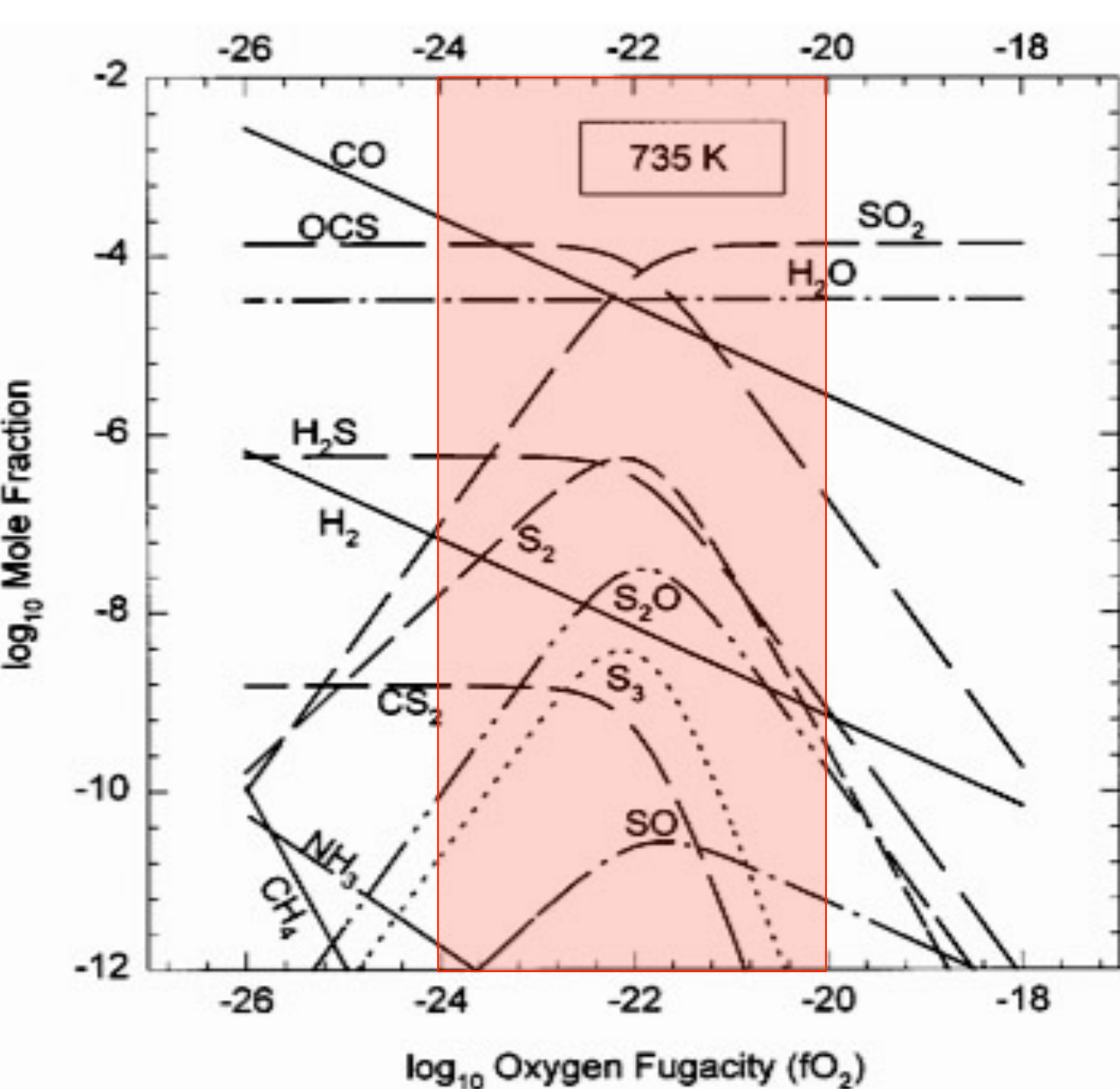


Figure 3. Atmospheric gases surface of Venus as a function of f_{O_2} . From [2].

f_{O_2} Sensor Operating Principle

Reference material of a known f_{O_2} (sample atmosphere/known oxide), (Fig. 4.)

The f_{O_2} differential between the known and unknown materials causes a diffusion of oxygen through the electrolyte, resulting in a small, measurable voltage.

Operating range of current ceramic sensors is high for Venus temperatures. (Fig. 5)

Intent is for FirefOx to be a primary sensor, following Nernst equation.

Directly relates the potential generated by the diffusing oxygen atoms through the sensor to f_{O_2} via a relationship similar to:

$$E = RT/4F \ln(P_{O_2}/P_{refO_2})$$

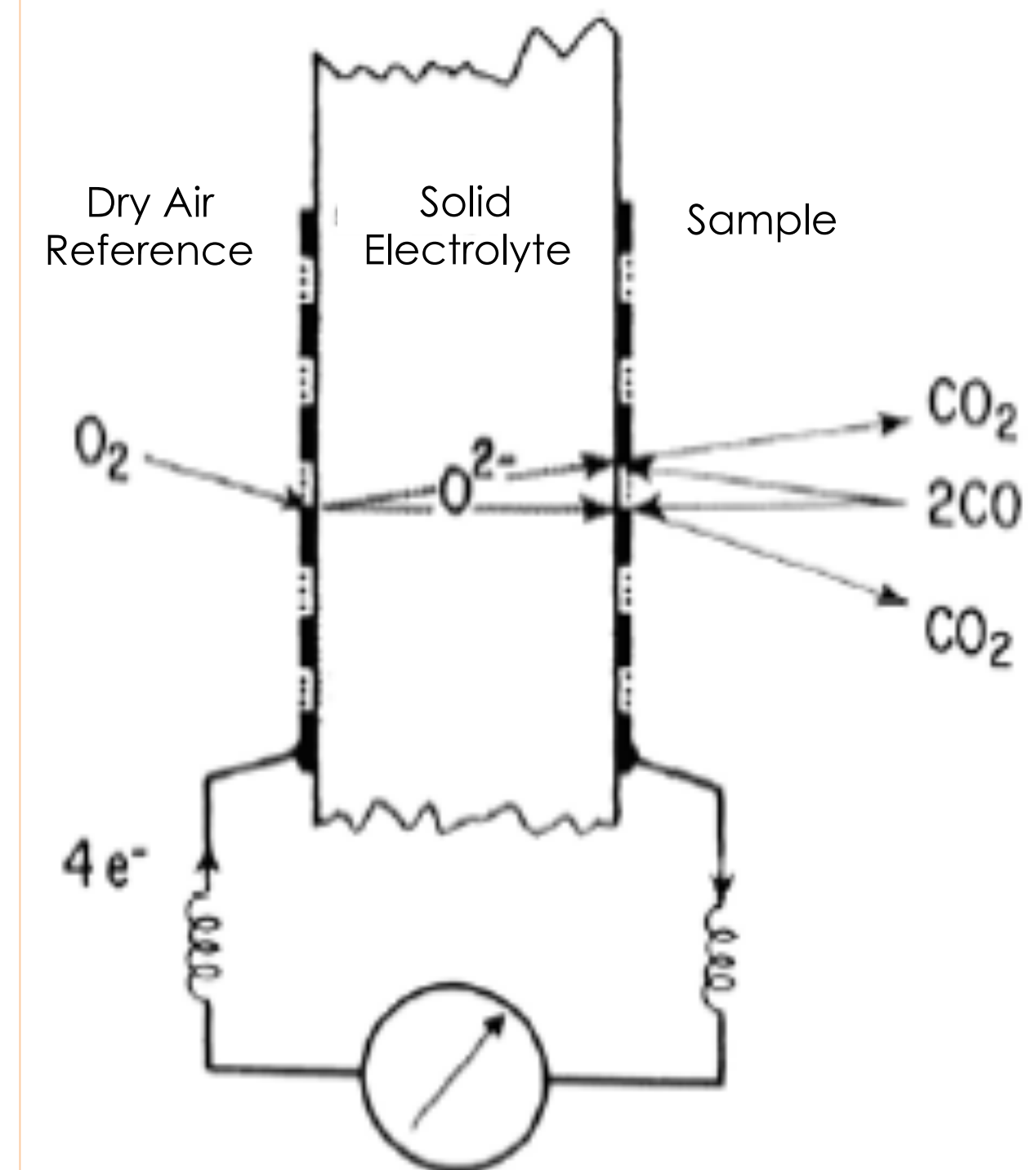


Figure 4. Sensor principle.

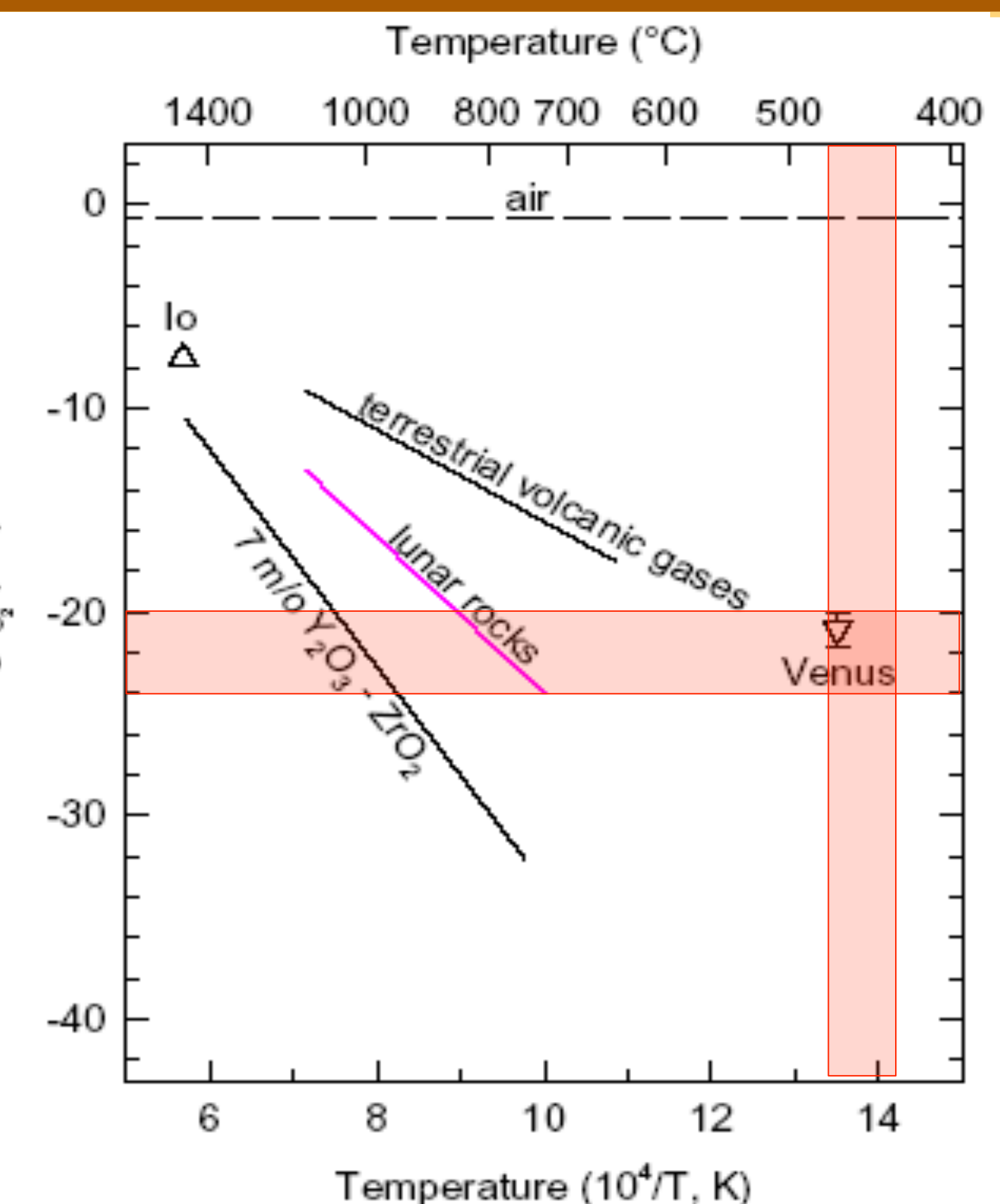


Figure 5. Operating range of ceramic sensors to be used for FirefOx sensors.

FirefOx Instrument

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

Type of data collected: **Voltage**

Transmission requirements: **1 Hz, ten bits/second**

Pressure vessel penetration: **2-4 wires per sensor**

Exterior hardware: **"Button" sensor. Mountable anywhere exposed to atmosphere.**

Interior hardware: **Minimal volume - Wire, single chip electronics.**

Mass: **~0.1-0.2 Kg max.**

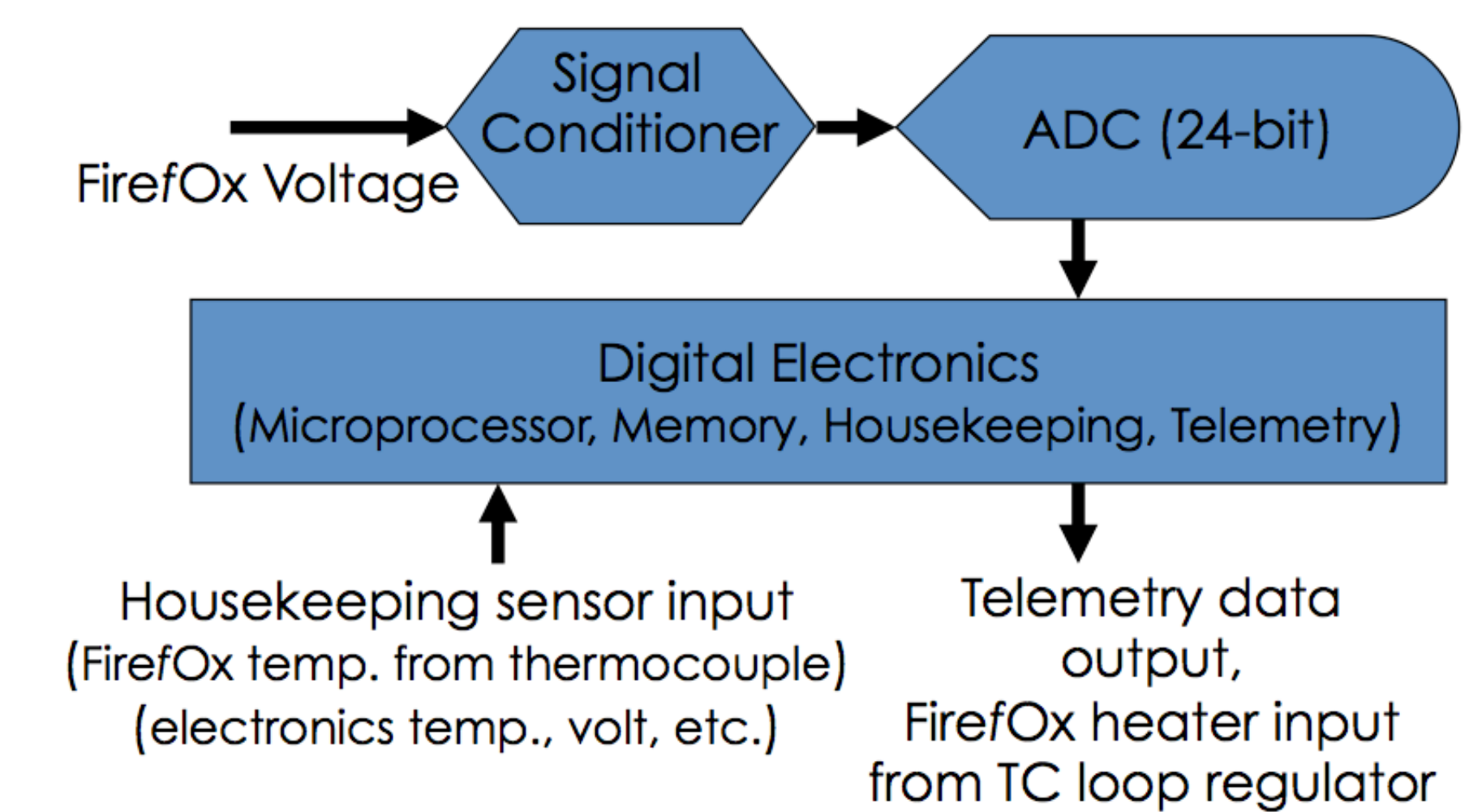


Figure 7. Preliminary electronics schematic for FirefOx sensor.

8% Yittria stabilized ZrO_2

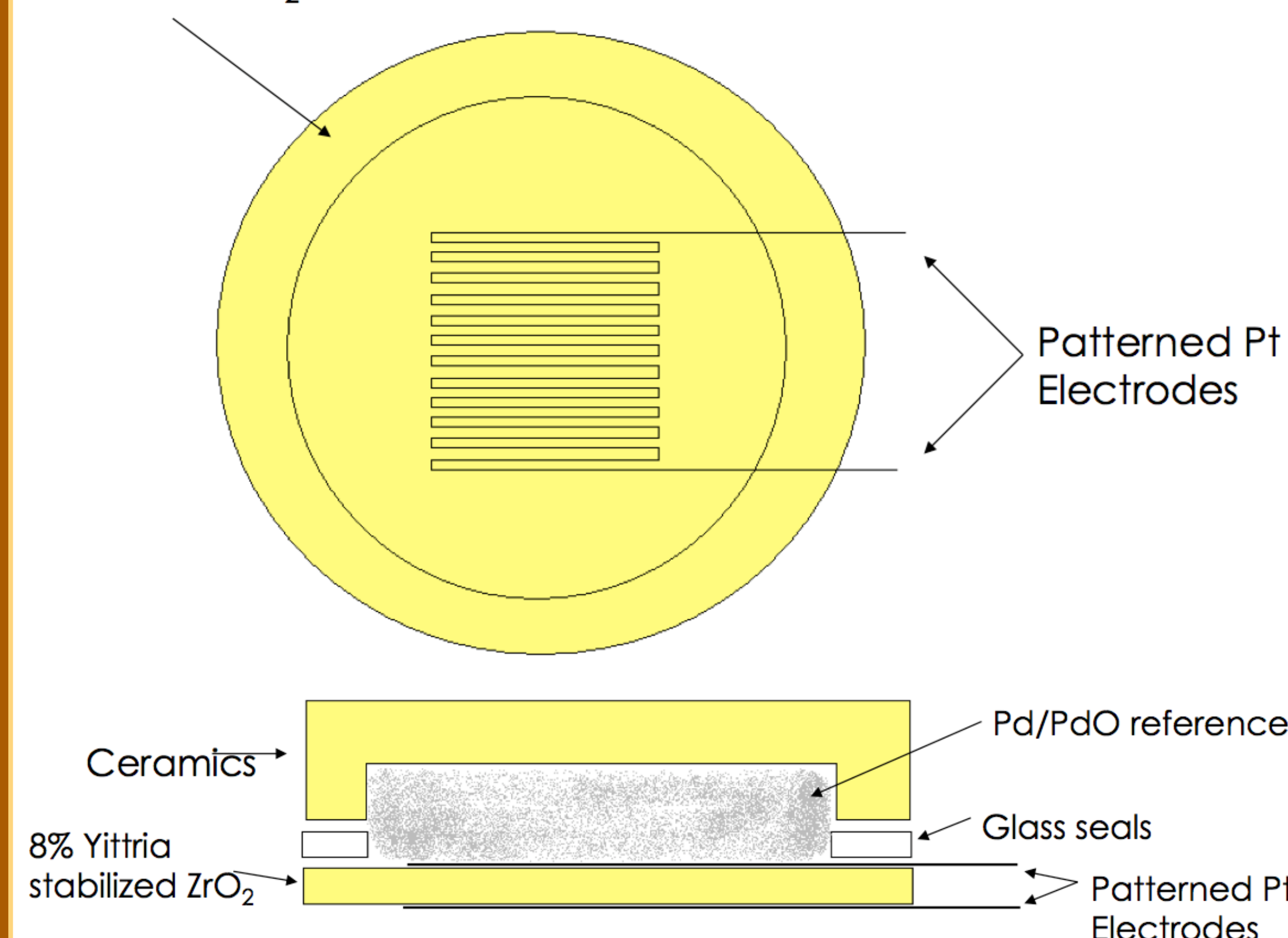


Figure 6. Preliminary design for FirefOx sensor prototype, bottom view and cut-away side view. Metal/Metal Oxide reference material is glass-sealed in ceramic "button" and capped by doped ZrO_2 . Pt electrodes on the ZrO_2 sensor measure the potential of the oxygen diffusion via the Nernst equation.

Table 2. Science Traceability

Science Question	What is the stable mineralogy and gas chemistry at the Venus surface-atmosphere interface?
FirefOx Objective	Determine oxygen fugacity of Venus atmosphere near surface (within 100m).
Science Mission Objective	f_{O_2}
Instrument Requirement	f_{O_2} measurement accuracy to $\pm 0.5 \times 10^{-24}$ of at 710-740 K over range of 10^{-18} to 10^{-24} bar.
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	f_{O_2} profile of the lower atmosphere of Venus.
Science Results	Stability regime for minerals and atmospheric gases near/at Venus surface.

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[1] Fegley and Trieman, (1992) Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions, 7-71. [2] Fegley et al., (1997). Icarus, 125(2), 416-439. [3] Mueller (1963), Science 141, 1046-1047.

FirefOx Investigation

- Linearly scalable
 - Redundancy/cross calibration
 - Sensor(s) on lander feet to measure f_{O_2} of contact surface.
- Flexible, low resource investigation
 - EPO possibilities with student teams
 - Inclusion as engineering system
 - "In the noise" for most cost/mass/power mission requirements
- Assumes accurate T and total P measurements from other sources. If not the case, sensor could be augmented.

FirefOx Roadmap

- Laboratory proof-of-concept at 1-atm complete.
- Sensor Development
 - Temperature sensitivity
 - Temperature control needed?
 - Interferences
 - Full Venus atmosphere simulation
 - IRAD / MatISSE
 - TRL 4 \rightarrow 6 in ~4 months of work
- Ready to use for multiple mission applications in short order.