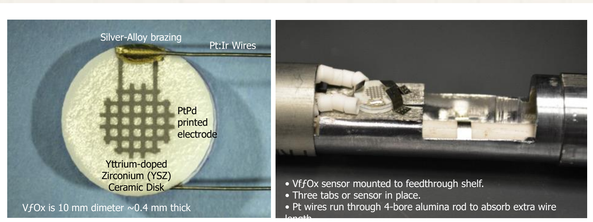
V*f*Ox In GEER:

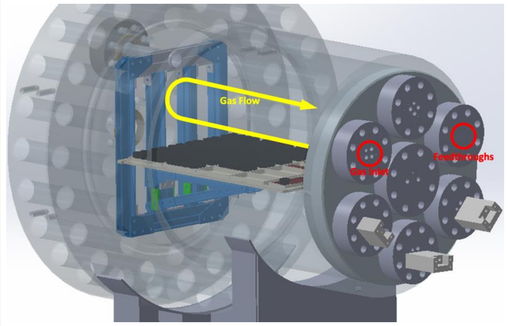
Functional Test of a Venus Oxygen Fugacity Sensor

Noam R. Izenberg[1], Martha S. Gilmore[2], Mark D. Sprouse[3] , Dorothy Lukco[4]
[1]Johns Hopkins University Applied Physics Laboratory, Laurel, MD (noam.izenberg@jhuapl.edu), [2]Wesleyan University, Middletown, CT, [3]NASA Glenn Research Center, Cleveland, OH , [4]HX5, LLC, Cleveland, OH.

DAVINCI
Deep Atmosphere Venus Investigation of Noble gases, Chemistry, and Imaging



1. V*f*Ox Sensor; and mounting in GEER

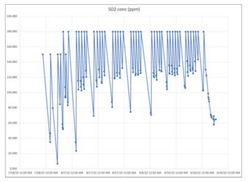


2. Glenn Extreme Environment Rig (GEER) schematic with MMT test sample tray, V*f*Ox location, and gas input flow diagram.

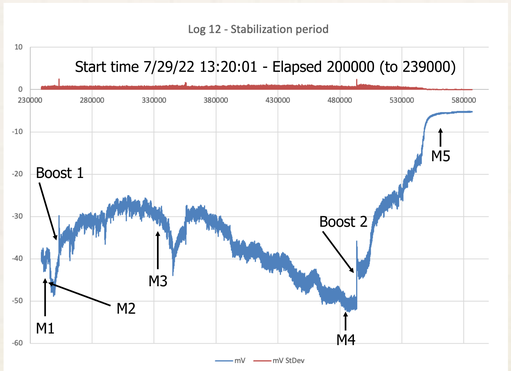
3. V*f*Ox measured voltage during heat-up phase of GEER test, with standard deviation (x100). V*f*Ox is un-powered. Its signal is generated by division of O^{-2} ions from the standard to the sample (GEER) atmosphere through the ceramic lid between electrodes. VfOx effectively "turns on" by itself when hot enough (over 250-260°C). Temperature peaked and leveled at ~460°C. VfOx voltage pinned the +/-25 mV gain on the data logger during heating, but settled to ~-50mV when chamber temperature and pressure stabilized.

INITIAL VALUES AT START OF TEST		
CO2	96.5 ± 0.8%	Requirements - maintain as measured by GC
N2	3.5 ± 0.8%	
SO2	150 ± 30 ppmv	
CO	17 ± 1.4 ppmv	Monitor with GC and perform best effort corrections.
COS	4.4 ± 1 ppmv	
H2S	3 ± 2 ppmv	
H2O	30 ppmv	Goals - if detectable, and mass spec indicates no signal, boost to starting concentrations.
HCl	0.4 ppmv	
HF	5 ppbv	
Pressure	1350 ± 15 psi	
Temperature	460 ± 2C	

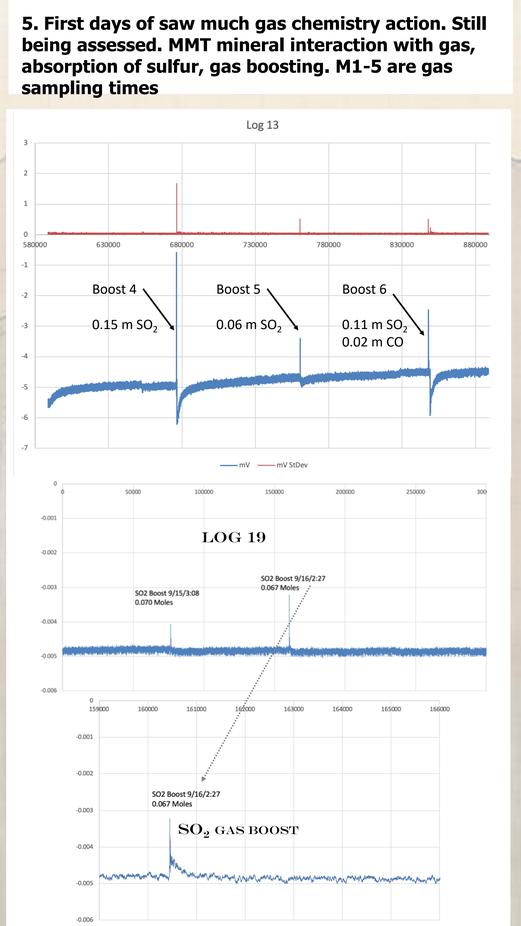
Date/Time	Delta Time (hrs)	Event	Const.	Temp (° C)	Pres (psia)	SO2 (ppm)	CO2 (mole %)	N2 (mole %)	COS (ppm)	CO (ppm)	H2S (ppm)
7/26/22 6:00 PM	0.0	Fill	All	RT		150.0	96.5	3.5	4.4	17.0	3.0
7/29/22 2:32 PM	68.5	M1		460.1	1349.1	34.9	95.8	3.7	41.5	5.0	N/A ***
7/29/22 3:26 PM	69.4	M2		460.1	1348.0	46.3	95.8	3.7	41.3	5.9	N/A ***
7/29/22 5:42 PM	71.7	Boost 1	SO2, CO*	460.0	1350.9	150.0				17.0	
7/30/22 2:57 PM	93.0	M3		460.0	1347.8	79.6	95.6	3.8	39.0	10.6	N/A ***
8/1/22 9:39 AM	135.7	M4		460.0	1346.1	6.5	95.7	3.7	37.5	12.9	N/A ***
8/1/22 12:00 PM	138.0	Boost 2	SO2	460.0	1351.1	150.0					
8/2/22 8:14 AM	158.2	M5		460.0	1349.8	84.7	95.8	3.7	36.6	5.4	4.4
8/2/22 2:17 PM	164.3	Boost 3	SO2	460.0	1350.7	150.0					
8/3/22 7:18 AM	181.3	M6		459.9	1349.1	58.1	95.7	3.7	36.1	5.8	4.2
8/3/22 9:47 AM	183.8	M7		460.1	1348.4	54.1	95.7	3.7	35.9	10.4	4.3
8/3/22 11:04 AM	185.1	M8		460.0	1347.2	52.9	95.7	3.7	35.8	3.2	4.5
8/3/22 12:20 PM	186.3	M9		460.0	1346.0	51.7	95.7	3.7	36.9	6.2	4.6
8/3/22 2:45 PM	188.8	Boost 4	SO2	459.9	1349.0	180.0					
8/4/22 7:21 AM	205.4	M10		459.9	1347.7	107.2	95.7	3.7	34.7	2.8	4.5
8/4/22 9:30 AM	207.5	M11		460.0	1346.9	93.7	95.7	3.8	35.6	3.6	4.4
8/4/22 10:52 AM	208.9	M12		460.0	1345.7	95.4	95.6	3.7	34.3	3.2	3.9
8/4/22 12:17 PM	210.3	M13		460.1	1344.1	93.3	95.7	3.6	34.8	3.5	3.7
8/4/22 2:06 PM	212.1	Boost 5	SO2	460.0	1345.1	150.0					
8/5/22 7:46 AM	229.8	M14		460.0	1343.6	83.2	95.7	3.7	34.3	7.5	3.6
8/5/22 11:19 AM	233.3	M15		460.0	1343.2	87.2	95.6	3.7	34.5	5.2	2.7
8/5/22 2:44 PM	236.7	Boost 6	SO2, CO*	460.0	1347.0	180.0				17.0	



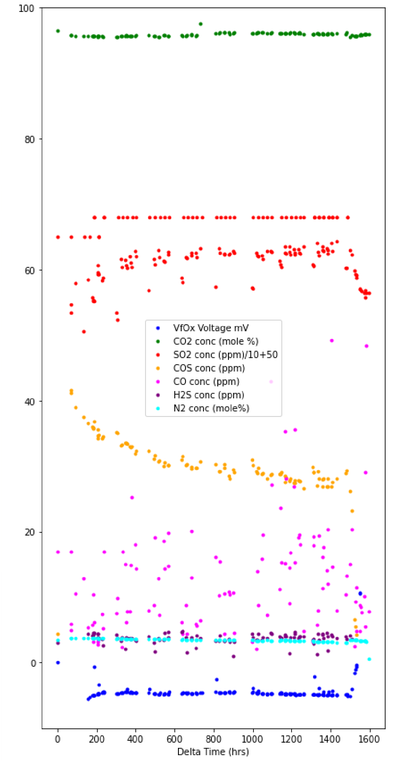
4. Initial gas mix in GEER for experiment; record of gas measurements with time; SO_2 gas boosts over time.



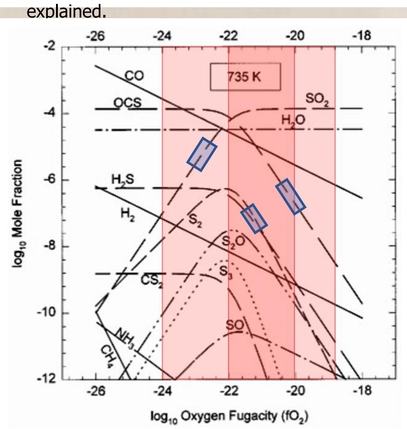
5. First days of saw much gas chemistry action. Still being assessed. MMT mineral interaction with gas, absorption of sulfur, gas boosting. M1-5 are gas sampling times



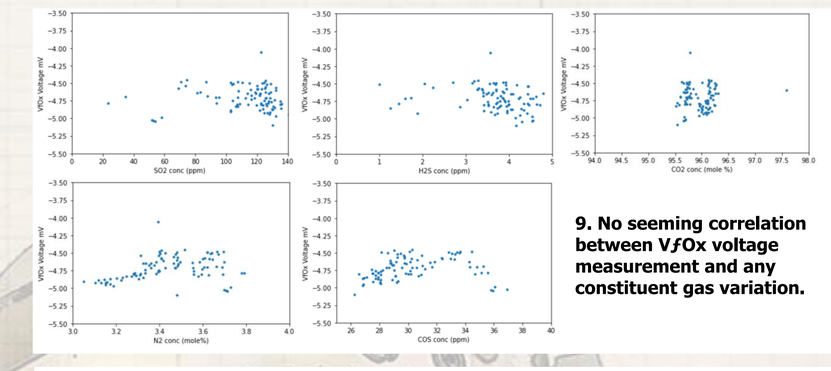
6. As test continued, equilibrium established. V*f*Ox signal stabilized, altered by gas boosts (usually SO_2, sometimes SO_2 + CO. Gas Boosts, decreased magnitude of voltage signal (possible temporary increase in chamber fO_2).



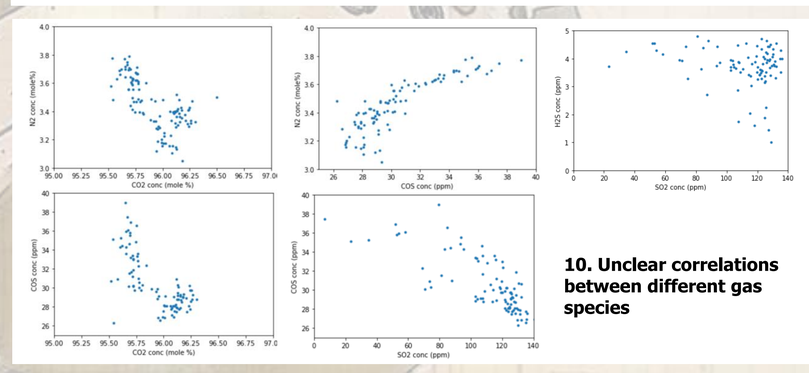
7. Measured gas quantities over time (see legend) and measured VfOx voltage though experiment. CO measurement is "presence-absence". SO_2 measurements show boosts (as in Fig. 4). COS decline is not yet explained.



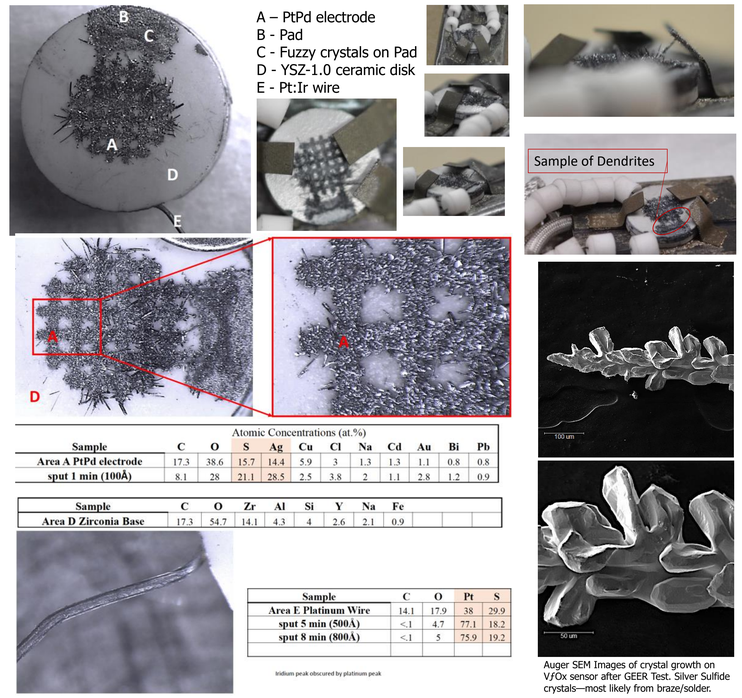
8. Potential fO_2 ranges based on measured gases from experiment. From 10^{-23} to 10^{-20}. GEER gases may never have been in the same equilibrium as calculated for Venus by [5].



9. No seeming correlation between V*f*Ox voltage measurement and any constituent gas variation.



10. Unclear correlations between different gas species



Atomic Concentrations (at.%)											
Sample	C	O	S	Ag	Cu	Cl	Na	Cd	Au	Bi	Pb
Area A PtPd electrode	17.3	38.6	15.7	14.4	5.9	3	1.3	1.3	1.1	0.8	0.8
sput 1 min (100Å)	8.1	28	21.1	28.5	2.5	3.8	2	1.1	2.8	1.2	0.9

Sample	C	O	Zr	Al	Si	Y	Na	Fe
Area D Zirconia Base	17.3	54.7	14.1	4.3	4	2.6	2.1	0.9

Sample	C	O	Pt	S
Area E Platinum Wire	14.1	17.9	38	29.9
sput 5 min (500Å)	<.1	4.7	77.1	18.2
sput 8 min (800Å)	<.1	5	75.9	19.2

Iridium peak obscured by platinum peak

Auger SEM Images of crystal growth on V*f*Ox sensor after GEER Test. Silver Sulfide crystals—most likely from braze/solder.

11. Post-test analysis of dendrite growth using X-ray photoelectron microscopy. Dendrites everywhere, some up to 2-3 mm long. All dendrites on sensor itself are silver sulfide, not platinum. The silver was highly mobilized over 60 days, spreading across the PtPd electrode. Some minor PtS growth seen on the Pt:Ir wire leads. Dendrite growth had no apparent effect on voltage measurement.

V*f*Ox stands for "Venus Oxygen Fugacity" and is the DAVINCI [1] mission's Student Collaboration Experiment (SCE). VfOx is a small single-objective sensor used to measure the partial pressure of molecular oxygen in Venus' lower atmosphere. Through the mission timeline, V*f*Ox will be designed, fabricated, tested, operated, and results analyzed by undergraduate and graduate students mentored by the SCE and DAVINCI teams in partnership with Johns Hopkins University and other institutions.

The principal of V*f*Ox [2] is a ceramic O_2 sensor derived from common applications, utilizing diffusion of O^{-2} ions between a standard (PdO) inside the sensor and the target atmosphere measured by a mW level voltage that depends directly on the standard/sample fO_2 ratio.

A 60-day environmental test of a prototype design of the sensor was conducted at the Glenn Extreme Environment Rig (GEER) [3] from August to October 2022, in which V*f*Ox (**Fig. 1**) was placed inside the experimental chamber (**Fig. 2**) and brought to Venus surface temperature (460 °C; **Fig. 3**) and pressure (92 bar) conditions, in a Venus like atmosphere (96.5% CO_2, 3.5% N_2) that included trace gases like SO_2, maintained by occasional "boosts" of extra gas during the experimental run (**Figs. 4-6**).

V*f*Ox "rode along" on this GEER run with an extensive set of minerals, including representatives of different oxygen buffer systems [4]. The post analysis of the mineral sets, combined with the recorded voltage record measured by V*f*Ox, and the pressure, temperature, and gas composition record of the GEER run itself are intended to determine V*f*Ox's sensitivity and stability, and suggest possible modifications to the sensor or its mode of use that the upcoming academic program can execute.

Experimental evaluation: **Figs. 3, 5, 6, 7, 9, 11** shows V*f*Ox data during and after the run. The GEER chamber temperature and pressure is held steady during this period, but two boosts of SO_2 were recorded regularly. In both cases, the measured voltage of V*f*Ox changes appreciably, temporarily as the balance of trace gases equilibrates. Analysis, including estimation of voltage dependence on fO_2 (**Fig. 8**), is ongoing. V*f*Ox voltage had no clear variation with major or minor gas constituent fluctuation throughout the test (**Fig. 9**). Some gas volumes appeared to be correlated (**Fig. 10**), but it is unclear if there is a dependency in evidence.

Post-test analysis (**Fig. 11**) shows significant growth of silver sulfide dendrites (not platinum sulfide) on across the Pt-Pd printed electrode of the sensor. This growth did not appear to interfere with the voltage measurement of the sensor.

References: [1] Garvin, J. B. et al. (2022), *Planet. Sci. J.*, 3.5: 117. [2] Izenberg N. R. et al. (2021) *AGU Fall Mtg*, V2021, P35H-2227. [3] Balcerski J. A. et al. (2021) *LPI Contributions*, 2628, 8054. [4] Santos and Gilmore, this session. [5] Fegley et al., (1996) *Icarus* 125,416-439.