White Paper on
Laboratory Studies in Support of Venus Exploration: Surface and Near-Surface

Laboratory experiments are crucial adjuncts to NASA's spacecraft exploration program, because spacecraft observations and data commonly can only be understood by comparison with controlled studies of analog materials in the laboratory. This assertion is especially true for Venus (*1*), where the atmosphere composition and surface conditions are unlike any place else in the solar system and are difficult to model (with few terrestrial analogs). The Decadal Survey can help advance Venus science by continuing its past support for laboratory experimental and analytical studies; specific studies are listed below.

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I. Laboratory Studies in Support of Venus Science

The surface and lower atmosphere of Venus are poorly understood, because of its thick, nearly opaque clouds and because its surface conditions (at 740K, and 92 bars CO_2 with significant SO_2) prevent most spacecraft lander operations. Venus' surface topography and geology cannot be observed except by radar (as by the Magellan orbiter) and through a few spectral windows in the near infrared. Its deep atmosphere is equally obscured by its thick cloud deck. And, unlike the Moon or Mars, we have no recognized meteorites from Venus.

Radar images and other data from Venus show a planet unlike other in the solar system, but possibly a model for similar exoplanets. Venus is geologically young, and likely has active volcanos and faulting; however, its tectonics are unlike Earth's (*2*). Geologically, Venus' surface shows low-elevation basaltic plains, basaltic central volcanoes, highlands of complex topography and thickened crust (possibly not basaltic), and even what might be a continent.

Because of its high temperatures and corrosive composition, Venus' atmosphere is chemically coupled to its surface, and Venus' surface conditions affect its interior processes. Since the properties of Venus' lower atmosphere, and the mineralogy and compositions of its surface cannot be determined from orbit, we must (for now) rely on laboratory experiments to understand how Venus works (*1, 3, 4*). Even if DAVINCI+ or VERITAS is selected as Discovery mission, laboratory experiments will still be needed to appreciate their results fully.

II. Topics for Laboratory Studies

A. Venus' Middle Atmosphere

For the most part, Venus' middle atmosphere (from the base of its cloud deck at 30 km to ~100 km) is beyond our scope. However, three aspects of the middle atmosphere are discussed here. First, is the identity and character of its 'UV absorber'; second is the locations and fates of trace elements, notably iron and phosphorus; and finally, the strong temporal variations of its SO_2 content, which is discussed in detail below under surface-atmosphere interactions.

UV-Absorber. An enduring mystery of Venus' atmosphere is its strong absorption of ultraviolet light (and longer wavelengths) by the so-called 'UV Absorber,' which is a crucial constraint on the atmosphere's thermal structure and photochemistry. Among the suggested UV-absorbing substances are $FeCl_3$, the molecule OSSO, and organic matter possibly related to life (*5-7*), each with different implications for the nature and evolution of Venus' atmosphere.

Because the nature and origin of the Absorber are not known, its relationship to the abundance and distribution of photochemical products and their diurnal and/or climatic chemical cycles is also unknown (*8-10*). Its cloud-top abundance is strongly affected by subsolar mixing and zonal transport rather than short-time scale chemical reaction (*8, 11*), but there may be linkages to SO_2 abundance at the cloud top (*10*). A key unknown about the UV Absorber is its distribution with height ; its elevation distribution is inferred from spectrography during a single descent spacecraft descent at a single local time (*12*). Inference from a single observation to the whole planet is fraught with uncertainty; to truly understand the UV Absorber (its origins, cycling, and effects), we need multiple optical observations in concert with mass spectra at multiple latitudes and local times.

Minor Elements. Related to the question of the nature and identity of the UV absorber is that of sources and lifetimes of minor elements in the middle atmosphere. If the UV absorber is $FeCl_3$, one must wonder what processes introduce Fe to the middle atmosphere, and remove it. Similarly, it is not clear whether $FeCl_3$ might be unstable, and react to form $FeSO_4 \cdot nH_2O$ or FeS_2.

Separate but related questions, raised by the prospect of extant life in Venus' middle atmosphere (*6*), are the abundance and cycling of phosphorus in the middle atmosphere. Phosphorus is commonly a limiting element for life-as-we-know; for Venus' atmosphere, it must be adequately abundant, bio-available, and replenished against losses to the surface (*13*). If the unknown UV absorber is linked to some sort of extant life in the middle atmosphere (*5*), then these questions are intimately connected to those of the nature and identity of the absorber.

Laboratory Experiments. The next probe through Venus's atmosphere will likely sample the gas where the UV-Absorber resides, and provide significant constraints on its origin. In preparation for this new data, laboratory infrastructure and experiments are needed to continue determining the optical properties of suspect molecules or substances. To understand the distribution and cycling of minor elements in Venus' atmosphere, we need to know whether they are mobile in the gas phase (e.g., as $FeCl_3$ molecules), and their stabilities and solubilities in the sulfuric acid droplets of Venus' clouds.

B. Venus' Deep Atmosphere

Understanding the physical and chemical properties of Venus's deep atmosphere, below its cloud deck (< 30 km), is important in many respects: chemical reactivity between the atmosphere and surface, heat and mass transfer with the upper atmosphere, and even power

generation for long-lived landers. The physical and chemical states of Venus' deep atmosphere is currently uncertain. Venus' atmosphere is ~96.5% CO_2, ~3.5% N_2, ~150 parts-per-million (ppm) SO_2, and smaller proportions of other species; at Venus' surface, this fluid is at ~740K temperature (T) and ~92 bars pressure (P), both covarying with elevation (*14*).

'Supercritical Fluid'? These T & P for Venus' surface are above the critical point for pure CO_2, and various workers have suggested special properties for this 'supercritical fluid,' by analogy with supercritical CO_2 at lower temperatures. Others have noted that these T & Pare low compared to those of metamorphism in the Earth, where fluid of this composition would be considered gaseous. Likewise, the effects of N_2 on CO_2 are unknown at these T & P. Some have suggested that N_2 and CO_2 may diffuse apart in the T & P gradient near Venus's surface (*15, 16*); if so, the gas composition at the surface would be different from that at elevation.

Physical Properties. This uncertainty about the state of fluid at Venus' surface implies uncertainty about its physical properties. A sure understanding of the atmosphere's viscosity and density are crucial for designing descent vehicles and balloons. Likewise, it would be important to know both for possible 'windmill' mechanisms for long-term power to landers.

Chemical Activity/Fugacity. These questions of gas versus supercritical fluid have implications for the chemical properties of the lower atmosphere. If the lower atmosphere is physically non-ideal (i.e., supercritical fluid with special properties), then its chemistry is not near ideality, and one cannot merely use the partial pressure of a gas (e.g., its molar proportion times the overall pressure) in calculations of chemical equilibria. For non-ideal mixtures, one must include multiplicative factors, fugacity coefficients, to account for the non-ideality. Fugacity coefficients can be large, and so could have significant implications for calculations based on the composition of Venus's lower atmosphere, including crucial questions of oxidation state at the surface, and hindered equilibration at lower temperatures.

Laboratory Experiments. Determining the chemical and physical properties of Venus' deep atmosphere will not be simple – the measurements must be done on analog atmosphere compositions at appropriate T & P. The simplest type of measurement is of pressure-temperature-volume, from which non-ideality is readily recognized and characterized; for instance (*17*) shows that P-T of CO_2 in the constant volume GEER chamber (NASA Glenn Extreme Environments Rig) is close to that of an ideal gas, and consistent with a van der Waals equation of state (to at least ~700K). Density and viscosity can perhaps be constrained by falling

sphere experiments, perhaps done in GEER or a synchrotron X-ray facility so the spheres could be imaged as they fell. Measurement of velocity and attenuation of pressure waves (sound) would also be useful. WHY

C. Surface-Atmosphere Chemistry

Surface-atmosphere reactions should dominate the current alteration mechanism on Venus. These reactions should include both oxidation and sulfurization and should produce thin coatings of magnetite, hematite, and/or sulfates on the surfaces of minerals and rocks. (*4, 18*)

Oxidation. Oxidation reactions of basalt and basaltic minerals with either a Venus-like atmosphere or a terrestrial atmosphere at Venus-temperatures produce iron-oxide coatings, as well as Fe^{3+} in the mineral structure. Recent work has shown that the rates of oxidation reactions on Venus should be quick – only weeks to months to coat mineral and rock surfaces with a NIR-opaque coating of iron oxides, particularly hematite but also possibly magnetite or maghemite (*19-21*). The speed of these oxidation reactions suggests that they could be quantified and extrapolated to Venus as measures of the ages of basalt lava flow.

Sulfate formation. The sulfur content of Venus' atmosphere above the cloud decks has varied significantly over time, with a pattern of very rapid increases followed by gradual, exponential-law, decreases (*22*). These variations are ascribed to volcanic eruptions that dump S-rich gas into the atmosphere, followed by chemical sequestration of sulfur to the surface, i.e., weathering of surface rocks. Preliminary experiments on reactions between SO_2-containing gas and rocks at Venus conditions produce, on laboratory timescales, thin coatings of sulfate minerals, dominantly $CaSO_4$ (anhydrite) with some alkali carbonates (*23, 24*).

Halogenation. Venus' atmosphere contains small proportions of HF and HCl, ~500 and 5 parts per billion respectively at the cloud tops. These halogens could react with surface rocks and possibly produce minerals like fluorite (CaF_2) and halite (NaCl)[1]. Such reactions could conceivably buffer the halogen content of the atmosphere (*23*). Another possible reaction would be production of chlorapatite [$Ca_5(PO_4)_3Cl$] from igneous fluorapatite, a reaction invoked to explain the radar properties of high elevations near Venus' equator (*25*).

Radar-reflective 'Snow'. The highest elevations of the mountains surrounding Ishtar appear very bright in Magellan SAR images (likewise, they have low emissivities in Magellan

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[1] Venus' surface temperature is above the boiling point of $FeCl_3$.

passive radar measurements). These radar-bright surfaces all begin at the same elevation, commonly called Venus' 'snow line.' The origin of this radar-bright 'snow' is not known; suggested causes include: rock reaction with the atmosphere to produce FeS_2 (pyrite) or other iron-rich phases (*26, 27*), deposition of metals or semi-metals (like Te) transported as vapor from hotter low elevations (*28*), and similar transport and deposition of chalcogenide or sulfosalt compounds, like BiTeS (*29, 30*). Results of some experiments have been published, but there is no consensus on whether any of these phases are stable, how common these phases would have to be to produce the radar measurements, or on how fast Venus' 'snow' might form.

Laboratory Experiments. Atmosphere-crustal interactions on Venus are being replicated in relatively simple laboratory experiments – immersing rock and mineral samples in atmosphere analog gas at T & P. Venus chambers like those at NASA Goddard and JPL are suitable for small-volume, short duration experiments, but do not (yet) have full control on internal gas compositions. The large GEER chamber at NASA Glenn is suitable for long-duration experiments and can produce and monitor complex gas compositions. Another approach is via experiments in cold-seal bombs (*21*), in which gas composition can be buffered but reaction progress cannot be monitored.

D. Venus' Near-subsurface

Rock-fluid interaction, as described above, should continue into Venus' near-subsurface, as atmosphere gases should penetrate porous rock, and as rocks are buried or dragged to depth. Conditions in this near-subsurface regime are poorly known, but are supremely important for understanding generation of Venus's magmas (are crustal volatiles involved?), its volcanic outgassing (is outgassed sulfur assimilated from the crust?), and its tectonics (what is the rheology of crustal rock?). These questions can only be answered through laboratory experiments, as even the most ambitious mission concepts don't yet include deep drilling and sample return.

The primary data one needs to know for these questions are the identities of minerals produced as Venus surface rocks weather and are brought to depth. Iron oxides and ionic sulfates are discussed above, and other products are possible. Thermochemical modeling suggests that aluminosilicates (Al_2SiO_5) and/or cordierite ($Mg_2Al_3(Si_5AlO_{18})$)) should form as weathering products; could scapolite minerals also be present? How do these weathering products, in addition to iron oxides and ionic sulfates, affect the rheology of the rock?

Given the abundance of CO_2 in Venus' atmosphere, one could reasonably wonder if carbonate minerals or carbonate-sulfate melts might occur in Venus' crust. One can point to Venus' canali – lava channels as long as 5000 km – which must have carried material that was molten at temperatures near those of Venus's surface. Venus' surface T & P are slightly above the eutectic for melting Na-K-Ca carbonate (*31*), and production of such melts (if carbonate solids were present) would have required surface temperatures only modestly hotter than they are now. Could Venus' climate have been hotter than it is now?

Laboratory Experiments. In the expected absence of deep drilling on Venus, laboratory experiments are the only way to learn about the chemistry and petrology of Venus' near-subsurface. The required experiments on mineral stabilities and reaction rates would be typical of standard methods in metamorphic petrology, albeit with fluid compositions rarely relevant to Earth systems. In the absence of water, reaction rates could be slow, and products would have to be analyzed in uncommon ways, e.g. by transmission electron microscopy (*21*).

III. Conclusion.

Venus is an extraordinarily difficult target for *in situ* exploration – its dense, caustic, and nearly opaque atmosphere, and the extreme temperature and pressure of its surface turn even the simplest analyses into severe technical challenges. In Earth-based laboratories, we can replicate most of the chemical conditions of the Venus atmosphere and surface in preparation for and in support of future missions to Venus. In support of understanding the surface and evolution of Venus, we strongly advocate for the following experimental studies in the upcoming decade:

1) Metamorphic reaction experiments relevant for Venus crust-atmosphere interactions to constrain both the rate of metamorphism and the minerals produced.
2) Experiments to constrain both the mineralogy and timing for the formation of the 'snow-line' on Venus mountain tops.
3) Explore the effects of halogens on crustal mineralogy, and radar and NIR emissivity.
4) Constrain the rate of atmospheric sulfur reacting out of the atmosphere into the crust producing sulfates.
5) Determine the chemical and physical properties of Venus' deep atmosphere.
6) Experimentally constrain the feasibility of environmental conditions required to support candidate UV absorbing species, including biogenic sources.

V. References.

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