Report on the LPI Workshop: "Venus Geochemistry: Progress, Prospects, and Future Missions," February 26-27, 2009.

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Summary

The Venus Geochemistry workshop was convened as a way to invigorate the Venus geochemistry community, and to provide assessment of the most crucial investigations for understanding the geochemistry of Venus. In brief, the recommendations of the workshop attendees include the following.

- Geochemical data are needed for all parts of Venus' surface, especially its highland areas. Venus' highlands are the oldest exposed areas, and thus have the greatest chance of revealing Venus' early history and climate.
- Geochemical investigations must address both the mineralogy of surface materials and their chemical compositions with greatly expanded elemental coverage and much improved precision (compared to prior analyses).
- Future geochemical investigations at Venus' surface will be facilitated and focused by laboratory investigations at Venus surface conditions and by studies of analog environments on Earth. These precursor studies would focus on: optical properties, E&M (Radar) properties, thermochemistry and reaction kinetics, and physical properties.
- These investigations will require pressure/temperature chambers, which could be small and specific to each investigation. Chambers suitable for spacecraft & instrument testing are not required for geochemical investigations, but would be enabling these studies if available to the science community
- NASA is encouraged to pursue every opportunity to enhance scientific and technological research relevant to Venus, as through programs in ROSES, SBIR, NESSF, and other vehicles for student support.

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Background

Venus is the "Terra Incognita" of the inner solar system –shrouded by a thick atmosphere, and with a surface so hot (the temperature of molten lead) that lander spacecraft have survived there for only hours. Yet, Venus remains supremely important for understanding the formation and evolution of terrestrial planets. Although it is Earth's twin in size (and possibly bulk composition), Venus is fundamentally different in its surface geology and tectonics, its geological history, and the composition and dynamics of its atmosphere. Why is Venus not like Earth? Or, why is Earth not like Venus? The differences between these near-twin planets must contain clues about the evolution of terrestrial planets in general, and will place constraints on potential habitability of terrestrial planets and the detectability and habitability of planets circling other stars.

We understand little of Venus' origins and evolution, in great part because we know little about the chemistry of its surface materials and near-surface environment. The few images and chemical analyses from the Venera and VEGA landers show that Venus' lowland plains are made of basalt lava rock, albeit with some unusual (and unexplained) compositions. We know nothing of the geochemistry of Venus' highlands, central volcanos, coronae, domes, etc. Venus' atmosphere provides significant constraints on the planet's history (e.g., noble gases and light isotopes), but its chemical interactions with surface materials are poorly constrained.

Purpose

Interest in Venus' surface and geochemistry has recently revived with recognition that Venus may be directly relevant to understanding Earth's climate and climate history, and that Venus may be an archetype for some planets around other stars (Grinspoon and Bullock, 2007). This increased interest in Venus was manifested in the 2006 Chapman Conference on '*Venus as a Terrestrial Planet*' and subsequent proceedings volume (Esposito et al., 2007), in creation of the Venus Exploration Analysis Group (VEXAG, http://www.lpi.usra.edu/vexag/) in 2007, and in the commissioning by NASA of a flagship mission study, the Venus Science and Technology Definition Team (Bullock et al., 2008). Thus, the Venus Geochemistry workshop was convened with several objectives:

- to assess current knowledge of Venus' geochemistry,
- to consider Earth-based investigations (laboratory and theoretical) that will enhance understanding of current data and enable future investigations,
- to explore concepts for spacecraft instruments and missions that will increase knowledge of Venus' geochemistry, and
- to energize and reconstitute the Venus geochemistry community in preparation for future spacecraft investigations.

Recommendations on the future path of Venus geochemistry were solicited in the formal presentations, and in an open discussion at the workshop's end. This report is a summary of those recommendations, suggested by scientists concerned with the geochemistry of Venus.

Summary of Sessions

The Venus Geochemistry Workshop, held at NASA Johnson Space Center's Gilruth Center in Houston, Texas, on February 26-27, 2009, was attended by approximately 65 planetary scientists with interests in Venus. The Venus Geochemistry Workshop consisted of oral sessions covering *Geological and Geophysical Constraints*, *Chemical Analyses and Planetary Inferences*, *Atmosphere and Surface-Atmosphere Interaction*, *Current Mission and Future Instruments*, and *Venus as a Terrestrial Planet – and What to Do About It*. A small number of posters was on display concurrently during the oral sessions.

Geological and Geophysical Constraints. The Venus Geochemistry Workshop began with an overview presentations about the geologic and geophysical features of Venus by W. Kiefer and the inferred petrogenetic diversity of Venus rock types based largely on the diversity of landforms (tesserae, shields, pancake domes, festoons, etc.). Three subsequent papers by M. Gilmore, V. Hansen, and M. Ivanov largely focused on tessera terrains, which constitute a significant fraction of the exposed surface. Some of the questions addressed included whether tessera terrains represent pre-volcanic shield basement rocks or are in some way genetically related to shield terrains; the extent to which they may record the deformational history of the Venusian crust; how sampling them could help illuminate the planet's geologic history; and whether they may represent an analog to continental (granitic, *sensu lato*) crust on Earth. The session concluded with a summary of volcanological features of the Venera and VEGA landing sites by J. Kargel, including inferences from lander data that some of these volcanic rocks are likely alkalic and silica-undersaturated, followed by a pair of papers on geophysical modeling of Venusian volcanic edifice construction (P. McGovern) and inferences for Venusian interior evolution using the Siberian Large Igneous Province as a Venus analog (L. Elkins-Tanton).

Chemical Analyses and Planetary Inferences. Three presentations by A. Treiman and J. Kargel focused on the planet's bulk and surface compositions as inferred from the limited data returned by the Soviet Union's Venus landers and from data collected by the Magellan spacecraft during Venus flyby. Although the uncertainties on these data are large, it seems clear that Venusian basalts are more akin to terrestrial compositions than are martian basalts, with FeO contents quite similar to terrestrial mid-ocean ridge basalts, for example. Another key feature that appears to be robust is that at least some Venusian basalts are alkalic and undersaturated with respect to silica. Some surface geomorphic features appear to be the consequence of flow of highly fluid liquid in narrow channels extending across hundreds to thousands of km, which could be produced by carbonatite-like melts. Papers by J. Filiberto and J. Jones focused on comparing experimental studies on terrestrial and extraterrestrial compositions to possible petrogenetic processes on Venus, examining the possible roles of water, crystal fractionation, and high-pressure sequestration of Fe into a core to explain Venusian basalt compositions. J. Head and A. Basilevsky contrasted the later history of Venus, as expressed by recent morphology and the limited geochemical data available, and the earlier history as indirectly inferred from atmospheric compositional features (previewing the emphasis of the workshop's second day). The session concluded with papers by Kiefer and Filiberto on attempts to infer mantle melting depths from future landed instrumental measurements, and by M. Kreslavsky on targeting such possible future mission landing sites to maximize the benefit of geologic context on whatever measurements can be made.

Atmosphere and Surface-Atmosphere Interaction. After an introduction to the Venus atmosphere by M. Bullock, Y. Yung summarized its likely sulfur chemistry in terms of reactions between sulfur species such as SO_3, H_2SO_4, SO_2, and carbonyl sulfides. A. Mahieux summarized current measurements of atmospheric constituents by instruments onboard the Venus Express mission, with emphasis on vertical compositional profiles in the middle atmosphere. S. Visscher introduced atmosphere-surface interactions with an overview focusing on the extent to which atmospheric composition is influenced by surface mineralogy and vice versa, and inferences about the possible existence of surface carbonates (including carbonatite lavas) and the roles of sulfurization and oxygen fugacity. A. Treiman presented preliminary numerical results on rock and mineral weathering in a Venus-like atmosphere, suggesting that anorthite component in plagioclase weathers to anhydrite + andalusite + quartz; diopside reacts to form anhydrite + orthopyroxene + quartz; and bulk basalt reacts to form anhydrite + cordierite + orthopyroxene + quartz (and possible iron oxide, at appropriate values of oxygen fugacity).

Current Mission and Future Instruments. This session began with a summary by N. Mueller of thermal emission measurements by the Venus Express VIRTIS instrument, suggesting lower emissivities from tessera highlands than from other terrains of similar elevation, possibly indicating felsic compositions. Higher emissivities are apparently correlated with regions of voluminous mafic lavas. J. Helbert presented a report on the development of a near-IR instrument that can survive Venus surface temperatures, and R. Grimm summarized the capabilities of a magnetotelluric sounding instrument that could be flown on a balloon in the middle atmosphere of Venus, where conditions are comparatively benign. A. Wang described a possible Raman spectrometer as part of a landed instrument package for investigating mineral-atmosphere interactions, in particular those involving sulfur. A related poster by S. Clegg summarized data from a Raman-LIBS spectrometer acquired under Venus pressure and temperatures.

Venus as a Terrestrial Planet – And What to Do About It. The final session of the workshop focused on the larger issues of Venus as a type example of terrestrial planet evolution. D. Grinspoon talked first on Venus's history, including the reasons for believing that it once had a (water) ocean, and the causes and timing of its transition to the current dry super-greenhouse climate. M. Bullock then spoke on the sulfur cycle in Venus' atmosphere, and the potential that measurement of atmospheric gas abundances can be 'inverted' to derive rates of climate change (i.e., by volcanic eruptions). Finally, M. Zolotov described geochemical models for the composition and evolution of Venus' early ocean, based on reasonable estimates of rock compositions and temperatures. That early ocean is predicted to have been a brine rich in Ca, Na, and Cl, and only slightly acidic. After the ocean evaporated, the residual chloride minerals could play significant roles in magma genesis and mantle tectonics.

Major Geochemical Issues

Based on presentations and discussions at the Venus Geochemistry Workshop, four general geochemical issues were discussed; these echo from, and are discussed further in the VEXAG (2007, 2009) and VSTDT (2009) reports.

First is the need for mineralogical and chemical analyses of many different types of terrains on the Venus surface, including: tessera highlands, Ishtar Terra and Lakshmi Planum, the highlands surfaces coated with radar low-emissivity material; coronae, shield volcanos and shield fields, and lava plains. Mineralogical analyses should include sensitivity to common silicate minerals, and to iron oxides and sulfides. Chemical analyses should include major and minor elements of basalts and common (terrestrial) rocks to a sensitivity adequate for identification and classification. Trace element abundances are of secondary importance, except for the heat-forming elements K, U, and Th.

Second is the need to understand the chemical composition and behavior of Venus' atmosphere near its surface. Most important are the abundances of C-O-H species, and of their reaction rates, both in the gas phase and by heterogeneous catalysis at the surface. Abundances of hydrogen-bearing species are crucial for understanding the past history of Venus, and cycling from the major cloud decks to the surface. Finally, it is important to determine abundances of volatile semi-metals, such as Pb, Te, and Bi, for their potential importance in forming the low-emissivity material of the highlands.

Third is the need to understand the rates and extents of atmosphere-surface interactions. What chemical components in the atmosphere are buffered by atmosphere-surface interactions? What are the mineral products in surface materials of atmosphere-surface interactions? What are the rates and extents of gas penetration into, and reaction with, Venus' subsurface?

And fourth is the need to understand Venus' past geochemical systems – the interacting atmosphere, lithosphere, and putative hydrosphere. How would those systems have behaved and interacted in Venus' ancient environments? And, how might we recognize, now, the existence and operation of such past geochemical systems?

Spacecraft Missions

Addressing these geochemical problems will require new analytical data from spacecraft at Venus, especially from landers and near-surface vehicles (e.g., capable of imaging the surface, probing the surface, and/or analyzing the near-surface atmosphere). Questions related to spacecraft mission design and instrumentation are not covered in this report, because they are discussed in the VEXAG reports (VEXAG, 2007, 2009), and because a model flagship-class spacecraft mission is described in the Venus Science and Technology Definition Team report (VSTDT, 2009).

Discussions at the Venus Geochemistry Workshop emphasized two top-level issues for spacecraft-based investigations.

1) The quality of geochemical data (i.e., elements and species analyzed, analytical accuracy and precision) must be significantly improved relative to those of the Pioneer, Venera, and VEGA missions. Current analytical instrumentation is likely to be far better than on the earlier missions, but operations in the Venus environment are difficult. Instrumentation must be chosen to match the mission's geochemical goals.
2) Site selection for data collection (i.e., latitude and elevation of atmospheric analyses, geologic setting of landing site) is critical. Many workshop participants emphasized atmosphere chemical analyses at the surface and below the cloud deck, and supported acquisition of surface geochemical analyses from carefully selected locations in the tessera terrain.

Precursor Investigations: Theory and Laboratory

The open discussion of geochemical questions for Venus centered on laboratory and theoretical studies, which provide paths toward understanding the data in hand, and predicting which future investigations are most likely to be fruitful. Many theoretical and laboratory investigations were suggested centering on five themes: optical (visible and near-infrared) properties of Venus materials at relevant pressure and temperature; E&M (radar) properties of Venus solid materials at relevant pressure and temperature; thermochemical and kinetic study of chemical reactions (gas phase, gas-solid, solid-magma) at relevant pressure and temperature; physical and mechanical properties of Venus surface materials; and studies of terrestrial environments and products that are analogous to those on Venus. It is important to note that spectrometric measurements of Venus surface materials and reactions will require calibrations and reference spectra taken in relevant physical and chemical environments. In many cases, interpretation of those data will require supplementary thermochemical data.

Optical Properties: Gases. Perhaps surprisingly, the experts present at the Venus Geochemistry Workshop agreed that the optical properties of Venus atmosphere gases are inadequately known. It was noted that the absorption and scattering properties of CO_2 at Venus-relevant pressures and temperatures are not known well, nor are those of important C-O-S species. It is not clear, either, that there are good data on scattering from particulates in the supercritical CO_2 fluid at the Venus surface.

Optical Properties: Solids. In general, there are limited data on the optical properties (reflectances and emissivities) of likely rocks and minerals at the Venus surface. This dearth of data is being addressed by several groups (e.g., Helbert et al., 2009; Yamanoi et al., 2009), but much work remains.

E&M (Radar) Properties. Considerable effort has been (and is being) expended to understand the radar properties of rocks and related planetary materials. The impetus for collecting these data is in studies of bodies at Earth-ambient or cold temperatures, like Mars and comets (e.g., Kofman et al., 2004; Herique et al, 2002). However, there seem to be few data on the radar properties of geological materials at high temperatures like that of the Venus surface (save a few incidental measurements on molten lava; Heggy et al., 2008).

Thermochemistry/Kinetics: Gases: Although the thermochemistry and stability of gas species in C-O-S (e.g., S_2, S_3, CO, COS) are known well, the kinetics of their reactions are poorly known at Venus pressure and temperature. Reaction kinetics are especially important for evaluating whether the low-emissivity material on Venus' highlands could be iron sulfide. If reactions are fast, iron sulfide is possible; if the reactions are slow, iron sulfide is unlikely (Visscher, pers. comm.).

Thermochemistry/Kinetics: Solids. The groundbreaking study of calcite stability in the Venus atmosphere (Fegley and Prinn, 1989) showed that solid materials at Venus' surface can react rapidly with its atmosphere. However, this effort needs to be extended by comprehensive laboratory studies of atmosphere-surface interactions at appropriate pressures and temperatures. Following are a selection of topics in need of thermochemical analysis (theoretical and laboratory) and kinetic studies (laboratory):

- Reactions between surface atmosphere and igneous glasses, including basaltic (tholeiitic through highly alkaline), andesitic, and rhyolitic (i.e., granitic) compositions;

- Reactions between surface atmosphere and individual minerals, such as might crystallize from igneous rocks (e.g., plagioclase, olivine, pyroxenes, silica, Fe-Ti-Cr oxides);
- Diffusion rates of cations and anions into/through likely rocks and minerals at Venus surface conditions;
- Diffusion/reaction of atmosphere into likely surface and subsurface materials (i.e., metasomatism);
- Stability and conditions of formation of ionic melts (carbonate-sulfide-halide) in the Venus crust; and
- Thermochemical data on selected compounds, like sulfate scapolite, and sulfate sodalite (haüyne).

In addition, many thermochemical/kinetic studies are crucial to understanding possible past geochemical systems and environments on Venus. On the theoretical side, there is a need for continuing investigation of geochemical/geophysical models of ancient Venus, e.g. formation and loss of a putative early ocean (e.g., Zolotov & Mironenko, 2009). On the experimental side, it is important to know how rapidly the products of an early geochemical system might be modified in the current Venus environment, and how these products might be recognized. In particular, one might consider modifications of: sedimentary textures; aqueously deposited carbonates and silica (biogenic or not); organic matter; and isotopic or chemical signatures characteristic of low-temperature or biological processes.

Physical/Mechanical Properties. Although studies of physical and mechanical properties are not inherently geochemical, they do provide crucial data for geochemical modeling, e.g., density, porosity, and viscosity (of likely surface flows). In particular, it would be important to understand how chemical reactions between Venus rocks and atmosphere affect properties such as volume (from incorporation of atmospheric S into the rock, and subsequent expansion and fracturing), porosity and permeability (for diffusion/reaction models above), and cohesiveness (possibly for understanding radar properties). Incorporation of data on viscosities of basaltic and, perhaps, ionic liquids may help understand some landforms and in turn provide added context for interpreting geochemical data.

Earth Analog Studies. The difficulties of field exploration on Venus are so large that efforts must be made to find comparable environments here on Earth – places where one can observe chemical processes and effects that occur in Venus-like conditions.

In igneous geochemistry, the limited analyses of the Venus basalts include ultrapotassic varieties, which are very rare on Earth. It would be important to look again at these basalt compositions in terms of terrestrial petrogenetic environments. Some of this work was done shortly after the Venera and VEGA landings, and could be updated with a modern appreciation of ultrapotassic rocks. Such studies could build on an existing, fairly substantial literature on the experimental phase relations of, and element partitioning in, alkaline magmatic systems.

In surface atmosphere interactions, analog environments may be found in some in settings of rock metamorphism. An example would be in water-absent 'hornfels-facies' metamorphism, which obtains (for the most part) in the shallow sub-surface near igneous intrusions. In such environments, one could assess relevant mineral equilibria, rates of reaction and of texture modification (e.g., obliteration of sedimentary textures), and obliteration of chemical and isotopic signatures of past environments.

Technology Enhancements

Lastly, workshop attendees discussed technology enhancements in service of geochemical investigations. Enhancements to spacecraft and robotic instrument technology are covered in other reports, including those of Kolawa (2007) and the VSTDT (2009). The Venus Geochemistry workshop attendees noted the need for environmental chambers that are capable of reproducing Venus surface conditions: pressure, temperature, and gas composition. Many such chambers are now in use in laboratories across the world, and can be specific to the needs of particular measurements or experiments. The attendees saw no need, from the perspective of geochemistry, for large chambers such as could be used for spacecraft system tests. However, if such chambers were available, they could be used to good advantage in geochemical precursor investigations.

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