



EXPERIMENTAL STUDIES OF ATMOSPHERE-SURFACE INTERACTIONS ON VENUS

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ABSTRACT

We review the sulfur cycle, oxidation state of the surface and near-surface atmosphere, and the decomposition rate of fossil hydrous minerals on the surface of Venus. For each of these chemical weathering processes we discuss what has been learned and what key questions remain unanswered. We focus on these three types of atmosphere-surface interactions because they appear to play major roles in determining the composition of the atmosphere, clouds, and the surface, e.g. by serving as a sink for SO₂, by controlling the extent and rate of basalt oxidation, or by acting as a sink/source for atmospheric water. Unfortunately, no direct mineralogical data exist for the Venusian surface. Currently, the only way to study atmospheric-surface chemistry on Venus is through laboratory experiments. The results from these experiments will help guide the design of future spacecraft experiments that could make direct mineralogical observations by using techniques such as XRD and/or imaging infrared reflectance spectroscopy. These experimental results along with direct mineralogical data could prove or invalidate models proposed over the years.

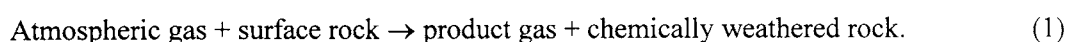
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INTRODUCTION

Venus and Earth have similar radii and densities and formed next to each other within the inner solar system, yet they have vastly different atmospheres and geology. Were these differences present from the very beginning (accretion) or did they develop over time? This is an important question in planetary science, but no conclusive answers have surfaced. In order to address this question, several missions and Earth-based observations were made over the past 50 years to gather information about Venus' atmospheric and surface chemical composition. The unusual mix of gases in Venus' atmosphere, along with the high temperatures and pressures, prompted numerous theoretical studies about possible reactions between the atmosphere and the surface. For example, thermodynamic modeling predicts the observed abundances of gases such as CO₂, HCl and HF using probable reactions between the atmosphere and reactive minerals on the surface. A theoretical framework for studying atmosphere-surface interactions on Venus has been developed and currently, we can only check these proposed interactions via laboratory experiments. Even though no direct mineralogical data exist for the Venusian surface, experiments could guide future observations made via landers, penetrators, rovers, and/or automated balloons (aerobots) by using techniques such as XRD and/or imaging infrared reflectance spectroscopy. Such mineralogical information and experimental results could prove or invalidate models proposed over the years.

Atmosphere-surface interactions play a significant role in determining the composition of both the atmosphere and surface. At Venus' modal radius, the surface temperature is ~ 740 K and the surface pressure is 95.6 bar (Lodders and Fegley 1998). This temperature/pressure field is similar to that for low-grade metamorphic regimes on the Earth (Klein and Hurlbut 1993). In the 1960s R. F. Mueller and J. S. Lewis theorized that reactions between the surface and the atmosphere of Venus buffered (or regulated) abundances of several gases (e.g. CO_2 , HCl, HF). Similar buffering reactions occur during metamorphism on Earth. Present knowledge shows that not all gases in Venus' atmosphere are controlled by buffering reactions. For example the abundances of SO_2 and OCS are apparently regulated by a balance (or imbalance) of sources (volcanism for SO_2 , iron sulfide weathering for OCS), and sinks (calcium sulfate formation for SO_2 , thermal and/or photochemical conversion to SO_2 for OCS). However, atmosphere-surface reactions play a key role in these cases as well.

Reaction (1), below, illustrates a schematic atmosphere-surface reaction on Venus:



One or more minerals in a rock on Venus' surface reacts with a gas in the overlying atmosphere to produce a chemically weathered rock (or "soil") and possibly a product gas. If reaction (1) reaches equilibrium in a short time period then it is said to be a buffering reaction. However, if reaction (1) does not reach equilibrium then the reaction rate, and not the equilibrium constant, is the key factor. In the latter case reaction (1) is a sink for the reactant gas and a source for the product gas.

Several detailed reviews have been written regarding these types of interactions (e.g., Fegley *et al.* 1997b, Fegley and Treiman 1992, Lewis 1970). Our goal in this paper is not to give an exhaustive review about all possible atmosphere-surface interactions on Venus. Rather, the goal is to briefly discuss three reactions that are important for determining the composition of Venus' atmosphere, clouds, and surface.

SULFUR CYCLE

Volcanoes on both Earth and Io emit sulfur dioxide and it is also expected to be an important volcanic gas on Venus. The model that describes the cycling of sulfur (as SO_2 , OCS, H_2SO_4 , etc.) through the atmosphere, the clouds and the surface is called the sulfur cycle. The sulfur cycle was proposed by van Zahn *et al.* (1983) and Prinn (1985) and a revised version of this cycle that incorporates information from experimental studies is given in Figure 1 (Fegley *et al.* 1995). The sulfur cycle is complex because gas-phase, gas-aerosol, gas-solid reactions, and volcanism are involved. Here we give a brief description of the processes that affect SO_2 . Volcanism emits SO_2 into Venus' atmosphere where it participates in a number of reactions. Two principal (and competing) reactions are photochemical conversion of SO_2 into H_2SO_4 aerosol droplets in the clouds and reaction of SO_2 with Ca-bearing minerals on Venus' surface to form anhydrite (CaSO_4). Together, volcanism and surface-atmospheric reactions control the SO_2 abundance on Venus.

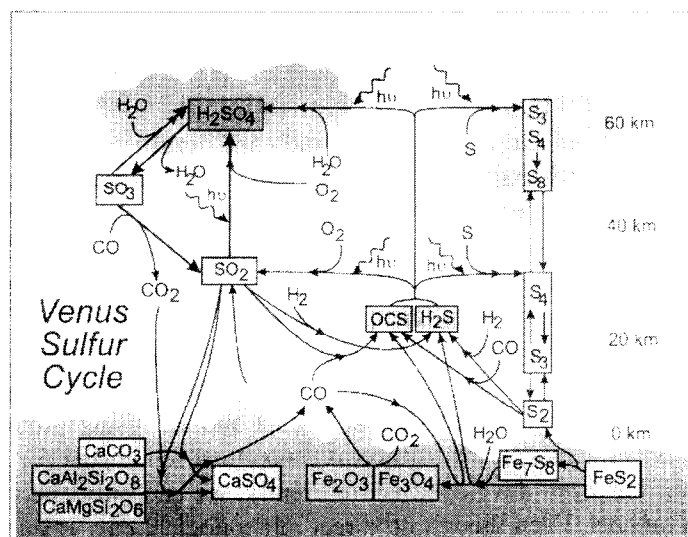
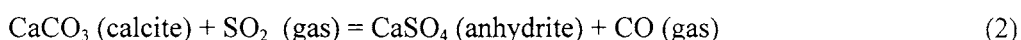


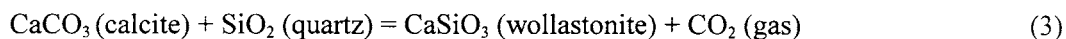
Fig 1. The Venus sulfur cycle proposed by von Zahn *et al.* (1983), Prinn (1985), and modified by Fegley *et al.* (1995).

Sulfur dioxide is the third most abundant gas (150 parts per million by volume = 150 ppmv) below the clouds of Venus with only CO₂ (96.5%) and N₂ (3.5%) being more abundant (Lodders and Fegley 1998). Sulfur dioxide is the principal sulfur gas in the atmosphere of Venus and UV sunlight photo-oxidation of SO₂ is the source of the global sulfuric acid clouds on Venus (Figure 1). Along with CO₂, sulfur dioxide is one of the most important greenhouse gases in Venus' atmosphere. In December 1978, gas chromatographs on Pioneer Venus and Venera 11, 12 spacecraft made the first observations of SO₂ below Venus' clouds and recorded ~150 ppmv of SO₂. Subsequent observations of SO₂ by Venera 13, 14 and Vega 1, 2 spacecraft found less SO₂ in Venus' lower atmosphere. However, later Earth-based IR observations of Venus' nightside showed about the same amount of SO₂ as originally reported by Pioneer Venus and Venera 11, 12. Therefore, the abundance of SO₂ in Venus' atmosphere below the clouds and variations (if any) of the SO₂ abundance with altitude and with time are in question.

An important part of the sulfur cycle is the interaction of atmospheric SO₂ with the surface. One such reaction occurs when SO₂ reacts with calcite to form anhydrite as shown in the following net reaction:



The observed abundance (~150 ppmv) of SO₂ on Venus is about 100 times larger than expected because reaction (2) between SO₂ and calcite should reduce the atmospheric abundance of SO₂ to the equilibrium value of a few ppmv if calcite and anhydrite coexist. Calcite is predicted to be present on the surface of Venus because it appears that the CO₂ pressure is buffered through the (Urey) calcite-wollastonite reaction (Lewis 1970):



There is excellent agreement between observed and calculated CO₂ pressures at Venus surface temperatures for the calcite-wollastonite equilibrium buffer (Fegley and Treiman 1992). This agreement is strong evidence that calcite does exist on Venus. Reaction (2) must be taking place on Venus today because the S/Ca atomic ratio (~0.2) measured by the Venera and Vega XRF analyses of Venus' surface is less than the ratio of unity expected if all Ca had been converted into anhydrite. Experimental work (Fegley and Prinn 1989) showed that reaction (2) is too slow to reach equilibrium at Venus' surface temperatures (660-740 K) but it is rapid on geologic timescales and would take about two million years to reduce the observed SO₂ abundance down to the equilibrium value. Volcanic outgassing of SO₂ is needed to replenish the SO₂ lost by anhydrite formation and the required volcanism rate depends on the sulfur content of the erupted material. If the erupted material has the same average S/Si ratio as the Venus surface at the Venera 13, 14 and Vega 2 landing sites where these two elements were analyzed, the implied volcanism rate is ~1 km³/year (Fegley and Prinn 1989). This rate is similar to the rate of sub-aerial volcanism on Earth and is about twenty times smaller than the rate of plate creation (18-20 km³/year) on Earth.

Calcite is not the only the Ca-bearing mineral that can react with SO₂. Other reactive minerals are Ca-bearing pyroxenes and feldspars. Both types of minerals are common in igneous rocks and would be expected to be found on Venus' basaltic surface. The computed (normative) mineralogies at the Venera 13, 14, and Vega 2 landing sites include Ca-bearing pyroxenes and feldspars (Barsukov *et al.* 1982, 1986). These minerals also serve as a sink for sulfur dioxide in the Venusian atmosphere (see Figure 1b of Fegley and Prinn 1989).

OXIDATION STATE

Another area of interest is the oxidation (redox) state of the surface and the lower atmosphere. The oxygen partial pressure (commonly called the oxygen fugacity) of the near-surface atmosphere controls the iron mineralogy and the trace gas chemistry at Venus' surface. The oxygen fugacity of the near-surface atmosphere controls the relative amounts of reduced versus oxidized carbon, sulfur and hydrogen gases via net chemical reactions exemplified by

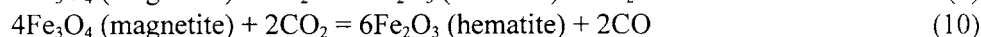
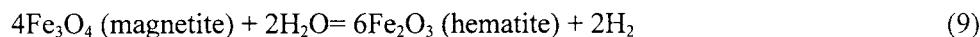


Sufficiently high oxygen fugacities favor CO_2 , SO_2 , and H_2O while lower oxygen fugacities favor CO , OCS , H_2S , and H_2 . Based on present knowledge of Venus' atmospheric composition, which is mainly derived from analyses at 12 km and higher, the crossover point between reduced (OCS) and oxidized (SO_2) sulfur gases is at about $\log_{10}f\text{O}_2$ (bar) ~ -22 (Fegley *et al.* 1997a).

In addition to regulating the type of gases found in the near-surface atmosphere, the oxidation state also controls the iron mineralogy of the surface. For example, magnetite is a black mineral that contains both Fe^{2+} and Fe^{3+} in the ratio of one Fe^{2+} to two Fe^{3+} . Upon oxidation, magnetite converts into the reddish mineral hematite where the Fe^{2+} has turned into Fe^{3+} . The net reaction can be written as

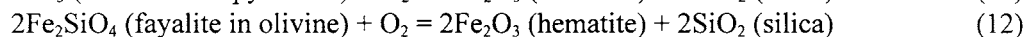
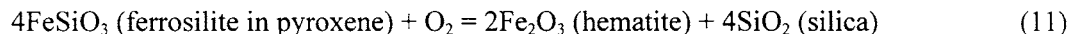


to emphasize the importance of the oxygen fugacity for the iron mineralogy of Venus' surface. Equivalently, reaction (8) can be expressed as



to emphasize the involvement of gases in Venus' atmosphere.

The Fe^{2+} present in igneous rocks (e.g., as the FeSiO_3 component in pyroxenes or as the Fe_2SiO_4 component in olivines) is also susceptible to oxidation. These types of reactions are schematically represented by



which could also be expressed as reactions involving CO_2 and H_2O to emphasize the involvement of atmospheric gases rather than the influence of oxygen fugacity (as done above).

Knowledge of the oxidation state of the lower atmosphere is necessary in order to predict what type of chemical weathering occurs on Venus' surface and what minerals we might expect to find. A recent study by Fegley *et al.* (1997a) examines the oxidation state of the lower atmosphere and surface of Venus. One of their conclusions that relate directly to atmosphere-surface reactions is that magnetite would be stable only on the lowest and hottest plains because the CO-CO_2 conversion is quenched at higher elevations (~ 0.7 km and above) where cooler temperatures exist. As a result the atmospheric oxygen fugacity is higher than predicted at chemical equilibrium and hematite forms instead of magnetite. The model of Fegley *et al.* (1997a) explains why spectral reflectance data indicated that hematite was present at the Venera 9 and 10 landing sites (Pieters *et al.* 1986). This is an ideal example of results from a theoretical study, confirmed by spectral data, that could be used to design future experiments sent to Venus.

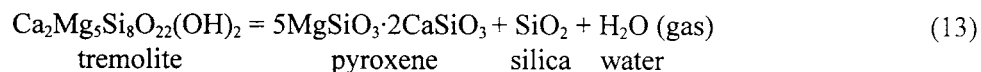
FOSSIL HYDROUS MINERALS

Venus' atmosphere has approximately 1000 times less atmospheric water than Earth's troposphere. The sub-cloud water content is 30-40 parts per million by volume (ppmv) compared to 1 - 4% for water in Earth's troposphere (Lodders and Fegley 1998). Even though Venus has a low water vapor abundance, water plays an important role because it is a major greenhouse gas, is the major reservoir of hydrogen in Venus' lower atmosphere and is an important factor in chemical weathering of the surface minerals (Fegley and Treiman 1992).

The high atmospheric deuterium/hydrogen (D/H) ratio of $(2.5 \pm 0.5) \times 10^{-2}$ in Venus' atmospheric water vapor (Donahue *et al.* 1997) suggests that Venus may have had more water in its past. The high D/H ratio implies a preferential escape of hydrogen to deuterium. The Venusian D/H ratio is 160 ± 32 times the D/H ratio of 1.56×10^{-4} in standard mean ocean water (SMOW) on Earth. The D/H ratio of Venus's atmosphere suggests that Venus once must have had the equivalent of at least a four meter deep global ocean and may have had as much as a 530 meter deep global ocean. However, some interplanetary dust particles, meteorites, and comets also have high D/H ratios (Irvine *et al.* 2000). Therefore, it is possible that Venus could have accreted matter with different D/H ratios than did Earth. Even though the high D/H ratio is a good indicator, by itself, it is only indirect proof that Venus was once wet. However, the existence of fossil hydrous minerals within the surface mineralogy would be irrefutable evidence that Venus did indeed have a wetter history.

For over thirty years the planetary community has debated the existence of hydrous minerals on Venus without knowledge of their decomposition rates (e.g., Mueller 1964, Lewis 1970, Zolotov *et al.* 1997). If there had been more water in Venus' past, it is possible that hydrous minerals formed on or within the surface. However, equilibrium thermodynamic calculations predict that these minerals are unstable at current Venusian surface temperatures and pressures (Zolotov *et al.* 1997). Johnson and Fegley (2000) give the first study of hydrous mineral decomposition rates with applications to Venus.

At Venus' elevated temperatures, these hydrous minerals must be thermally stable in order to retain water. One such thermally stable group is the amphiboles, a hydrous silicate mineral group found in igneous and metamorphic rocks (Deer *et al.* 1997) For example, tremolite is a simple amphibole that is characteristic for low-grade metamorphosed ultrabasic rock. In order for tremolite to be stable on the plains of Venus at 740K, the atmospheric partial pressure of water vapor for the decomposition reaction (13) must be approximately 6 bar.



This value is approximately 2,000 times greater than the current H₂O partial pressure on Venus (about three millibar), therefore tremolite should decompose. However, the existence of tremolite on Venus cannot be summarily dismissed because the rate of reaction (13) is unknown. For example, diamond is thermodynamically unstable at the Earth's surface, yet diamonds do not turn into lumps of graphite. If tremolite formed on or (more likely) below the surface during a wetter era in Venus' past, the results suggest that tremolite can survive for geologic timescales under current Venus surface conditions.

Johnson and Fegley (2000) examined the kinetics of reaction (13) by isothermally heating tremolite powder samples of known weight, surface area and composition in dry flowing CO₂ or N₂ gas under one atmosphere of pressure. Carbon dioxide and N₂ are the two most abundant gases in Venus' atmosphere and data show that tremolite decomposes at the same rate in both gases. When tremolite is heated and decomposes, it loses water. Over 250 experiments, ranging in duration from hours to over sixteen months, were done at temperatures of 1045-1238K.

The extent of reaction was measured as a function of time by measuring the weight (water) loss. Typical decomposition weight loss curves are shown in Figures 2 and 3. Decomposition of tremolite to the expected reaction products, namely two pyroxene solid solutions (enstatite saturated diopside and diopside saturated enstatite), the cristobalite form of SiO₂, and water vapor was confirmed by electron microprobe, X-ray diffraction (XRD), mid-infrared spectroscopy, and scanning electron microscope (SEM) analyses. Figure 4 shows the decrease of the mid-infrared hydroxyl (OH) peak (3674 cm⁻¹) versus extent of decomposition.

The Avrami-Erofe'ev kinetic rate model best describes what was observed in the SEM images. The model rate equation is $kt = (-\ln(1-\alpha))^{1/2}$ where k is the rate constant (hr⁻¹), t is in hours, and α is the fraction reacted of the sample ($\alpha = \% \text{ wt. loss} / \% \text{ theoretical wt. loss}$, which is 2.22%). This model takes

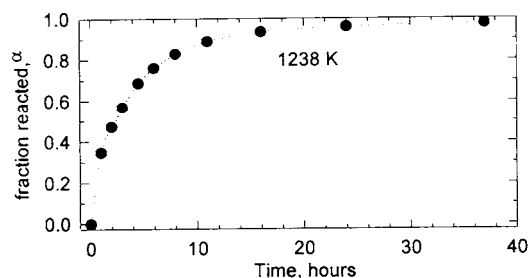


Fig. 2. A typical weight loss curve for tremolite decomposition at 1238 K in carbon dioxide at ambient pressure.

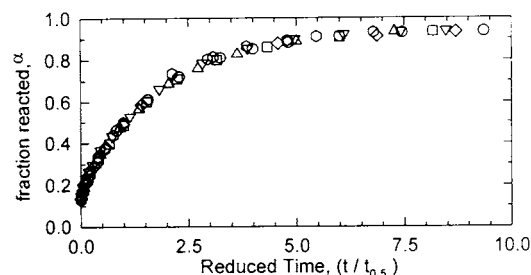


Fig 3. Fraction reacted versus time normalized to 50% decomposition time ($t_{0.5}$) for tremolite heated in CO_2 . Temps: \triangle 1238K, \square 1213K, \circ 1196K, ∇ 1178K, \diamond 1148K, \diamond 1120K

into account random nucleation and growth given that as the nuclei grow, nucleation sites are both generated and removed (Bamford and Tipper 1980). The Arrhenius plot in Figure 5 shows the linear relationship between the log of reaction rate constants and inverse temperature. Analysis of the data gives the rate equation

$$\log_{10}k \text{ (hr}^{-1}\text{)} = 17.85(\pm 0.21) - 23,299(\pm 1,215) / T \quad (14)$$

where T is in Kelvin with a corresponding activation energy of $446 \pm 23 \text{ kJ mol}^{-1}$.

The rate of reaction (13) was extrapolated to Venus surface temperatures ($\sim 660\text{--}740\text{K}$) using this rate equation (14). It becomes increasingly difficult for tremolite to decompose as the temperature decreases. If powdered tremolite such as used in these experiments were placed on Venus' lowlands at 740K today, the grains would reach 50% decomposition in 3.8 billion years. Furthermore, the normalized time plot in Figure 3 shows that complete decomposition of tremolite takes several to ten times longer than the time required for 50% decomposition. Figure 3 shows the fraction of tremolite reacted versus time normalized to the time required for 50% decomposition of the tremolite (i.e., $t/t_{0.5}$). This type of plot (e.g., see Bamford and Tipper 1980) shows that tremolite decomposition follows the same kinetic behavior and occurs by the same mechanism (although at a different rate) at the temperatures studied. One tremolite sample, currently being heated at 740K, recently passed its two year reaction anniversary and has not decomposed. Further heating of this sample is ongoing, but any decomposition is not expected to occur. The findings suggest that tremolite grains do not decompose in geologic timescales at current Venusian surface conditions.

The conclusion that tremolite, once formed, would survive on Venus is robust. However, computer models that are currently under debate, indicate that Venus might have been 100K hotter in the past than

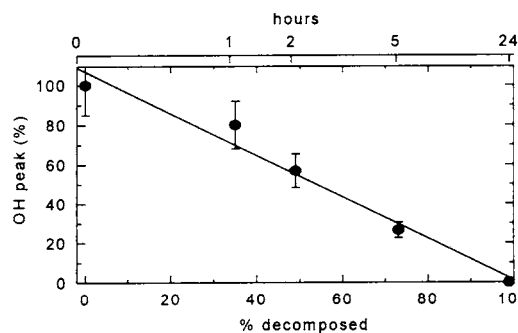


Fig. 4. Decrease of the tremolite hydroxyl (OH) peak (3674 cm^{-1}) with extent of decomposition as measured by mid-IR spectroscopy. Error bars are $\pm 15\%$.

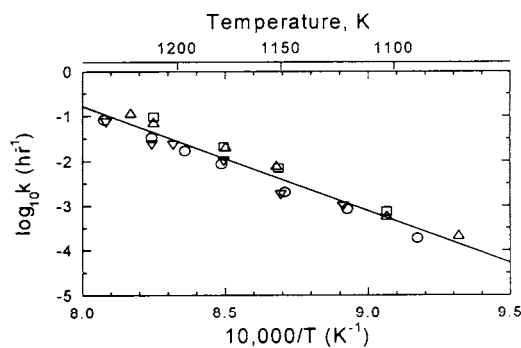


Fig. 5. An Arrhenius plot of the rate constants (hr^{-1}). The symbols represent different sets of experiments.

today (Bullock and Grinspoon 1999). This high temperature excursion may have persisted for 100Ma to 400Ma. Even so, the chances of tremolite survival are still good. In the Venusian highlands, at the 100 degree higher temperature (760K), these grains would reach 50% decomposition in 500Ma, which is longer than the duration of the higher temperatures. Complete decomposition would take ~5.0 billion years (see Figure 3). Larger grains would take even longer to decompose.

Yet, the question remains, how much tremolite could have formed on Venus in the past? This depends on how much water was available. This question can be answered by using mass balance. For example, if Venus once had ~1,100 micrograms of water per gram of rock (Zolotov *et al.* 1997 and references therein), and all this water were in tremolite, then tremolite would exist at ~5.0 mass %. Although this is probably an upper limit, percent levels of tremolite are plausible. If we refer to terrestrial geology, metamorphic rocks typically contain a few percent amphiboles.

It is reasonable to postulate that hydrous minerals could have formed on Venus. On Earth, we find tremolite in low grade metamorphic ultrabasic rocks and in contact metamorphosed siliceous carbonate rocks (Deer *et al.* 1997). Geochemical arguments suggest the presence of both rock types on Venus (Fegley *et al.* 1992, Kargel *et al.* 1994, Fegley *et al.* 1997b). Tremolite also occurs as an alteration product of pyroxenes that interact with water-enriched magmatic fluids (Deer *et al.* 1997). Under sufficiently high water partial pressure, it is possible that tremolite would have formed in localized areas of Venus' crust via magmatic heating. Zolotov *et al.* (1999) also discuss potential locations for hydrous mineral formation on Venus.

Regions that might favor the survival of amphiboles are the highlands, tesserae and/or crater ejecta blankets. The mineralogy of the tesserae, which cover ~8% of Venus' surface (Ivanov and Head 1996), is unknown. If the tesserae are metamorphic, as proposed by Nikolaeva *et al.* (1992), they may be a good locale for preserving tremolite-bearing rocks. The highlands and tesserae are at higher elevations that have cooler temperatures which favor tremolite preservation. Lastly, crater ejecta blankets could contain amphiboles from older excavated layers that were brought to the surface upon impact.

If we are able to detect amphiboles or other thermally stable hydrous minerals (Zolotov *et al.* 1997) on the surface, we will have ground truth confirming that Venus had more water in its past. Such a discovery would answer the long-standing question posed in the introduction with the response: Venus became the way it is today over time. This experimental study shows that tremolite can survive decomposition on Venus over geologic timescales. Therefore, future spacecraft to Venus should have the ability to detect hydrous minerals. If it were not for these decomposition experiments, it is unlikely that the existence of hydrous minerals would even be considered for detection in future missions.

THE FUTURE

Unfortunately, no direct mineralogical data exist for the Venusian surface. The only geochemical data we have for the surface are abundances of Mg and heavier elements measured by X-ray fluorescence spectrometers on the Venera 13 and 14 and Vega 2 landers (Surkov *et al.* 1984, 1986). Unlike the Moon and Mars, there are no known samples from the Venusian surface, that is, meteorites. What information we have about the surface mineralogy was derived through thermodynamic studies and orbital radar (Pettengill *et al.* 1982, Barsukov 1992, Fegley and Treiman 1992, Fegley *et al.* 1992, Kargel *et al.* 1994, Brackets *et al.* 1995, Fegley *et al.* 1997b).

Direct mineralogical measurements that can identify minerals include XRD and/or infrared reflectance spectroscopy (Blake *et al.* 1994, Rossman 1988). Indirect methods such as *in situ* neutron spectroscopy or thermogravimetric/differential thermal analysis (TGA/DTA) can be used to detect hydrous minerals, but these techniques are unlikely to be useful on Venus (Zolotov *et al.* 1997). These instruments could be carried by via landers, penetrators, rovers, and/or automated balloons (aerobots). For example, the detection of sulfates and carbonates on the plains would be evidence for a SO₂ sink on the surface. The distribution of magnetite and/or hematite as a function of elevation would constrain the oxygen fugacity of the near-surface atmosphere and allow for better models of surface weathering. It may

also be possible with such measurements to obtain unambiguous proof that Venus did have more water in the past if hydrous minerals could be detected.

The three examples of atmosphere-surface reactions presented here exemplify the value of continuing both theoretical and experimental studies. The results not only help us to better understand the chemical processes occurring on the surface and in the lower atmosphere, but also guide the development of future spacecraft instruments. It has been over a generation since any in situ chemical analyses have been made of Venus' atmosphere and surface. Ideally, future instruments would measure the mineralogy, and chemical and atmospheric composition simultaneously and directly. It is also important for these instruments to be mobile and analyze several different locations because a single sample would be of limited value. Regardless, it is vital that both experiments and theory continue to explore the Venusian atmosphere-surface interactions. It is only with a strong understanding of the fundamental reactions and processes on Venus that we will know what type of equipment should be sent to Venus and where to sample. The combination of theory, experiments, and observations and their interpretations ultimately brings us closer to deciphering why Venus and Earth are similar yet, at the same time, so very different.

ACKNOWLEDGEMENTS

This work was supported by the NASA Planetary Atmospheres Program.

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