Lithospheric and Atmospheric Interaction on the Planet Venus

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ABSTRACT

A host of interesting problems related to the probability of a global process of chemical interaction of the Venusian atmosphere with that planet's surface material has emerged in the wake of flights by the Soviet space probes, "Venera-4, -5, -6, and -7" (1967-70). It was disclosed during these flights that the temperature of Venus' surface attains 750 K, pressure is approximately 90 atm., and CO_2 constitutes 97% of the atmosphere. We shall explore several of these issues which were discussed in the pioneering works of Mueller (1963, 1969) and Lewis (1968, 1970):

- Is Venus' troposphere in a state of chemical equilibrium?
- Can we assume that the chemical composition of the troposphere is buffered by the minerals of surface rock?
- What are the scales and mechanisms involved as exogenic processes take place?
- To what degree is the composition of cloud particles tied to the process of lithospheric-atmospheric interaction?

We have succeeded in resolving a number of these problems over the past 20 years. At the same time, critical issues such as the chemical constituents of the near-surface layer of Venus' atmosphere, cloud particle chemistry, and the mineralogy of iron and sulfur in surface rock obviously cannot be definitely resolved until further landing craft will have been sent to the surface of Venus.

Several research projects have been conducted in the USSR and the United States, which used physical-chemical and thermodynamic methods

for computing multi-component systems. These projects have helped us to understand the particularity of the natural process occurring on the surface of Venus (Lewis and Kreimendahl 1980; Barsukov *et al.* 1980; Volkov *et al.* 1986; and Zolotov 1985).

Factual material from the studies of the atmosphere and surface of Venus, gathered with the "Venera" series spacecraft and during the "Pioneer Venus" mission, can be used to compare our view of the distribution, chemical composition, and physical properties of products of lithospheric-atmospheric interaction on Venus.

MANIFESTATION OF EXOGENIC PROCESSES USING PHOTOGEOLOGICAL DATA

The following conclusions on the nature and scope of exogenic processes were made after the probes "Venera-15" and "Venera-16" finished mapping Venus:

- The present surface relief of Venus was formed as a result of the combined processes of crater formation, volcanism, and tectonic activity;
- The rate of renewal of Venus' relief is estimated to take a million years for the first several centimeters (in the last three billion years), as compared to hundreds of meters on Earth and the first several meters on Mars (Nikolaeva *et al.* 1986);
- There is no evidence of exogenic processes on a global scale, such as lunar regolith;
- There are no traces of fluvial or aeolian processes having occurred on a scale that matches the resolution of the radar images (one kilometer).

At the same time, microscale exogenic processes have been quite clearly manifested. TV-panoramas from "Venera-9" and "Venera-10" recorded three types of processes: the formation of cracks; degradation with the emergence of desert aeolian weathering ridges; and corrosion, akin to porous aeolian or chemical weathering. The "Venera-13" and "Venera-14" images show laminated formations which have been interpreted (Florenskiy *et al.* 1982) as aeolian-sedimentation rock. Their formation can be described as a cycle: weathering—transport—deposition— lithiphication—weathering. . .

Experiments to estimate such physical properties of surface rock on Venus as porosity, and carrying capacity such as "Venera-13" and "Venera-14" (Kemurdgian *et al.* 1983) confirmed the existence of loose, porous bedrock. Loose, porous bedrock with an estimated thickness of 10 centimeters exists at the landing site of the Soviet "Venera-13" and "Venera-14" probes. The question of their geological nature is still unanswered: Are they products of chemical weathering or aeolian activity?

There is no direct evidence of the existence of aeolian forms as yet. No global aeolian, martian-type structures were revealed in the area mapped by the radars of the "Venera-15" and"Venera-16" probes. Nor do any of the four TV-panoramas show aeolian forms.

Experimental simulation (Greely *et al.* 1984) demonstrated that in an atmosphere of CO_2, with a pressure of approximately 100 atm. and wind speed of up to 3 m/sec^{-1}, signs of rippling occur when saltation of particles of up to 75 μm in diameter takes place. Theoretical estimates of the threshold rates of the separation of particles of varying dimensions produced similar results. Dust fraction, transported as suspension, will have a diameter of < 30 μm.

Scrupulous investigation of the TV-panoramas, incorporating data from measurements of the optical properties of the near-surface atmosphere, have demonstrated that the formation of dust clouds from the aerodynamic landing of Soviet probes is a reality. It is considered that the nature of particle behavior during wind activity on Venus is similar to the sorting of material at the bottom of the ocean at a depth of about 1000 meters.

Let us sum up the information on exogenic processes that was generated by research on the morphology and properties of the surface of Venus:

- The rate of exogenic processing of the Venusian surface relief is extremely low; the morphology of the ancient (0.5 to one billion years) relief has been excellently preserved;
- physical weathering (the equivalent of terrestrial, geological processes) has not been found: there is no aqueous water, living matter, or climatic contrasts;
- Regolith-like forms of relief are not developed;
- Aeolian activity on present-day Venus does not lead to the formation of global forms which can be differentiated on radar maps;
- The television images show traces of chemical weathering in the form of rock corrosion and degradation.

The findings from X-ray-fluorescent analyses on the Soviet "Venera-13" and "Venera-14" and "Vega-2" probes and K, U, and Th determinations on the Soviet "Venera-8, -9, and -10," and "Vega-1, and -2" probes (Surkov 1985) have given us information regarding the chemical nature of the surface rock. It is merely important for this paper to note that all of this rock belongs to the basalt group and contains almost 10 times more sulfur than their terrestrial equivalents.

THE CHEMICAL COMPOSITION AND A CHEMICAL MODEL OF THE TROPOSPHERE OF VENUS

It became clear, following the flight by the Soviet "Venera-4" probe in 1967, that CO_2 accounts for 97% of the Venusian troposphere, N_2 is approximately 3%, and the remaining constituents account for approximately 0.1% (by volume). Unfortunately, we lack instrumental data on chemical composition at elevations below 20 kilometers. This creates considerable difficulty as we attempt to understand the chemical processes at the boundary between the atmosphere and the surface.

The troposphere of Venus can be seen as a homogenous, well mixed, gaseous envelope for the major constituents (CO_2 and N_2) and the inert gases. It is clear that complex relationships exist between the physical (turbulent mixing, and horizontal and vertical planetary circulation of gas masses) and chemical (condensation and vaporization of cloud particles, gas-phase reactions, and gas-mineral types of interaction) processes in the atmosphere which lead to the existence of vertical and horizontal gradients of microconstituent concentrations (H_2O, SO_2 and CO; see Figure 1).

Venus' high surface temperature can be regarded as a factor which enhances the chemical interaction of the atmosphere with surface rock and, as a consequence, yields a dependency of the atmosphere's composition on heterogenic chemical reactions at the atmosphere-surface boundary.

Mueller (1964) proposed 25 years ago that three zones may exist in the vertical profile of Venus' atmosphere, depending on the predominance of varying types of chemical processes:

- The zone of thermochemical reactions in which the composition of the atmosphere is buffered by surface rock minerals;
- The zone of "frozen" chemical equilibrium, where the composition of gases corresponds to their equilibrium ratios in the near-surface layer of the troposphere;
- The zone of photochemical reactions in the upper atmosphere.

According to this model, chemical reactions at the planet's surface take place amid a constant influx of reactive matter from the crust reservoir, as geological and tectonic activity also occur. Using the principle of global chemical quasiequilibrium in the atmosphere-crust system, we can apply thermodynamic computations to estimate the equilibrium concentrations of atmospheric gases that are not accessible to direct measurements.

Lewis (1970) obtained more complete data on calculations of the chemical composition of the near-surface atmosphere; he took into account the results of the atmospheric analyses performed by the Soviet "Venera-4, -5 and -6" probes. Unlike Mueller (1964), he only considered chemical equilibrium at the atmosphere-surface boundary (Table 1). Both of the

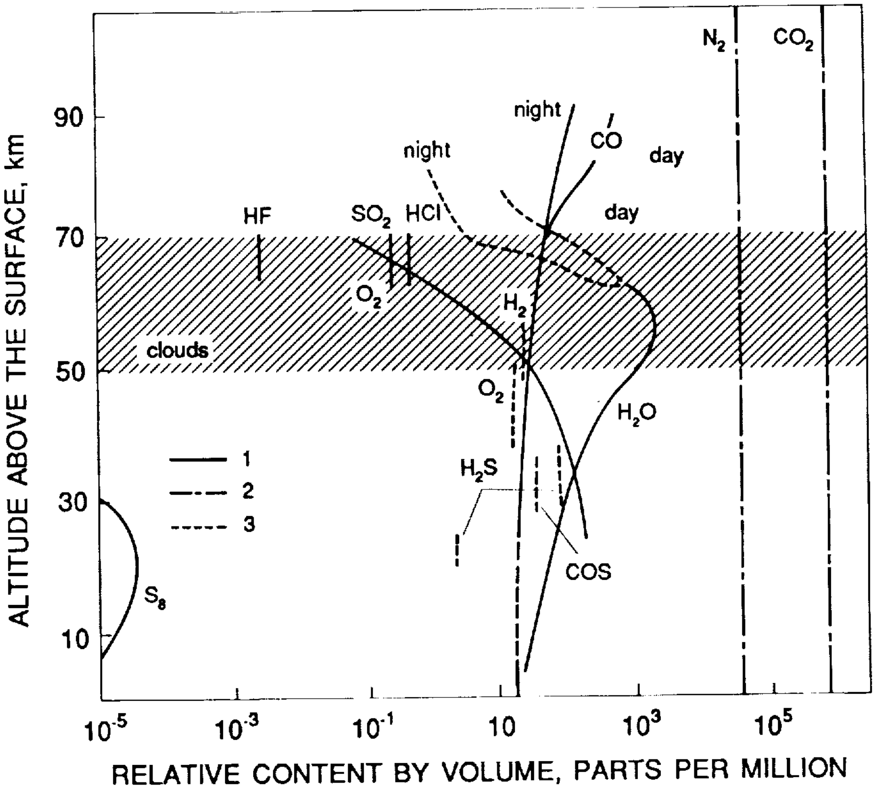

FIGURE 1 A schematic vertical cross-section of the troposphere of Venus. It shows the distribution of macro- and microconstituents based on data from measurements performed by the "Venera" series and the "Pioneer Venus" probes. 1: microconstituents; 2: macroconstituents; 3: data requiring refinement.

above models used the existence of chemical equilibrium throughout the troposphere, to its upper cloud boundary.

The literature has been discussing Urey's (1951) hypothesis for quite some time. He proposed "Wollastonite" equilibrium as a mechanism for buffering P_{CO_2} in the global, equilibrium atmosphere-crust system (Mueller 1963; Vinogradov and Volkov 1971; Lewis and Kreimendahl 1980):

$$CaCO_3 + SiO_2 \Leftrightarrow CaSiO_3 + CO_2$$

calcite quartz Wollastonite

The thermodynamic calculations performed in these studies demonstrated that the mineral association of calcite-quartz-Wollastonite on the surface of Venus can buffer P_{CO_2} (~ 90 bar) at a temperature of 742 K. This is virtually

TABLE 1 Chemical Models of Venus' Troposphere

Authors	Quasi-Zone of Chemical Equilibrium	Zone of "Frozen" Chemical Equilibrium	Initial Data
R. Mueller 1963, 1969	Troposphere + lithosphere	Troposphere to an altitude of 80 km*	Spectroscopic measurements of CO, HCl, HF, and H_2O
J. Lewis 1970	Troposphere + surface rock	" "	Spectroscopic measurements of CO, HCl, HF; H_2O ("Venera-5 & -6" data)
Florenskiy *et al.* 1976	" "	Troposphere to lower cloud boundary	Chemical analysis of the atmosphere on Soviet "Venera -4 & -10" probes
Khodakovskiy *et al.* 1979	" "	Near-surface troposphere	Chemical analysis of the atmosphere on Soviet "Venera -11 & -12" probes & "Pioneer Venus"
Krasnopol'skiy and Parshev 1979	" "	Troposphere to an altitude of 60 km**	" "

*Upper boundary of the cloud layer
**According to Krasnopol'skiy and Parshev (1979): to the "zone of photochemical reactions"

commensurate with the surface conditions. However, interpretation of the multisystem computations has shown that carbonates are unstable. Yet, the high concentration of SO_2 in the troposphere is one of the determining factors of this process (Zolotov 1985; Volkov *et al.* 1986). Consequently, "Wollastonite" equilibrium can scarcely be seen as the basis for a chemical model of Venus' atmosphere.

Florenskii *et al.* (1976) developed the idea in 1976 that there may be chemical equilibrium in the subcloud portion of the troposphere. The lower atmosphere was divided into three zones:

- The stratosphere with an upper layer of clouds, which is the zone of photochemical processes;
- The main cloud layer zone, where photochemical (above) and thermochemical (below) processes compete;
- The portion of the troposphere below the cloud base, which is the zone where thermochemical equilibria are predominant.

This model brought us to a closer understanding of the Venusian troposphere as a complex, predominantly nonequilibrious system, even though numerical estimates of microconstituent concentrations (primarily SO_2) departed greatly from the actual values (Table 2).

TABLE 2 Chemical Composition of the Venusian Near-Surface Troposphere from Computational Data (Relative Levels of Microconstituents by Volume).

Gas	1	2	3	4	5	6
CO	$\underline{2\cdot10^{-4}}$	$\underline{5\cdot10^{-5}}$	$\underline{1.7\cdot10^{-5}}$	$\underline{1.5\cdot10^{-5}}$	$7.2\cdot10^{-6}$	$1.7\cdot10^{-5}$
H_2O	$\underline{5\cdot10^{-4}}$	$\underline{3.2\cdot10^{-4}}$	$\underline{2\cdot10^{-5}}$	$\underline{2\cdot10^{-4}}$	$\underline{2\cdot10^{-5}}$	$2\cdot10^{-5}$
SO_2	$3\cdot10^{-7}$	$8\cdot10^{-6}$	$\underline{1.3\cdot10^{-4}}$	$\underline{1.3\cdot10^{-4}}$	$\underline{1.3\cdot10^{-4}}$	$1.3\cdot10^{-4}$
H_2S	$5\cdot10^{-6}$	$1.2\cdot10^{-6}$	$5.2\cdot10^{-8}$	$3\cdot10^{-7}$	$8\cdot10^{-9}$	$8\cdot10^{-5}$
COS	$\underline{5\cdot10^{-5}}$	$\underline{3.2\cdot10^{-5}}$	$2.3\cdot10^{-5}$	$2\cdot10^{-5}$	$3\cdot10^{-6}$	$4\cdot10^{-5}$
S_2	$2\cdot10^{-8}$	$4\cdot10^{-8}$	$1.8\cdot10^{-7}$	10^{-7}	$\underline{1.3\cdot10^{-8}}$	$2\cdot10^{-8}$-$8\cdot10^{-7}$
H_2	$7\cdot10^{-7}$	10^{-7}	$2.4\cdot10^{-9}$	$2\cdot10^{-8}$	10^{-9}	$2.5\cdot10^{-5}$
O_2	$8\cdot10^{-26}$	10^{-24}	10^{-23}	--	10^{-23}	$1.8\cdot10^{-5}$

Notes: The underlined figures are initial data of measurements on space probes or ground-based facilities; 1: Mueller (1969); 2: Lewis (1970); 3: Khodakovskiy *et al.* (1979); 4: Krasnopol'skiy and Parshev (1979); 5: Zolotov (1985).

Column 6 tabulates data of measurements made on the "Venera" and "Pioneer Venus" probe series; no measurements were performed below an altitude of 20 kilometers (Figure 1).

Following measurements of the chemical composition of the troposphere by the Soviet "Venera-11 and -12" probes and the "Pioneer Venus" probe, the computational and experimental values of microconstituent concentrations were compared. Khodakovskii *et al.* (1979) and Krasnopol'skii and Parshev (1979) concurrently and independently proposed models (Table 2). These models were the first to compare gas-phase reaction rates with troposphere mixing rates. These consequences were generated:

- The troposphere is generally in nonequilibrium, with the exception of the near-surface layer with a thickness of the first kilometer, where the highest temperatures are dominant. However, the processes of heterogeneous catalysis at the atmosphere-surface boundary may favor the establishment of chemical equilibrium in relation to certain constituents;
- The chemical composition of the microconstituents in the vertical cross-section below the cloud base region of the troposphere does not vary: it corresponds to the "frozen" equilibrium at the atmosphere-surface boundary ($T = 735$ K; $P = 90$ atm).

The principal of "frozen" equilibrium was applied in order to theoretically estimate the chemical composition of cloud particles; this enables us to better understand the sulfur and chlorine cycles in the atmosphere-crust system (Volkov 1983; Volkov *et al.* 1986).

The lack of instrumental determinations of microconstituents in the troposphere at altitudes below 20 kilometers prevents us from solving the critical problem of the ratio of gaseous sulfur: $H_2S + COS > SO_2$ (Lewis 1970) or $H_2S + COS < SO_2$ (Khodakovskii *et al.* 1979; see Table 2). Furthermore, gas chromatographic determination of oxygen by the Soviet "Venera-13, and -14" probes cannot be reconciled with the concurrent presence in these same samples of 80 ppm H_2S and 40 ppm COS (see Volkov and Khodakovskii 1984 for greater detail). The only original attempt to experimentally estimate the oxidation-reduction regime on Venus' surface, using a "Kontrast" detector on the Soviet "Venera-13, and -14" probes (Florenskii *et al.* 1983) pointed to the presence in the near-surface layer of the troposphere of a reducing agent (CO). However, it does not give us a clear-cut solution to the oxygen problem.

The results from estimations of the chemical composition of the troposphere and the nature of the processes occurring in its near-surface layer can be summarized in three conclusions:

(1) Chemical equilibrium in the troposphere of Venus has generally not been reached.

(2) The vertical gradients of SO_2, H_2O and CO concentrations are a function of the competition between physical and chemical processes in the troposphere.

(3) The near-surface troposphere can be seen as a layer in a state of "frozen" chemical equilibrium.

Unfortunately, we have yet to resolve the question of the oxidation-reduction regime on Venus' surface, as well as the problem of the existence of free oxygen in the troposphere.

THE MINERAL COMPOSITION OF SURFACE ROCK ON VENUS

Many investigations have attempted to estimate the possible mineral associations on the surface of Venus using chemical thermodynamic methods.

Mueller published the first such study as a component of the aforementioned chemical model of the atmosphere (Mueller 1963) and obtained the following results:

- Temperature and pressure on Venus' surface are consistent with silicate-carbonate equilibrium, and carbon is bound in the rock in $CaCO_3$ form;
- Oxygen partial pressure is buffered by Fe-containing minerals;
- Graphite and the native metals are not stable;
- Nitrogen is not bound in the condensed phases;

- A number of chlorine- and fluorine-containing minerals are stable at the surface.

Lewis (1970) calculated 64 mineral equilibria in order to estimate P and T on the surface before the probes performed these measurements. One out of three proposed options for the P and T values was in satisfactory agreement with the actual values obtained a year later. Lewis yielded the following, additional forecast estimates:

- Surface rock contains H_2O molecules bound in the form of tremolite;
- sulfur is bound in the cloud layer in the form of mercury sulfides. Carbonyle-sulfide is the dominant form in which sulfur is found in the troposphere. This prediction proved only partially true: sulfur is actually the main component of cloud particles, but the latter consist primarily of H_2SO_4.

A series of studies to calculate mineral composition was conducted in 1979-83 at the V.I. Vernadskiy Institute using the computation of the phase ratios in multicomponent, gaseous systems, modeling the atmosphere/surface-rock system. The computations were based on troposphere chemical analysis data from the Soviet "Venera" series of probes, "Pioneer Venus," thermodynamic constants of about 150 phases, the chemical components of terrestrial magmatic rock, and the results of x-ray-fluorescent analysis of rock at three probe landing sites ("Venera-13," "Venera-14," and "Vega-2"). Compilation of this material can be found in Volkov *et al.* (1986). It should be stressed that three important predictive conclusions were made before the first data on the chemical composition of Venus' bedrock were obtained:

- Sulfur may be bound as sulfates ($CaSO_4$) and/or sulfides (FeS_2), and its concentration greatly exceeds known sulfur levels in terrestrial equivalents;
- Water-containing minerals are unstable;
- Carbonates are unstable;
- Magnetite Fe_3O_4 must be a widespread constituent both as primary and as altered bedrock.

These conclusions were generally confirmed, albeit with some refinement, by comparing them with X-ray-fluorescent analyses at "Venera-13," "Venera-14" and "Vega-2" landing sites, and by further, more detailed theoretical investigations (Zolotov 1985, 1989).

Sulfur at the surface probe landing sites, if we judge from the data of additional, postflight calibration investigations (Surkov *et al.* 1985), is in an anhydrite form ($CaSO_4$). Sulfur content may serve as a measure of convergence to the state of chemical equilibrium relative to SO_2 in the atmosphere-crust system (Lewis and Prinn 1984; Volkov *et al.* 1986). It may be possible that rock with a maximum level of sulfur (1.9 mas. %, "Vega-2") were in contact with the atmosphere longer than the bedrock at the landing sites of the Soviet "Venera-13" and "Venera-14" probes.

In his 1985 study, Zolotov conducted thermodynamic assessments of carbonate stability depending on the concentration of SO_2, since a reaction such as:

$$CaCO_3 + 1.5SO_2 \Leftrightarrow CaSO_4 + CO_2 + 0.25S_2$$

takes place in Venus surface conditions free of kinetic constraints. As it turned out, the presence of SO_2 in quantities exceeding 1 ppm excludes the existence of calcite and dolomite. However, magnesite ($MgCO_3$), as a product of the alteration of pure forsterite, $MgSiO_4$ (Fo_{100}), may be stable at altitudes of 1.5 to eight kilometers.

Zolotov demonstrated in this same study (1985) that hematite (Fe_20_3) may even be stable at an altitude of more than 1.5 kilometers (Figure 2), in addition to magnetite (Fe_3O_4) (the product of water vapor-driven oxidation of Fe-containing silicates, CO_2 and SO_2). Hematite stability is apparently confirmed by the results obtained from interpreting the surface color on the TV images from "Venera-13 and -14" (Shkuratov *et al.* 1987).

Nevertheless, in their 1980 study Lewis and Kreimendahl retain the conclusion regarding calcite ($CaCO_3$) and wüstite (FeO) stability, while allowing for the prevalence of H_2S and COS over SO_2 in conditions of total chemical equilibrium at the surface-atmosphere boundary. They come to the same logical conclusion that in this case, the surface rock of Venus' crust is characterized by an extremely low degree of oxidation (Fe+3/Fe+2 at one to two orders lower than the terrestrial value). Strictly speaking, the ultimate solution to the problem of the oxidation of Venus' crust has not been found due to the lack of instrumental data.

In 1975, Walker (1975) drew attention to the possible dependence of the mineral constituents of Venus' surface on the hypsometric level. The pressure ($\approx$ 65 atm.) and temperature ($\approx$ 100 K) gradients are actually so great that they may alter the composition of the phases of rock during their exogenous cycle, that is, under the influence of aeolian transport. If we take into account the fact that our knowledge of Venus' mineralogy does not go beyond the framework of theoretical forecasting, the factor of "hypsometric control" must still be considered hypothetical.

Let us summarize the theoretical investigations of the chemical interaction of Venus' rock with its atmosphere.

- Alteration of the composition of Venus' basalts during interaction with the atmosphere is highly probable;

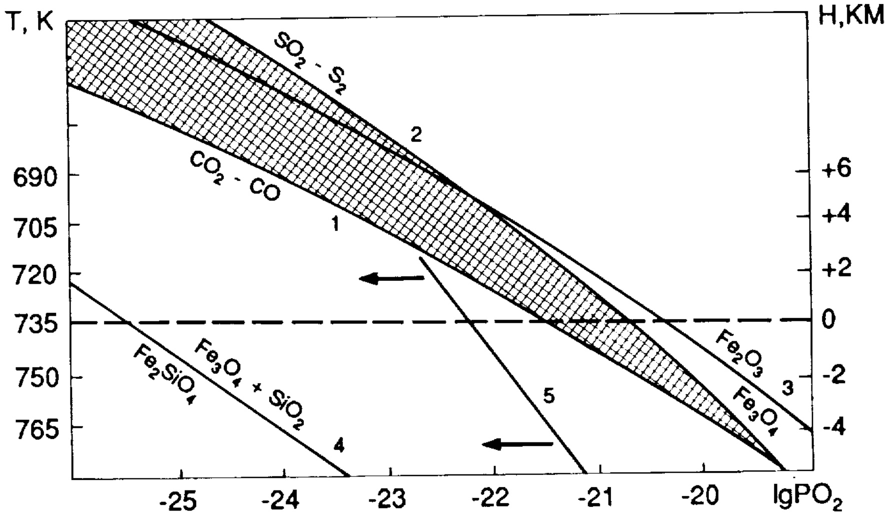

FIGURE 2 Estimates of the oxidation-reduction regime in the troposphere and on the surface of Venus from data produced by measurements (1,2,5) and computations (3,4). (Zolotov 1985). 1. $CO_2 = CO + \frac{1}{2}O_2$ ($C_{CO_2} = 96.5\%$; $C_{CO} = 20$ ppm). 2. $SO_2 = \frac{1}{2}S_2 + O_2$ ($C_{SO2} = 130 \div 185$ ppm; $C_{S2} = 20$ ppb). 3. $3Fe_2O_3 = 2Fe_3O_4 + \frac{1}{2}O_2$ (buffer HM). 4. $2Fe_3O_4 + 3SiO_2 = 3Fe_2SiO_4 + O_2$. 5. "Kontrast" detector (Florenskiy *et al.* 1983).

- Apparently, the primary outcome stemming from this interaction will be the sink of sulfur in the crust as anhydrite ($CaSO_4$) and/or iron sulfides (FeS and FeS_2);
- The existence of carbonates (besides $MgCO_3$), free carbon and nitrogen compounds on the surface of Venus is thermodynamically prohibited;
- The lack of complete factual data prevents our making a clear-cut conclusion as to the stability of water-bearing minerals and the degree of oxidation of the Venusian crust.

THE CYCLES OF VOLATILE COMPONENTS

Interpretation of data on Venus' atmospheric chemistry, and in particular, consideration of the photochemical processes in the stratosphere (Krasnopolskii 1982; Yung and De More 1982) demonstrated that nitrogen and carbon cycles are completed in the atmosphere. The H_2O cycle poses more problems, since we are not yet clear on the vertical profile of H_2O concentrations in the near-surface atmosphere.

Clearly, sulfur is the only volatile element on Venus which, in the

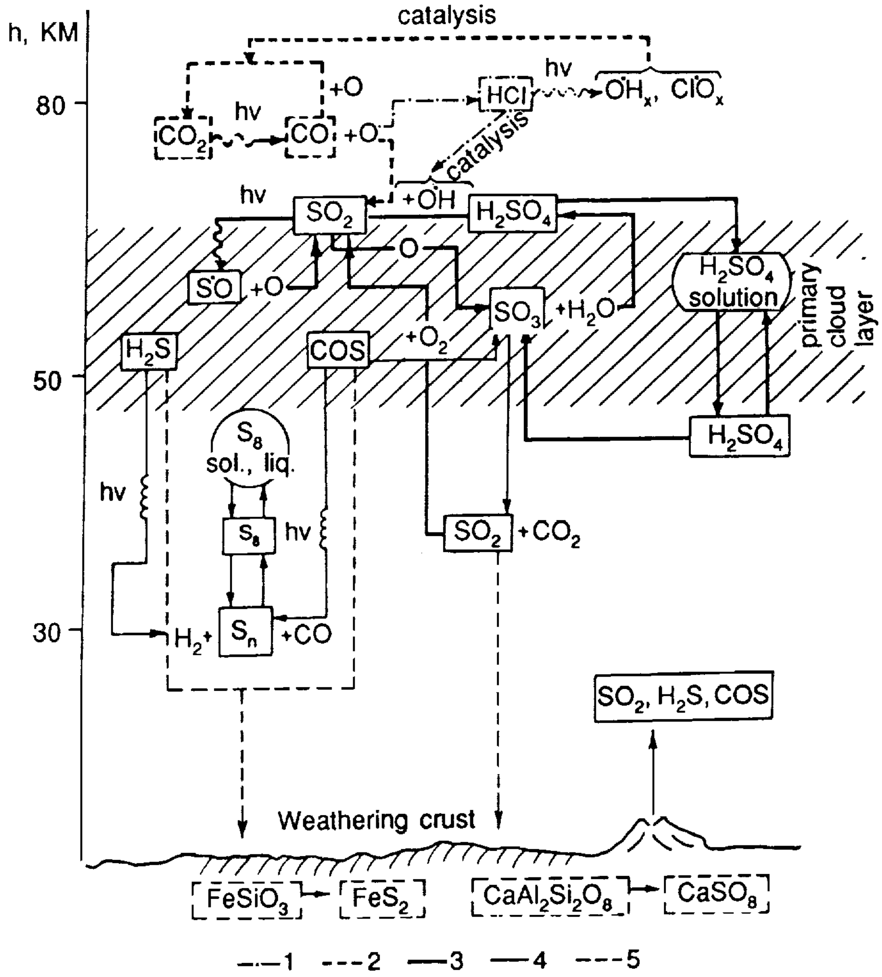

FIGURE 3 Diagram of the cycles of CO_2, sulfur and chlorine in the Venusian atmosphere 1: chlorine cycle; 2: CO_2 cycle; 3: rapid sulfur cycle; 4: slow sulfur cycle; 5: sulfur flux into the crust.

contemporary geological epoch, participates in the cyclical mass exchange between the atmosphere and the crust. Sulfur's behavior as a constituent of the cloud layer essentially determines its structure and dynamics. Three cycles (Figure 3) have been discerned, depending on the rates at which these processes unfold (Lewis and Prinn 1984).

The rapid cycle takes place in the stratosphere and the clouds and sets the stage for the photochemical emergence and thermal destruction of sulfuric acid aerosols. The residence time for the SO_2 molecule is estimated

TABLE 3 Mineral Composition of Venusian Surface Rock Based on Theoretical Assessments (Secondary Minerals)

1	2	3
Carbon in $CaCO_3$ $C_{(graphite)}$ is unstable	Carbonates Ca and Mg	Carbonates are unstable $MgCO_3$ (?)
H_2O in amphiboles and micas	H_2O in amphiboles	Amphiboles (?)
Fe_2O_3, Fe_3O_4	FeO, Fe_3O_4 where $X_{COS} + X_{H2S} > X_{SO2}$	Fe_3O_4, Fe_2O_3 (?) where $X_{COS} + X_{H2S} < X_{SO2}$
Sulfur in sulfides of Fe and anhydrite ($CaSO_4$)		Predominantly $CaSO_4$, sulfides of Fe are stable
Nitrogen-bearing minerals are unstable Chlorine- and fluoride-bearing minerals are stable (fluorite/apatite?)		

1. Mueller 1963, 1969
2. Lewis 1970; Lewis and Kreimendahl 1980
3. Khodakovskiy *et al.* 1978; Volkov 1983; Zolotov 1989.

to be from several hours to several years. Two alternative scenarios are proposed in Table 4. It is difficult to select between the two because of the lack of experimental data on the rates of certain photochemical reactions.

The slow atmospheric cycle is most likely a function of photochemical and thermodynamic reactions in the lower atmosphere which lead to the existence of reduced forms: H_2S and COS and elementary sulfur. Apparently, the stratosphere is the region of H_2S and COS flux: they either photodissociate there or are oxidized by molecular oxygen to SO_3. The time span of sulfur molecules in the cycle is estimated to be several dozen years (Lewis and Prinn 1984).

The mass exchange between Venus' crust and its atmosphere is carried out in a "geological" sulfur cycle. The source of sulfur is crust matter which produces sulfur-bearing gases through both volcanism and the interaction of minerals with atmospheric gases, such as FeS_2 with CO_2, H_2O, and CO.

These gases repeatedly participate in photo- and thermodynamic processes in the atmosphere. The rapid atmospheric cycle brings about the long-term existence of a cloud cover made up of condensed H_2SO_4 particles. The competition of photo- and thermochemical reactions in the slow cycle apparently support the existence of SO_2 as the dominant form of sulfur in the atmosphere. An excess of SO_2 compared with its equilibrium concentration in the atmosphere-crust system create an SO_2 flux in the form of sulfates in surface rock.

Two factors determine the scales and rates of flux:

TABLE 4 Sulfur Cycles on Venus

Cycle		
Timeframe	I. Fast cycle (stratosphere and cloud layer)	
	(Winick and Stewart 1980)	(Krasnopol'skiy 1982)
	$CO_2 + hv \rightarrow CO + O$	$SO_2 + hv \rightarrow SO + O$
< 10 yrs.	$SO_2 + O + M \rightarrow SO_3 + M$	$SO + O + M \rightarrow SO_2 + M$
	(OH, HO_2 are catalysers)	$SO_2 + O + M \rightarrow SO_3 + M$
	$SO_3 + H_2O \rightarrow H_2SO_4$ (Sol)	$SO_3 + H_2O \rightarrow H_2SO_4$ (Sol)
	II. Slow cycle (lower atmosphere and cloud layer)	
	$SO_3 + 4CO \rightarrow COS + 3SO_2$	$SO_3 + H_2 + 3CO \rightarrow H_2S + 3CO_2$
$\gtrsim$ 10 yrs.	$COS + hv \rightarrow CO + S$	$H_2S + hv \rightarrow \dot{H}S + \dot{H}$
	$COS + 1.5O_2 \rightarrow SO_3 + CO$	$H_2S + 1.5O_2 \rightarrow SO_3 + H_2$
	III. Geological Cycle	
	$CaSiO_3, CaA1_2Si_2O_8 + SO_2 \rightarrow CaSO_4$	
> 10^6 yrs.	$FeSiO_3, Fe_3O_4 + COS (H_2S) \rightarrow FeS(FeS_2)$	

The time frame for a cycle to run its course depends on:
1) Mineral $\leftrightarrows$ gas reaction rates on the planet's surface
2) Length of time during which mineral particles are in contact with the atmosphere such as surface relief renewal rates

- The rate of heterogeneous mineral = gas reactions on the planet's surface;
- The residence span in which mineral particle are in contact with the atmosphere, for example, the surface relief renewal rate.

The completing of the "geological" cycle probably occurs as the altered surface rock (rich $CaSO_4$) is re-melted in the deep regions of the crust. Attenuated volcanic and tectonic activity on Venus ultimately reduces the thickness of the cloud layer because sulfur is fixed in the crust and depleted in the atmospheric reservoir.

GENERAL CONCLUSIONS

We can cite at least four firmly established facts that determine the existence of the chemical interaction of Venus' atmosphere with its surface rock. These are:

- Loosely porous rock on the planet's surface is developed; massive rock display traces of corrosion and degradation;
- There is no global regolith; aeolian transport on a limited scale is supported by weak winds in the near-surface atmosphere;
- The troposphere contains reactive gases (microconstituents): SO_2, H_2O, CO, and others;- Venus' basalts contain one to 1.5 more orders of sulfur than their terrestrial equivalents.

We can make the following conclusions based on our interpretation of the entire set of observational data:

(1) The processes of lithospheric-atmospheric interaction substantially alter primary basalts and subject them to chemical weathering. The scale of this process cannot be estimated;

(2) The troposphere is generally not in a state of chemical equilibrium with the surface rock, and the chemical composition of the near-surface layer may correspond to a "frozen" equilibrium which is buffered by the minerals.

(3) Sulfur is in a state of cyclical mass exchange between the atmosphere and the crust.

(4) Nitrogen and oxygen in the crust's rock do not form stable phases. Their cycles become completed in the atmosphere.

REFERENCES

Barsukov, V.L., V.P. Volkov, and I.L. Khodakovsky. 1982. The crust of Venus: theoretical models of chemical and mineral composition. J. Geophys. Res. 87(suppl. Part 1):A3-A9.

Florenskiy, K.P., A.T. Bazilevskiy, and A.S. Selivanov. 1982. Panoramas of the landing sites of "Venera-13" and "Venera-14" (a preliminary analysis). Astron. Vestnik. 16(3):131-138.

Florenskiy, K.P., V.P. Volkov., and O.V. Nikolaeva. 1976. Towards a geochemical model of the troposphere of Venus. Geokhimiya 8: 1135-1150.

Florenskiy, K.P., O.V. Nikolaeva, V.P. Volkov, *et al.* 1983. On the oxidation-reduction conditions on the surface of Venus, based on data from the "Kontrast" geochemical detector deployed on the "Venera-13" and "Venera-14" probes. Kosmich. issled. 21(3):351-354.

Greely, R., J. Iverson, R. Leach, *et al.* Windblown sand on Venus: preliminary results of laboratory simulations. Icarus 57(1):112-124.

Kemurdjian, A.L., P.N. Brodskiy, V.V. Gromov, *et al.* 1983. Preliminary results in determining the physical and mechanical properties of bedrock by the Soviet automated "Venera-13" and "Venera-14" probes. Kosmich. issled. 21(3):323-330.

Khodakovskiy, I.L., V.P. Volkov, Yu.I. Sidorov, *et al.* 1978. The mineralogical composition of bedrock, and the processes of hydration and oxidation of the outer envelope of the planet Venus (a preliminary forecast). Geokhimiya 12:1821-1835.

Khodakovskiy, I.L., V.P. Volkov, Yu.I. Sidorov, *et al.* 1979. A geochemical model of the troposphere and crust of the planet Venus, based on new data. Geokhimiya 12:1748-1758.

Krasnopol'skiy, V.A. 1982. Photochemistry of the atmospheres of Mars and Venus. Nauka, Moscow.

Krasnopol'skiy, V.A., and V.A. Parshev. 1979. On the chemical composition of the Venusian troposphere and cloud layer, based on measurements made by "Venera-11 and -12" and "Pioneer Venus." Kosmich. issled. 17(5):763-771.

Lewis, J.S. 1968. An estimate of the surface conditions of Venus. Icarus 8(3):434-457.

Lewis, J.S. 1970. Venus: atmospheric and lithospheric composition. Earth Planet. Sci. Lett. 10(1):73-80.

Lewis, J.S., and F.A. Kreimendahl. 1980. Oxidation state of the atmosphere and crust of Venus from Pioneer-Venus results. Icarus 42(3):330-337.

Lewis, J.S., and R.G. Prinn. 1984. Planets and their atmospheres. Origin and evolution. Academic Press, Orlandi.

Mueller, R.F. 1963. Chemistry and petrology of Venus: preliminary deductions. Science 141(3585):1046-1047.

Mueller, R.F. Planetary probe: origin of the atmosphere of Venus. Science 163(3873):1322-1324.

Nikolaeva, O.V., L.B. Ronka, and A.T. Bazilevskiy. 1986. Circular formations on the plains of Venus as evidence of its geological history. Geokhimiya 5:579-589.

Surkov, Yu.A. 1985. Cosmic investigations of the planets and their satellites. Nauka, Moscow.

Surkov, Yu.A., L.P. Moskaleva, O.P. Shcheglov, *et al.* 1985. The method, equipment and results from determinations of the elementary composition of the Venusian bedrock made by the "Vega-2" space probe. Astron. Vestnik. 19(4):275-288.

Shkuratov, Yu.G., M.A. Kreslavskiy, and O.V. Nikolaeva. 1987. A diagram of the albedo-color of a parcel on the surface of Venus and its interpretation. Astron. vestnik. 21(2):152-154.

Urey, H.C. 1951. The origin and development of the Earth and other terrestrial planets. Geochim. et Cosmochim. Acta. 1(2):209-277.

Vinogradov, A.P., and V.P. Volkov. 1971. On Vollastonite equilibrium as a mechanism determining the composition of Venus' atmosphere. Geochimiya 7:755-759.

Volkov, V.P. 1983. The Chemistry of the atmosphere and surface of Venus. Nauka, Moscow.

Volkov, V.P., and I.L. Khodakovskiy. 1984. Physical-Chemical modeling of the mineral composition of the surface rock of Venus. Pages 32-37. In: Geokhimiya i kosmochimiya. Papers at the 27th session of the Int'l. Geol. Congr. Section C. 11. Nauka, Moscow.

Volkov, V.P., I.L. Khodakovsky, and M.Yu. Zolotov. 1986. Lithospheric-atmospheric interaction on Venus. Chemistry and physics of terrestrial planets. Adv. Phys. Geochim. 6:136-190.

Walker, J.C. 1975. Evolution of the atmosphere of Venus. J. Atm. Sci. 32(6):1248-1256.

Winick, J.R., and A.I.F. Stewart. 1980. Photochemistry of SO2 in Venus' upper cloud layers. J. Geophys. Res. 85(A 13):7849-7860.

Yung, Y.L., and W.B. de More. 1982. Photochemistry of the stratosphere of Venus: implications for atmospheric evolution. Icarus 51(2):199- 247.

Zolotov, M.Yu. 1989. Chemical weathering on Venus and Mars: Similarities and Differences. Pages 71-79. In: Cosmochemistry and comparitive planetology. Proceedings of Soviet scientists for the 28th session of the Int'l. Geol. Congr. Nauka, Moscow.

Zolotov, M.Yu. 1985. Sulfur-containing gases in the Venus' atmosphere and stability of carbonates. Pages 942-944. In: Abstr. XVI Lunar and Planet. Sci. Conf. Houston, part 2.