

The stability of climate on Venus

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Abstract. The climate of Venus is to a large degree controlled by the radiative properties of its massive atmosphere. However, volcanic outgassing and surface-atmosphere interactions may moderate the atmospheric abundances of CO₂ and other radiatively important volatiles. Recently, work on the interpretation of the impact cratering record has placed limits on the magnitude of the volcanic flux. Additionally, recent laboratory data on the equilibria and kinetics of possible surface-atmosphere reactions under Venus-like conditions provide important insights into the role that they may play in moderating Venus' climate. The surface temperature and pressure on Venus coincide approximately with the P-T equilibrium of the calcite-wollastonite mineral reaction, and atmospheric sulfur species are probably involved in rapid heterogeneous reactions with the surface. Perturbations to the atmospheric inventory of radiatively active species may have a significant impact on the climate of Venus and upon the stability of the greenhouse effect. Through the use of a Venus climate model that couples atmospheric radiative-convective equilibrium with surface processes, we show that it is likely that Venus' climate is at or near a state of unstable equilibrium. Furthermore, we show that only moderate perturbations in the abundances of radiatively active volatiles may be sufficient to precipitate changes to new climate regimes.

Introduction

Venus absorbs less sunlight than does the Earth, yet its surface temperature is about 735 K, due to a strong greenhouse effect (Pollack *et al.* 1980; Sagan 1960; Wildt 1940). The first indications that Venus' atmosphere had evolved to a temperature much higher than ours was from Earth-based radio observations (Mayer *et al.* 1958). Further confirmation of high atmospheric temperatures were provided by centimeter wavelength measurements from the Mariner 2 spacecraft (Barath *et al.* 1963). Using existing laboratory data, (Sagan 1960) showed that water vapor and CO₂ absorbed in complementary parts of the thermal infrared and together could produce a greenhouse effect sufficient to explain the high surface temperature. The first nongray greenhouse model of Venus' atmosphere was developed by (Pollack 1969a; Pollack 1969b), in which CO₂, H₂O, and N₂ were responsible for the infrared opacity. This one-dimensional radiative-convective model incorporated an adiabatic temperature profile in a layer beneath optically thick water clouds. Although some pressure-induced bands of CO₂ were considered, the radiative properties of CO₂ at high temperatures and pressures were poorly constrained by the available data. Pollack concluded that an H₂O mixing ratio of 0.5% was needed to explain the observed temperature distribution in Venus' atmosphere. Although the model was consistent with the available spacecraft data (from the Venera 4 mission) on H₂O abundances (Nature 1967), later H₂O measurements from the Venera 11 and 12 spacecraft in 1977 and from Pioneer Venus in 1980 indicated a far lower abundance of about 100 ppm (Moroz *et al.* 1978; Oyama *et al.* 1979; Oyama *et al.* 1980). Pollack *et al.*

[1980a] published an improved radiative transfer model, utilizing updated solar flux, gaseous composition, temperature, and cloud structure measurements from Pioneer Venus. SO₂, CO, and HCl were added as sources of infrared opacity, as well as several pressure-induced transitions of CO₂. They were able to reproduce the observed surface temperature and lapse rate structure of Venus' atmosphere very closely with a greenhouse model that contained water vapor abundances consistent with measurements from the Pioneer gas chromatograph and Venera spectrophotometer.

The major component of Venus' atmosphere is CO₂, with a mixing ratio of 0.965. Although CO₂ is a greenhouse gas on Earth, its low abundance in the atmosphere is controlled by life and the CO₂ geochemical cycle. In addition, there is clear evidence that the terrestrial abundance of atmospheric CO₂ is currently being affected by anthropogenic sources (Houghton *et al.* 1990). A comparison of the total inventories of CO₂ (Fegley and Lodders 1992; Wildt 1940) shows that the atmosphere of Venus contains approximately the same amount of CO₂ as on Earth, including carbonates formed by sedimentation and biological processes, as well as the CO₂ in the atmosphere. At the temperatures and pressures found at Venus' surface, it is likely that much of the planet's total carbon inventory resides in the atmosphere. However, just as on Earth and Mars, a CO₂ geochemical cycle probably exists or did exist on Venus. Evidence for volcanism, from the striking radar images of the surface sent by the Magellan spacecraft, is widespread (Head *et al.* 1991; Head *et al.* 1992). Recently, carbonate-sulfate volcanism has been proposed to explain the extraordinarily long canali on Venus, as well as striking fluvial features (Kargel *et al.*

1994). Volcanism represents the dominant source in both the terrestrial and martian CO₂ cycles, and it may be inferred that during periods of large-scale volcanism, CO₂, SO₂, H₂O, and other radiatively important volatiles are injected into Venus' atmosphere. UV spectroscopic measurements (Esposito 1984) show approximately an order of magnitude decrease in cloud top SO₂ abundances from 1978 to 1983. It was suggested that this temporal variability could have been the result of major volcanic activity prior to the Pioneer Venus mission.

The high temperatures and pressures (~92 bars) at the surface of Venus have led to the suggestion that surface-atmosphere interactions may play an important role in buffering CO₂ and other volatiles. Urey [1952] first proposed that atmospheric CO₂ on Venus could be buffered through reactions with surface minerals and Rasool and de Bergh [1970] proposed that heterogeneous reactions may have important implications for the evolution of climate on Venus. They showed that the surface temperature and pressure on Venus coincide approximately with the P-T equilibrium of the calcite-wollastonite-CO₂ mineral reaction. Recent laboratory data on the equilibria and kinetics of possible surface-atmosphere reactions under Venus-like conditions provide important insights into the role that they may play in moderating Venus' climate (Fegley *et al.* 1995; Fegley and Treiman 1992). Small changes in radiatively active atmospheric species can change the magnitude of the Venus greenhouse effect and shift the equilibrium points of key mineral buffers, resulting in an important climate feedback mechanism. If this is the case, perturbations to the atmospheric inventory of radiatively active species, caused by volcanic eruptions, may have a significant impact on the climate of Venus and upon the stability of the greenhouse effect. Heterogeneous reactions between SO₂ and the surface are likely, since the deep atmosphere abundances are 1 to 2 orders of magnitude higher than can be accounted for by equilibrium with surface minerals (Fegley and Treiman 1992). If surface reactions are indeed active in altering atmospheric SO₂ and CO₂ and if reaction rates are significant on geologic timescales, it is of interest to assess the impact they may have on the climate of Venus. This paper discusses the development and results of a Venus climate model that takes into account the interaction between radiative and chemical processes in the atmosphere, and surface-atmosphere interactions.

Venus Climate Evolution Model

We have sought to address questions regarding the stability of Venus' climate by developing a coupled surface-atmosphere climate model. A one-dimensional radiative-convective model is employed for atmospheric temperature structure calculations. Laboratory equilibrium and kinetic data for selected heterogeneous reactions are used to couple geochemical cycles to the atmospheric radiative-convective equilibrium calculations. The model admits equilibrium solutions, wherein the atmosphere and

surface are in thermochemical equilibrium with an atmosphere in radiative-convective equilibrium. By using heterogeneous reaction kinetics, however, the model also allows the determination of dynamical solutions. In this way, we are able to explore both the stability of the model over a wide range of pressures and temperatures and timescales for climate change on Venus due to surface-atmosphere interactions.

Radiative Transfer Model

In order to model the radiative-convective equilibrium state of Venus' atmosphere over a wide range of molecular abundances, we developed and used several simplifying parameterizations. The spectral data base we used was developed by Pollack *et al.* [1980a] for greenhouse models of Venus' atmosphere and subsequently updated and improved upon for high temperatures (Watson and Rothman 1992). The database contains spectral information on the permitted transitions of CO₂, H₂O, SO₂, CO, HCl, HDO, COS, HF, and H₂S, as well as several pressure-induced transitions of CO₂ and hot bands of CO₂ and H₂O. Using the correlated-k method (Goody *et al.* 1989; Lacis and Oinas 1991), broadband opacities were calculated for 68 spectral intervals from 1.7 to 250 μm. Average correlated absorption coefficients for spectral interval j and gas species l , k_{jl}^{tot} were calculated by including continuum and particle absorption:

$$k_{jl}^{tot} = k_{jl}^{gas} + k_l^{cont} + k_j^{part}$$

In order to perform rapid calculations of model atmosphere temperature structures, Rosseland mean absorption coefficients were used, where the average absorption coefficient is given by

$$\langle \kappa \rangle = \frac{\sum_j \frac{\partial B(\tilde{\nu}_j, T)}{\partial T} \Delta \tilde{\nu}_j}{\sum_j \left[\left(\frac{\partial B(\tilde{\nu}_j, T)}{\partial T} \right) \Delta \tilde{\nu}_j \right] \sum_l \left(\frac{1}{k_{jl}^{tot}} \right) W_l}$$

B is the Planck function, whose derivative is evaluated at the center of each spectral interval, $\Delta \tilde{\nu}_j$, and W_l are the normalized Gauss weights for the Gauss point k_{jl}^{tot} . For the climate model, we are concerned primarily with the evolution of surface temperatures over a wide range of conditions.

Rosseland mean opacities were calculated for 12 model atmospheres representing a wide range of temperatures, pressures and atmospheric mixing ratios. Opacities for arbitrary model atmospheres were then obtained by interpolation, using a power law fit to the atmospheric mixing ratios, $\{X_i\}$,

$$\begin{aligned} \langle \kappa(P, \{X_i\}) \rangle = & aX_{CO_2} + bX_{H_2O} + cX_{SO_2} + dX_{CO} \\ & + e(X_{CO_2} X_{H_2O})^g + f(X_{CO_2} X_{SO_2})^h \end{aligned}$$

Parameterizing the effects of band overlaps in the calculation of the Rosseland mean opacities as power laws allowed for a well-determined fit to the 12 model atmospheres with different mixing ratios and temperatures. For each value of pressure and temperature, a matrix solution was sought to evaluate the coefficients $a-h$. Any value of the Rosseland mean absorption coefficients can therefore be described as a point in a six-dimensional space $\kappa(P, T, X_{\text{CO}_2}, X_{\text{H}_2\text{O}}, X_{\text{SO}_2}, X_{\text{CO}})$ and is uniquely determined.

Solar flux deposition for the present Venus atmosphere was taken directly from Pioneer Venus solar flux measurements, using the solar flux radiometer (Tomasko *et al.* 1979; Tomasko *et al.* 1980). For the purpose of adopting these data for different climate regimes, a simple scheme was employed. Solar flux absorption for Venus is poorly understood, since the identity of the absorber or absorbers is not known (Esposito 1980; Pollack *et al.* 1980). Inferring the solar flux absorption for other climate regimes, therefore, is somewhat arbitrary, since the changes in abundances of the absorber would be driven by unknown chemical processes in the atmosphere. Therefore the simple approach of truncating the solar absorption profile for lower pressures, and linearly extrapolating the solar absorption in the logarithm of P for higher pressures has been employed. In the radiative transfer model, the total amount of absorbed sunlight is described as

$$f(P) = 1 - \frac{F(P)}{F(0)}$$

where $F(P)$ is the solar flux at pressure level P and $F(0)$ is the solar flux entering at the top of the atmosphere; $f(P)$ is therefore the total fraction of sunlight absorbed above a given pressure level. Total opacities τ at a given level are described in terms of the Rosseland mean absorption coefficients (which are calculated in bar^{-1}) as

$$d\tau = \langle \kappa \rangle dP$$

Using the gray-Eddington approximation and the above descriptions of the opacities and solar flux deposition, the temperature structure may be determined from

$$\sigma T^4 = \sigma T_e^4 \left(\frac{1}{2} + \frac{3}{4} \tau \right) (1-f)$$

where σ is the Stefan-Boltzmann constant and T_e is Venus' effective temperature. Therefore the surface temperature is given by

$$T_g = T_e \left[\left(1 + \frac{3}{4} \tau^* \right) (1-f^*) \right]^{\frac{1}{4}}$$

where τ^* is the total atmospheric infrared opacity and $1-f^*$ is the fraction of sunlight that reaches the surface of Venus. A convective adjustment was made by calculating the adiabatic lapse rate,

$$\Gamma = \frac{g}{c_p}$$

where g is the gravitational acceleration and C_p the specific heat, is also a function of pressure, and was obtained from the Venus International Reference Atmosphere (Kliore *et al.* 1986). Where the radiative equilibrium lapse rate was found to be less than the convective lapse rate, the temperature profile was set to the local adiabat. For the current Venus atmosphere, the above calculations provided a good fit to temperature profiles from Pioneer Venus data. The results of this initial calculation are shown in Figure 1.

Surface-Atmosphere Interactions

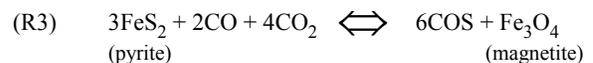
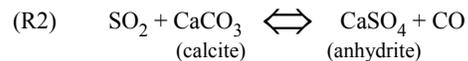
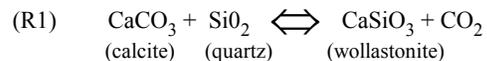
For the purpose of modeling the effects of surface-atmosphere interactions on the climate of Venus, heterogeneous reactions were selected by employing the following criteria:

1. Surface minerals involved in reactions with the atmosphere should have a high probability of being present under current Venus conditions. Venera 13/14 and Vega 2 Xray fluorescence measurements were used to determine abundances of elements heavier than Mg. Likely normative mineral compositions for these landing sites were then derived (Barsukov *et al.* 1986; Surkov *et al.* 1984; Surkov *et al.* 1986).

2. Equilibrium values for proposed reactions should be close to those found at Venus' surface. The extensive study of possible surface-atmosphere reactions by (Fegley and Treiman 1992) discusses a large number of such reactions and predicts the stability of many possible mineral assemblages at Venus' surface.

3. Only reactions for which laboratory kinetic data were available were considered. Although this severely restricts the number of reactions under consideration, atmospheric buffers can only be effective if they are kinetically favored. A number of potential buffering mechanisms for such important volatiles as H_2O , HCl , and HF have been proposed (Fegley and Treiman 1992; Lewis 1970; Volkov *et al.* 1986) but must await laboratory determinations of reaction rates before their impact on Venus' climate can be ascertained.

Of the hundred or so surface-atmosphere reactions considered in the literature, only three meet the above three criteria. They are



Reaction (R1), the calcite-wollastonite- CO_2 reaction, was originally proposed (Urey 1952) as a key mechanism for

the buffering of CO₂ on Venus. Subsequent laboratory investigations of equilibrium values of this and other possible CO₂ buffering mechanisms (Fegley and Treiman 1992) as well as improved determinations of Venus' surface conditions have confirmed that this reaction may indeed be a very important geochemical mechanism for the regulation of CO₂ on Venus. The calcite-wollastonite reaction involving CO₂ is an important metamorphic process in the Earth's crust and is a key part of the carbonate-silicate geochemical cycle. CO₂ is liberated by this reaction, as it is dissolved in magmas which eventually find their way to the surface through volcanism. It is remarkable that the equilibrium point for this reaction coincides nearly exactly with the temperature and pressure found on the surface of Venus. *Mueller and Kridelbaugh* [1973] attempted to determine the rate of this reaction under Venus-like conditions. Although their work has been criticized by *Fegley and Treiman* [1992] as being inapplicable to Venus due to faulty analysis of the laboratory data, it will be shown here that with the proper formalism, the results are roughly scalable to Venus.

Mueller and Kridelbaugh [1973] proposed a rate constant for the decarbonation of calcite by directly measuring its rate of decomposition. Their data are in the form of an Arrhenius plot, which yields the activation energy, and therefore a rate constant in s⁻¹, from

$$R = Ae^{-\frac{AE}{RT}}$$

Fegley and Treiman [1992] have asserted that this cannot be applicable to a planetary problem, since a heterogeneous surface reaction rate, which depends on the ability of CO₂ to diffuse to new surfaces, was not directly measured. However, given the conditions at which the experiments took place, we employed a simple reaction-diffusion equation to deduce a plausible surface reaction rate. If n is the atmospheric number density of CO₂, z is the depth into the soil, and D is the diffusion coefficient for CO₂ in the soil pore space, the atmospheric number density of CO₂ at the surface due to this reaction may be described by

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial z^2} + \frac{n}{\tau}$$

Here, the rate constant R , derived in the laboratory, is simply $1/\tau$. Solving the reaction/diffusion equation, the instantaneous surface reaction rate is simply the net flux of CO₂ into the soil, or

$$F = n \left(\frac{D}{\tau} \right)^{\frac{1}{2}}$$

and depends on the atmospheric number density, the lifetime, τ , and on the diffusion coefficient (*Bullock et al.* 1994). Diffusion of CO₂ into or out of the soil proceeds due to the concentration gradient set up by its reaction with mineral surfaces. For the diffusion of atmospheric CO₂ through soil pore space, we take $D = \epsilon D_o$, where D_o is the usual gas-gas diffusion coefficient derived from kinetic

theory and ϵ is the soil porosity. The assumption is that molecular diffusion is the dominant method of transport, which is correct when the mean free path of the gas is less than the soil pore space size. This condition is easily met under Venus surface conditions, even for soil pore sizes of much less than 1 μm . The direct application of laboratory kinetic data yields the interpretation of a reaction rate that is temperature, but not concentration dependent. Over geological timescales, the progress of a given geochemical sink will obviously be dependent upon the atmospheric column abundance. Using the above flux, derived by considering both the diffusion and reaction of an atmospheric species in the soil, a more accurate analysis of the effectiveness of a given buffering reaction on the climate feedback is made possible.

By using reaction-diffusion kinetics to adapt the *Mueller and Kridelbaugh* [1973] laboratory data for the decarbonation rate of calcite under Venus surface conditions, it is found that the calcite-wollastonite-CO₂ buffer reaction proceeds with surface reaction rate of

$$R_1 = 10^{15.91} e^{-\frac{11356}{T}} \text{ molecules/cm}^2 \text{ s}$$

Fegley and Prinn [1989] directly measured the surface reaction rate of the SO₂ anhydrite buffer, reaction (R2). Their results were derived for current Venus surface conditions ($T = 735 \text{ K}$, $P_{\text{SO}_2} = 12 \text{ mbar}$) and was found to be

$$R_2 = 10^{19.64} e^{-\frac{15248}{T}} \text{ molecules/cm}^2 \text{ s}$$

In order to scale these laboratory data to other climate regimes (i.e., other temperatures and partial pressures), a scheme similar to that employed for reaction (R1) was used. Thus the net effect of the proposed SO₂-anhydrite buffering mechanism on Venus' climate is dependent upon temperature through both the reaction rate and the diffusion coefficient. Furthermore, through the flux equation, the surface reaction rate is also dependent directly upon the atmospheric concentration found at the surface.

One of the striking results from the Magellan spacecraft mission to Venus was the observation of areas of extremely low microwave emissivity in the highlands. It has been proposed (*Pettengill et al.* 1982) that this is due to minerals consisting of inclusions of conducting material dispersed in a more insulating matrix. Pyrite is an excellent candidate due to the correspondence of the equilibrium point of reaction (R3) with the temperatures and pressures found in the Venus highlands (*Fegley and Treiman* 1992). The kinetics of pyrite weathering under Venus conditions has been determined in the laboratory (*Fegley et al.* 1995). They report activation energies and rate constants for the decomposition of pyrite under a variety of temperatures and CO₂-dominated atmospheric compositions. These data may easily be converted to a temperature-dependent surface reaction rate under Venus conditions. Using an activation energy of $1.5 \times 10^6 \text{ J/mol}$ and a reaction rate of 4×10^{-4}

cm/hr, the reaction rate in terms of the number of sulfur atoms is

$$R_3 = 10^{25.81} e^{-\frac{18050}{T}} \text{ molecules/cm}^2 \text{ s}$$

This reaction may have important consequences for the atmospheric abundances of COS, and therefore on tropospheric chemistry. The reaction may be important for feedbacks between atmospheric chemistry, volatile abundances, and climate, so it is included in the present model.

Equilibrium data for the above three reactions is widely available, although has only recently (Fegley and Treiman 1992) been obtained accurately for Venus-like conditions.

Clouds

The global energy balance of Venus' atmosphere is controlled by the deposition of solar energy. Clearly, a dramatic change in the scattering and reflection of sunlight by cloud particles can have a direct effect on the effective temperature, through the energy balance

$$\sigma T_e^4 = (1 - A) F_o / 4$$

where T_e is the effective temperature, A is the albedo, and F_o is the solar flux. Significant changes in cloud composition or morphology are likely to produce changes in solar energy deposition, as well as global albedo. Changes in atmospheric abundances of SO₂ and H₂O, in addition to their radiative effects on Venus' climate, may thus also be involved in cloud albedo feedback. However, Venus' 23 km thick cloud decks currently have a visible optical depth of 35-50 (Esposito *et al.* 1983; Grinspoon *et al.* 1993). Enormous changes in cloud morphology would therefore be necessary before the global albedo would be affected. Furthermore, it is not clear to what magnitude cloud mass loading would be affected by large changes in atmospheric abundances of either SO₂ or H₂O. H₂SO₄ aerosols in Venus' clouds currently account for only 0.1% of the columnar mass of SO₂ and perhaps 1% of the columnar mass of H₂O. Clearly, an evolutionary photochemical model of Venus' clouds is required before addressing questions concerning the role of clouds in climate feedback. So for the present work, the bolometric albedo of Venus is taken to be constant, even though large changes in atmospheric abundances could have an undetermined effect on the clouds and albedo of the planet. Cloud thickness in our modeling is assumed to be defined by the evaporation of H₂SO₄-H₂O droplets at the lower boundary and by sufficient SO₂, H₂O and UV flux at the upper boundary. Thermal infrared opacity due to cloud aerosols is assumed to be constant throughout the climate evolution model.

Results

In order to explore the stability characteristics of the climate, the system was allowed to evolve statically in

order to determine equilibrium states for both the atmosphere and surface. In general, these two equilibrium fields will not coincide. This is shown in Figure 2 for calculations involving conditions that are consistent with the present atmospheric abundances. The solid line represents the surface pressure and temperature that is achieved by allowing the three surface-atmosphere reactions to simultaneously be in equilibrium. The overall surface pressure is dominated by the calcite-wollastonite-CO₂ equilibrium with a small, but significant, contribution due to the SO₂-anhydrite buffering mechanism. The dotted line represents the surface conditions that result from radiative-convective equilibrium that is achieved with atmospheric partial pressures that are consistent with the surface mineral buffering.

With the climate feedbacks that are considered in this model, it can be seen that these two curves intersect at only two points. At about 95 bars of surface pressure and 735 K, equilibrium between the surface mineral buffers and radiative-convective processes is achieved. The intersection at the lower right of the P-T diagram corresponds roughly to the surface temperature and pressure that exists on Venus today. Another equilibrium point exists at an atmospheric state where most radiatively active species have returned to surface reservoirs, and only water and inert gases (i.e., N₂) remain. This is state corresponds to the intersection of the dotted and solid lines at the upper right of the plot. An extremely important point here, and one that is robust to many of the details of the model, is that the current equilibrium point is unstable. This is due chiefly to the relative slopes of the radiative and mineral equilibria curves. Small perturbations in the climate system, such as an injection of radiatively active volatiles through volcanism or the removal of a constituent through buffering, will precipitate a catastrophic change in climate to a much hotter or much cooler state. A good candidate for initiating a cooling trend, for example, would be the uptake of SO₂ though the SO₂-anhydrite buffer, since Venus' lower atmosphere currently contains 10 to 100 times as much SO₂ as can be accounted for by equilibrium with surface rocks (Fegley 1988; Fegley and Treiman 1992; Volkov *et al.* 1986).

Nominal values for the thermodynamic constants of the three surface-atmosphere reactions considered here place Venus' present atmosphere on the cooler side of the mineral equilibrium curve. However, uncertainty in these data could place Venus' current conditions on either side of this unstable equilibrium. Recent Magellan images have shown that Venus has an extensive, and very likely ongoing, history of volcanism. Rates of extrusive volcanism, as determined by the Monte Carlo simulations (Bullock *et al.* 1993) show that an extrusive flux of about 0.4 km³/yr is consistent with the observed impact cratering record. Rates of intrusive volcanism are unknown but relevant; if the ratio of intrusive to extrusive fluxes is assumed to be about 10 (consistent with estimates for terrestrial volcanism), then outgassing of volatiles occurs from approximately 5 km³/yr of magma. Although volatile

abundances of Venus magmas are poorly constrained, estimates of water abundances from the residence times of atmospheric water (Grinspoon 1993), and the observed temporal variability of SO_2 (Esposito 1984), show that significant sources of radiatively active gases may be currently active. It is possible, therefore, that the nominal cooling trend that is demonstrated in the model is offset by sources that are presently active. If this is true, Venus' climate may be in a kind of steady state, with volcanism providing sources of infrared opacity to the atmosphere and geochemical sinks removing them.

If, on the other hand, the Venus surface-atmosphere system were on the other (hot) side of the separatrix, a rapid escalation of temperature and pressure would ensue due to a strong positive feedback between the surface buffering reactions and radiative-convective equilibrium. The viability of such a runaway situation is predicated on the assumption that both sulfur and carbon reservoirs are capable of continuously supplying volatiles to the atmosphere. This may not be the case for CO_2 , since the current atmospheric inventory of CO_2 on Venus is nearly the same as the combined oceanic-crustal-atmospheric inventory on Earth. At some point in this runaway scenario, therefore, one or more of the surface buffers must switch off, and the climate of Venus would be "pegged" at a high temperature and pressure state, with all surface reservoirs depleted.

Understanding the sensitivity of the climate model system may be explored by considering the effect of a single large-scale injection of volatiles into the atmosphere. Therefore the model was allowed to evolve in a number of runs by increasing the initial amounts of SO_2 and H_2O in the atmosphere. Recent work (Grinspoon 1993), employing estimates of the current H_2O escape rate and volcanic flux (Bullock *et al.* 1993), has resulted in an estimate of the water abundances of Venus lavas. This estimate places a rough upper bound on the water abundance of about 50 ppm. Although far less than terrestrial abundances, even moderate volcanic fluxes could precipitate a climate catastrophe in the climate evolution model. Taking SO_2 abundances appropriate for terrestrial lavas (about 0.2%) and H_2O abundances of 50 ppm, it was found that a single volcanic event of about $18 \times 10^6 \text{ km}^3$ is sufficient to push the climate system through the unstable equilibrium point to one with a high surface temperature and pressure. Magellan images have shown that Venus' basaltic flood plains are large, covering about 80% of the planet (Head *et al.* 1991), and individual edifices themselves are massive compared with terrestrial ones. Moderate to large igneous provinces on Earth, such as the Deccan traps, are as large or larger than the $18 \times 10^6 \text{ km}^3$ event required to drive the Venus climate model into a high-temperature, high-pressure runaway state.

Using the laboratory kinetic data that are available for the buffering reactions and the reaction-diffusion kinetics developed here, the model was also allowed to evolve dynamically in time. The idea was to determine the timescales involved in the evolution of the system to new

climate regimes. The dynamic response of the model for the present atmosphere, without sources, is depicted as the dot-dashed line in Figure 2. This line represents 100 My of evolution and shows how the surface conditions evolve in P-T space. Although the initial trajectory away from the equilibrium point is rapid (the 10 My point is marked with a cross), evolution to the cooler, 3 bar regime slows greatly due to kinetic inhibition of the surface-atmosphere reactions at lower temperatures. Evolution of the atmospheric temperature profile and abundances of major atmospheric constituents are shown in Figures 3 and 4. CO_2 and SO_2 abundances decrease with time, but their exact rates of decrease are determined by the nonlinear nature of the feedbacks between surface-atmosphere interactions with atmospheric radiative-convective equilibrium. The evolution of surface temperature is shown more clearly on a plot that is linear with time in Figure 5.

The dynamics of the climate model in response to a single injection of SO_2 and H_2O into the atmosphere, as discussed above, is shown in Figure 6. Calculations were for a much shorter time period, since at these higher temperatures and pressures, the surface and atmosphere rapidly equilibrate. The total timescale was 2×10^5 years, after which the catastrophic evolution of the model produced instabilities in the calculations. The corresponding mixing ratios and surface temperature are shown in Figures 7 and 8.

We also considered the case where the climate of Venus is in a steady state between surface buffering reactions, continual injection of radiatively active gases, and exospheric escape. The dynamics of the model were altered by including constant source terms for of SO_2 and H_2O . These source terms can be viewed as a constant volcanic flux; atmospheric H_2O is in steady state with exospheric escape while SO_2 is in steady state with surface-atmosphere reactions. By starting with the current Venus conditions, and by including a source of $4 \times 10^{14} \text{ g}$ of SO_2 per year, it was found that the climate system would enter a steady state near its current unstable equilibrium point. This corresponds to volcanic flux of about $57 \text{ km}^3/\text{yr}$, given the estimates of lava volatile content discussed above. The evolution of the system in P-T space is shown in Figure 9, and the corresponding evolution of atmospheric abundances and surface temperature are shown in Figures 10 and 11.

Conclusions

The purpose of this work has been to illustrate how climate feedbacks may arise on Venus due to surface-atmosphere interactions and atmospheric radiative-convective equilibrium. Although the atmospheric evolution and geochemical cycles in a planetary system are naturally extremely complex, by modeling the behavior of key elements of the climate and its feedbacks, it is possible to deduce some general stability properties that the Venus climate system may possess. This approach has been

applied to the climate of Venus to show that with respect to perturbations of Venus' atmospheric inventory of radiatively active gases, Venus' climate is unstable. A more complete understanding of Venus' climate must necessarily involve a great number of factors that can be progressively introduced into the kind of approach discussed here. In particular, additional modeling, involving exospheric escape processes, atmospheric photochemistry and cloud physics, and a more complete set of heterogeneous reactions with the surface must be developed to provide a much richer set of feedback loops than exist in the present model.

By modeling the Venus climate system using this simplified approach, certain dynamical behaviors are illustrated:

1. Assuming no sources of volatiles, the current Venus climate appears to be in a state of unstable equilibrium. This conclusion is robust with respect to the uncertainties in the laboratory thermodynamic data. For nominal values of the thermodynamic and kinetic data, timescales for significant climatic cooling due to surface-atmosphere interactions are 10^7 to 10^8 years.

2. A sufficiently large instantaneous source of radiatively active volatiles can precipitate a climate catastrophe in the model towards a much higher surface temperature and pressure. A single volcanic eruption of $18 \times 10^6 \text{ km}^3$, assuming an SO_2 abundance of 0.2% and an H_2O abundances of 50 ppm in erupting lavas, is sufficient to initiate a runaway greenhouse effect. In reality, an instability like this would most likely be curtailed by the depletion of all surface reservoirs of radiatively active species. This "pegged" climate state may be an accurate description of the current climate on Venus.

3. Current Venus climate conditions may be in a steady state due to a continual source of radiatively active gases exsolved by volcanism, surface-atmosphere interactions, and exospheric escape. A volcanic flux of $57 \text{ km}^3/\text{yr}$, assuming a terrestrial-like SO_2 abundance of 0.2% in erupting lavas and steady state atmospheric H_2O abundance, was found to be sufficient to keep the current Venus climate system in steady state. However, the long-term effects of photochemistry and exospheric escape processes, as well as cloud chemistry and albedo feedbacks were not considered.

The present model is viewed as a first step in the systematic modeling of the climate evolution of the planet Venus. Understanding the evolution of Venus' climate will be greatly improved by incorporating an evolutionary cloud physics model in an enhanced version of the current model. More accurate laboratory data of the heterogeneous chemistry that is likely to be occurring at the surface of Venus are essential to understanding geochemical cycles that affect climate. Above all, improved data, from both Earth-based observations and spacecraft missions to Venus, are essential for measuring the deep atmospheric

abundances and temporal variability of radiatively important species.

Acknowledgments. This work is dedicated to the memory of the late Jim Pollack, who was an active participant in all phases of this research. The work was supported by grants from NASA's Planetary Atmospheres Program (NAGW-3584) and NASA's Graduate Student Researchers Program (NGT-51294). The authors would like to thank Richard Freedman for his part in the atmospheric Rosseland mean opacity calculations and Kevin Zahnle, Bruce Jakosky, and Bruce Fegley for their helpful suggestions.

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Paper number 95JE03862
0148-0227/96/95JE-03862\$05.00

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(Received September 12, 1995; revised December 12, 1995; accepted December 14, 1995.)

Figure 1. Temperature structure calculation for the current Venus atmosphere. The solid line shows the model result, and the dotted line shows the temperature profile from Pioneer Venus (Venus International Reference Atmosphere).

Figure 3. Evolution of the temperature structure using initial conditions identical with the current Venus atmosphere. Calculations are for 100 My and each dashed line shows 10 My of evolution. The atmosphere is undergoing cooling, so it is evolving to the left.

Figure 2. Mineral equilibria and radiative-convective equilibrium curves for surface pressures and temperatures. The solid line represents the equilibrium values of surface temperature and pressure for the three surface-atmosphere reactions combined. The dotted line shows the surface temperatures and pressures that result from atmospheric radiative-convective equilibrium that is achieved with atmospheric mixing ratios that are consistent with the mineral equilibria. A dynamical solution to the Venus climate model, employing reaction-diffusion kinetics, is given by the dot-dashed line. Initial conditions are for the present Venus atmosphere. The dot-dashed line shows 100 My of evolution of the surface in P-T space, assuming no sources. The cross marks evolution after 10 My.

Figure 4. Evolution of the surface partial pressures of major atmospheric constituents for 100 My, starting with the current Venus atmosphere.

Figure 5. Evolution of surface temperature, starting with the current Venus atmosphere.

Figure 7. Evolution of the partial pressures of major atmospheric constituents for 2×10^5 years, starting with a Venus atmosphere that has been enhanced in H_2O by 15% and SO_2 by 15%.

Figure 6. Dynamical solution of the Venus climate model, employing surface reaction-diffusion kinetics for SO_2 . Initial conditions are for a Venus atmosphere that has been enhanced in H_2O by 15% and SO_2 by 15%. The solid and dotted lines are the same as in Figure 3. The dot-dashed line shows 2×10^5 years of evolution of the surface in P-T space, assuming no sources.

Figure 8. Evolution of surface temperature, starting with a Venus atmosphere that has been enhanced in H_2O by 15% and SO_2 by 15%.

Figure 9. Dynamical solution of the Venus climate model, employing surface reaction/diffusion kinetics for SO_2 and steady state water abundance. Conditions are for a Venus atmosphere that has a constant source of 4×10^{14} g SO_2 per year. Water approaches steady state with a constant flux of 10^{13} g/yr. The solid and dotted lines are the same as in Figure 3. The dot-dashed line shows 1 My of evolution of the surface in P-T space, describing part of a closed cycle around the unstable equilibrium point.

Figure 11. Evolution of surface temperature with a constant source of 4×10^{14} g SO_2 per year and water in steady state.

Figure 10. Evolution of the partial pressures of major atmospheric constituents for 1 My, with a constant source of 4×10^{14} g SO_2 per year and water in steady state.