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Stabilization of Venus' climate by a chemical-albedo feedback

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It has been suggested that the atmospheric concentration of SO_2 observed on Venus coincides with the equilibrium concentration over pyrite-magnetite assemblage (pyrite-magnetite buffer). If the atmospheric SO_2 abundance is controlled by the chemical reaction at the planetary surface, we expect coupling between the atmospheric SO_2 abundance and the surface temperature. Here, we propose that the pyrite-magnetite buffer combined with cloud albedo feedback controls the surface temperature on Venus. We show that this mechanism keeps the surface temperature in a rather narrow range around the presently observed value against large variations of solar luminosity and total atmospheric mass.

1. Introduction

The climate of Venus has been examined by the climate models which combine radiative and chemical processes (e.g., Bullock and Grinspoon, 1996; Hashimoto *et al.*, 1997). These studies have shown that surface chemical reactions have a large influence on the climate.

Bullock and Grinspoon (1996) construct a model of Venus' climate and argue that at present Venus is at a state of unstable equilibrium. Starting with the current venusian atmosphere, catastrophic cooling of the climate takes place in the climate model of Bullock and Grinspoon (1996). The catastrophe is caused by feedbacks between surface chemical reaction and the greenhouse effect. The following two chemical reactions assumed by Bullock and Grinspoon (1996, 1998) induce the catastrophe:

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2(\text{gas}), \tag{1}$$

$$SO_2(\text{gas}) + CaCO_3 = CaSO_4 + CO(\text{gas}). \tag{2}$$

The catastrophe is initiated by the uptake of atmospheric SO_2 through reaction (2), because Venus' atmospheric SO_2 abundance is much higher than the equilibrium value produced by reaction (2) (e.g., Fegley and Treiman, 1992; Klose *et al.*, 1992). Since the SO_2 greenhouse effect decreases with the decrease of atmospheric SO_2 abundance, the surface temperature drops. Then, atmospheric CO_2 begins to decrease through reaction (1), since temperature drop promotes calcite formation. Once the atmospheric CO_2 decreases, a runaway climate drift proceeds by the collaboration of the fixation of atmospheric CO_2 and cooling of the atmosphere.

The occurrence of instability in the model of Bullock and Grinspoon (1996) results from their assumption that there are large deposits of carbonate rock on the surface. No observation has confirmed the existence of carbonate on Venus' surface, though the hypothesis of a carbonate buffer favors the existence of carbonate. The carbonate buffer has been postulated to account for the CO_2 abundance of Venus' atmosphere. However, carbonate buffer cannot buffer the CO_2 abundance in the atmosphere when we take CO_2 greenhouse effect into account, since temperature change caused by CO_2 greenhouse effect disturb the chemical equilibrium (Hashimoto *et al.*, 1997). Moreover, if carbonate exists, it seems there is not much probability of our observing the current Venus' climate, since it would be difficult to maintain the observed SO_2 abundance for a geological timescale. According to the experimentally determined rate of SO_2 consuming reaction (2) (Fegley and Prinn, 1989), it takes about 2 Myr to reduce the observed SO_2 abundance to the equilibrium value predicted by reaction (2). The climate state should change on this timescale if there were no replenishment of SO_2.

In this study, we develop a climate model on the assumption that no carbonate exists on the Venus' surface, since there is no observational evidence for carbonates on the Venus' surface. Based on the observation of composition and temperature of the venusian atmosphere and thermodynamical considerations, we also assume that the atmospheric SO_2 abundance is controlled by the equilibria with the pyrite-magnetite assemblage:

$$\begin{aligned} &3\,FeS_2 + 16\,CO_2(\text{gas}) \\ &\quad = Fe_3O_4 + 6\,SO_2(\text{gas}) + 16\,CO(\text{gas}). \end{aligned} \tag{3}$$

The experiments performed by entry probes and near-infrared observations of the nightside of Venus (e.g., Bézard *et al.*, 1993; Bertaux *et al.*, 1996; Suleiman *et al.*, 1996) detected about 150 ppmv of SO_2 in the lower atmosphere of Venus. This observed mixing ratio of SO_2 is close to the equilibrium mixing ratio over pyrite-magnetite assemblage (e.g., Zolotov, 1991; Klose *et al.*, 1992) calculated from the observed CO concentration (Pollack *et al.*, 1993) and thermochemical data (Robie *et al.*, 1979; Chase *et al.*, 1985). In the following we call this as the pyrite-magnetite buffer.

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When the pyrite-magnetite buffer controls the atmospheric SO_2 abundance, we expect there to be coupling between the atmospheric SO_2 abundance and surface temperature, because SO_2 is an optically active gas and makes a contribution to the greenhouse warming (Pollack *et al.*, 1980). Suppose that the surface temperature is increased, then additional SO_2 gas is released from the surface rocks through reaction (3). An increase in atmospheric SO_2 raises the surface temperature. This positive feedback is suggested by Klose *et al.* (1992), and they concluded that the climate system would not be stabilized. We call this as a chemical-greenhouse feedback.

However, there exists another feedback loop by way of cloud formation. Since SO_2 is a precursor of the Venus' cloud, SO_2 abundance would be closely related to cloud. A decrease in surface temperature removes some atmospheric SO_2 and reduces the production of H_2SO_4 and H_2SO_4 cloud. We have to consider a changes both in the cloud greenhouse and albedo effects and greenhouse effect to examine the stability of the climate. Though the former forms a positive feedback loop, the later forms a negative feedback loop, as the decrease of atmospheric SO_2 reduces the cloud albedo and raises the surface temperature. The reduced cloud reduces planetary albedo, and then, raises the surface temperature. Similar negative feedback will also operate against an increase of the surface temperature. We call this the chemical-albedo feedback.

If the chemical-albedo feedback surpasses the chemical-greenhouse feedback, the Venus' climate would be stabilized. In this paper we construct a model of Venus' climate that incorporates a chemical model, a cloud model, and an atmospheric model and evaluate the stability of the Venus' climate.

2. Climate Model

Our climate model consists of three parts: chemical model, cloud model, and atmospheric structure model.

2.1 Chemical model: Pyrite-magnetite buffer

In our climate model, the pyrite-magnetite buffer controls the atmospheric SO_2 abundance. The pyrite-magnetite buffer requires that there be pyrite and magnetite on the surface of Venus. However, neither the existence nor the non-existence of pyrite and magnetite is supported by the observations, since no observation was performed to determine the mineralogy of the Venus' surface. The material of the Venus' surface can be inferred from the results of the radio and radar observations. High altitude surficial deposits of pyrite and magnetite have been suggested to account for the high radar reflectivity observed on the mountaintops (Pettengill *et al.*, 1982, 1988; Ford and Pettengill, 1983; Klose *et al.*, 1992). These models were abandoned because it turned out that these models cannot account for the result of the bistatic radar observations (Pettengill *et al.*, 1996). However, the radio and radar observations do not rule out the existence of pyrite and magnetite.

In order to model the chemical interaction between the atmosphere and crust, we assume that the crust consists of "soil" and "rock". The "soil" is equilibrated with the atmosphere, whereas the "rock" has no chemical interaction with the atmosphere. To determine the atmospheric SO_2 abundance, we only have to consider the partitioning of sulfur between the atmosphere and the "soil".

Chemical equilibrium calculations predict pyrite (FeS_2) and anhydrite ($CaSO_4$) as candidates for sulfur bearing minerals on the surface of Venus (Fegley and Treiman, 1992; Klose *et al.*, 1992). Those studies also indicate that all of the calcium in the "soil" is packed in $CaSO_4$ at equilibrium (Klose *et al.*, 1992). Since $CaSO_4$ dissociates only at extremely elevated temperature (Fegley and Treiman, 1992), we may assume that calcium minerals do not change the atmospheric sulfur abundance as long as the temperature variation is moderate. By contrast, FeS_2 will be closely related to the variation of atmospheric SO_2 abundance. At the present atmospheric condition, $CaSO_4$ is a stable phase all over the surface, but FeS_2 can occur only above a critical altitude where temperature is relatively low. At low altitudes Fe_3O_4 appears instead of FeS_2. Since the stability of FeS_2 is sensitive to the change in the surface temperature, even a small change in the surface temperature affects the stability of FeS_2. The formation and destruction of FeS_2 will consume and release the SO_2 and change the atmospheric SO_2 abundance.

In the calculation, we assumed that the SO_2 abundance is given by the equilibria of the pyrite-magnetite buffer. To attain chemical equilibrium, reaction rate must be fast enough. Decomposition of FeS_2 is experimentary ensured that it occurs in a relatively short time compared with the geological time scale (Fegley *et al.*, 1995). The rate of the FeS_2 forming reaction is not measured yet. When the surface temperature decreases, however, the critical altitude also decreases and fresh magnetite is exposed between the previous and current critical altitude. This would enhance pyrite formation.

The partitioning of sulfur between SO_2 and FeS_2 is subject to the constraint that the total mass of sulfur is conserved.

$$S_{\mathrm{atm}} = S_{\mathrm{tot}} - S_{\mathrm{max}} \cdot H(z_{\mathrm{pyrite}}) \tag{4}$$

where S_{atm} is the atmospheric abundance of sulfur, S_{tot} is the total abundance of sulfur in the atmosphere and FeS_2 in the "soil", S_{max} is the maximum abundance of sulfur potentially fixable as FeS_2 in the "soil", $H(z)$ is the area with an altitude above z, and z_{pyrite} is the critical altitude of FeS_2. S_{tot} represents the sum of the sulfur in the atmospheric SO_2 and the FeS_2 in the "soil". The hypsometric curve of Venus, $H(z)$, is given by the observation of Pioneer Venus (Masursky *et al.*, 1980).

Since S_{tot} and S_{max} are not yet measured, S_{max} is estimated from the elemental abundance of the Earth's crust, and S_{tot} is calculated from Eq. (4). If Venus' near surface S/C ratio is the same as that of the Earth, $S/C = 3.1 \times 10^{-2}$ (Ronov and Yaroshevskiy, 1967), the total abundance of surficial sulfur on Venus would correspond to 3.1 volume % as atmospheric SO_2 concentration. Since the present atmospheric concentration of SO_2 is 150 ppmv, we expect most of surficial sulfur is fixed in minerals. The host phases of sulfur in the "soil" are $CaSO_4$ and FeS_2 (Fegley and Treiman, 1992; Klose *et al.*, 1992), but most of the sulfur is fixed as $CaSO_4$ at present, because FeS_2 is stable only at the mountaintops which covers 7.6% of the planetary surface at the present atmospheric condition. In the region where FeS_2 is stable, the ratio of $FeS_2/CaSO_4$ would be the same with that of Fe/Ca, since

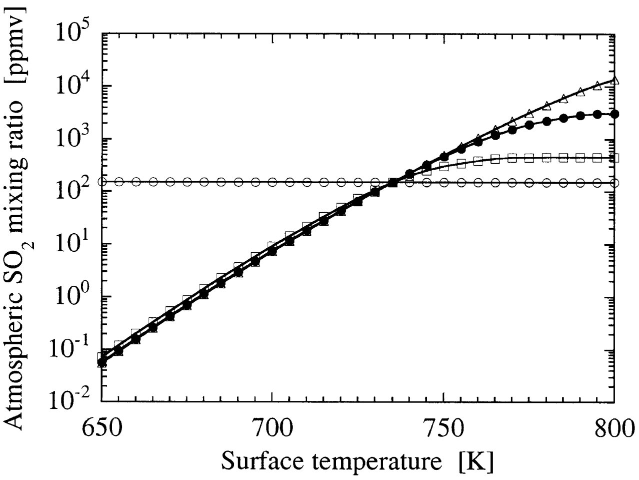

Fig. 1. Atmospheric SO_2 mixing ratio as a function of the surface temperature. Several cases for different S_{max} are shown. The standard value of S_{max} is 4.0 volume % (closed circle). S_{max} is enhanced ten times (open triangle), and reduced one tenth (open square). In case of no sulfur fixation in FeS_2, SO_2 mixing ratio keeps constant value (open circle). Fe_3O_4 and FeS_2 are assumed to have unit activity. We fix the CO/CO_2 at the observed value of 11.5×10^{-6} (Pollack *et al.*, 1993) and used thermochemical data compiled by Chase *et al.* (1985), Robie *et al.* (1979).

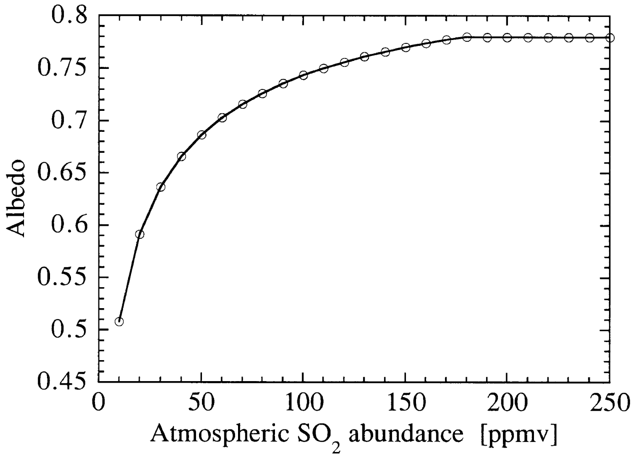

Fig. 2. Cloud albedo calculated for a given SO_2 mixing ratio in the Venus' lower atmosphere. The atmospheric structure is fixed.

the mineral assemblages at the chemical equilibrium calculated by Klose *et al.* (1992) demonstrated that all calcium is packed in $CaSO_4$ and almost all iron is packed in FeS_2. Using the Fe/Ca ratio of the Earth's crust, Fe/Ca = 0.72 (Ronov and Yaroshevskiy, 1967) and $H(z_{pyrite}) = 0.076$, the sulfur fixed in FeS_2 in the "soil", $S_{max} \cdot H(z_{pyrite})$, is calculated to be 0.305 volume % as atmospheric SO_2 concentration, which is 0.11 times as much as that fixed in $CaSO_4$ on the present Venus. Then, the maximum abundance of fixable sulfur in FeS_2 in the "soil", S_{max}, is calculated to be about 4.0 volume % as atmospheric SO_2 concentration, and the total abundance of surficial sulfur, S_{tot}, is calculated to be 0.32 volume %.

We use $S_{tot} = 0.32$ volume % and $S_{max} = 4.0$ volume % as the standard values, respectively. Although these values are chosen arbitrarily, the change of S_{atm} as a function of temperature is insensitive to the values of S_{tot} and S_{max} as shown in Fig. 1. In doing this calculation, the effect of topography is included (Hashimoto *et al.*, 1997). The details of this calculation are described in Hashimoto *et al.* (1997). When the surface temperature is low, almost all SO_2 is removed from the atmosphere by forming FeS_2. In such a case, z_{pyrite} is determined to yield $0 \approx S_{tot} - S_{max} \cdot H(z_{pyrite})$, and z_{pyrite} for a large S_{max} is higher than that for a smaller S_{max}, since a small change in z_{pyrite} is enough to fix the atmospheric SO_2 when S_{max} is large. When the surface temperature is low, the larger value of S_{max} leads to a smaller atmospheric SO_2 concentration, since z_{pyrite} is higher and the atmospheric SO_2 is equilibrated with the colder surface.

2.2 Cloud model

To calculate the influence of SO_2 variation on the cloud, a cloud model developed by Hashimoto and Abe (1996a, b) is used. The model combines the processes of transport, diffusion, and evaporation in the cloud layer. The cloud model determines the vertical distribution of H_2O vapor, number density and diameter of cloud particles when H_2SO_4 production rate, atmospheric structure, and atmospheric composition are given. Although this model is very simple, it reproduces the presently observed cloud very well. Calculated vertical structure of the cloud is similar to the observation (Hashimoto and Abe, 1996a). Albedo and optical depth for 550 nm wavelength obtained by our model are 0.87 and 34.8, respectively. These results show good agreement with the observation (Hashimoto and Abe, 1996a).

H_2SO_4 is formed through the hydration of SO_3 in the upper atmosphere where SO_2 is photooxidized. The column-integrated production rate of H_2SO_4, $P_{H_2SO_4}$, should be proportional to the product of the number densities of SO_2, N_{SO_2}, and H_2O, N_{H_2O}, at the production region:

$$P_{H_2SO_4} = A \cdot N_{SO_2} \cdot N_{H_2O}. \tag{5}$$

Using the number densities of SO_2 and H_2O at 16600 Pa (62 km altitude at present atmospheric structure), we set $A = 7.1 \times 10^{-22}$ [molecule^{-1} m^4 s^{-1}] so that the calculated production rates corresponds to 1.0×10^{16} [molecule m^{-2} s^{-1}] (Yung and DeMore, 1982) at the present condition. N_{H_2O} is estimated from the cloud model of Hashimoto and Abe (1996a, b). N_{SO_2} is calculated from the ratio of transportation efficiency of SO_2 to H_2O in the present Venus' cloud and the SO_2 concentration in the lower atmosphere.

The production of H_2SO_4 consumes the precursor materials and depletes them in the upper atmosphere. The higher the rate of H_2SO_4 production is, the more depleted the precursor materials become. Since the abundance of precursor materials in the upper atmosphere cannot be negative, the rate of H_2SO_4 production should be reduced to avoid the negative abundance. We reduce the rate of H_2SO_4 production when either the abundance of H_2O or SO_2 become negative, even though Eq. (5) gives a higher production rate. When the atmospheric SO_2 abundance increases, H_2O is depleted and the rate of H_2SO_4 production is usually determined by this rule. That is, the rate of H_2SO_4 production is determined by the less abundant of the two precursor materials.

Optical properties of the cloud are evaluated by using the Mie scattering code (Bohren and Hoffman, 1983), optical constants of 75% H_2SO_4-H_2O solutions, and two-stream approximation. The cloud albedo calculated by the model is shown in Fig. 2. The cloud albedo is nearly proportional to the SO_2 mixing ratio. Although SO_2 is a minor component of the venusian atmosphere, halving of the mixing ratio results in 20% increase of the atmospheric absorption of the solar radiation. On the other hand, when the SO_2 mixing ratio is larger than 190 ppmv, cloud formation is independent of the SO_2 mixing ratio, because cloud formation is limited by H_2O abundance. H_2O abundance is constant at the present value of 30 ppmv during the calculation (DeBergh *et al.*, 1991; Donahue and Hodges, 1993; Pollack *et al.*, 1993).

2.3 Atmospheric structure model

The atmospheric structure and tropopause are determined by a radiative-convective equilibrium model of the gray atmosphere (Nakajima *et al.*, 1992). The troposphere is approximated by a polytrope with polytropic exponent of 1.21. The polytropic exponent is estimated from the present lapse rate of the Venus' lower atmosphere. We include four sources of infrared opacity: CO_2, H_2O, SO_2 and cloud. The infrared opacity of cloud is computed by a method described in Subsection 2.2. To incorporate the greenhouse effect of SO_2, the effective absorption coefficient of gas is given as a function of the atmospheric SO_2 abundance. The surface temperature of a hypothetical SO_2-free atmosphere is 52K lower than that of the present (Pollack *et al.*, 1980). For the present and the SO_2-free atmospheres, we obtain the effective absorption coefficients that reproduce the surface temperature. Then, the coefficient is interpolated for other SO_2 abundances using the path-length dependence of the Rosseland mean value calculated from the broadband opacity data of CO_2, H_2O (Pollack *et al.*, 1980) and SO_2 (Eberstein *et al.*, 1969).

Since the entire Venus is covered by cloud, the planetary albedo can be represented by the cloud albedo. Thus, once the cloud albedo is estimated as a function of SO_2 concentration, we can calculate the planetary radiation that is radiated from the radiatively-convectively equilibrated atmosphere through the following equation:

$$F_{pl} = F_S(1 - A)/4 \qquad (6)$$

where F_{pl} is planetary radiation, F_S is solar flux, and A is planetary albedo. Taking into account the greenhouse effect of the atmosphere and cloud, we calculate the surface temperature from F_{pl}. Then, we obtain the SO_2 concentration from the pyrite-magnetite buffer. By iterating this process we can estimate the self-consistent surface temperature, albedo, and SO_2 concentration. We obtained the same solution when the calculations were performed from both initially warm and cold surface temperatures. Although the system may have multiple-equilibrium states, the state that we obtained is a stable one, which can be most easily reached.

3. Stability of Venus' Climate

Figure 3 shows the response of Venus' surface temperature against the change in solar flux calculated from our model. Both the greenhouse effect of SO_2 and cloud, and cloud albedo affect the surface temperature. It is widely believed that the solar luminosity has increased by about 30% since the Sun entered the main sequence (e.g., Gilliland, 1989). In case of smaller solar flux than present, we find that the chemical-albedo feedback overcomes the chemical-greenhouse feedback and the surface temperature is insensitive to the variation of the solar flux (Fig. 3(a)). Despite that the solar luminosity is 30% lower than the present, the decrease of the surface temperature is as small as 35 K. Without the chemical-albedo feedback (and also chemical-greenhouse feedback) the temperature change is as much as 60 K. The decrease in the solar constant is compensated by the decrease in planetary albedo (Fig. 3(b)) caused by decrease in the abundance of atmospheric SO_2. This indicates that the chemical-albedo feedback is very efficient in stabilizing the surface temperature for smaller solar radiation. The total abundance of the surficial sulfur on Venus affects the effectiveness of the chemical-albedo feedback only weakly. Even if the surficial sulfur on Venus were ten times larger or smaller than that of the standard value, the efficiency of the chemical-albedo feedback does not change (Fig. 3).

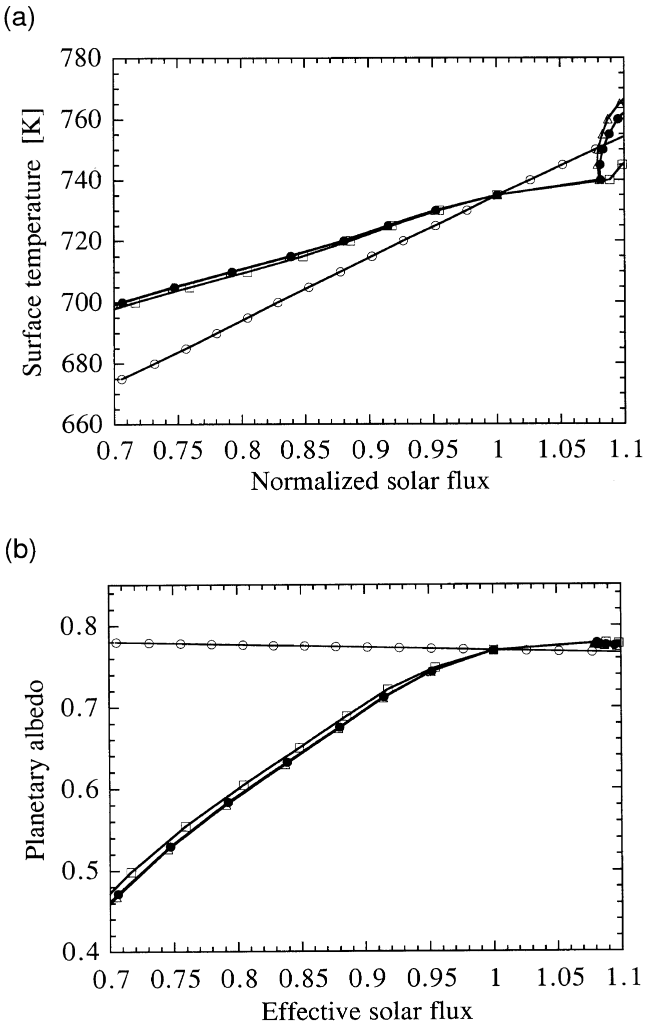

Fig. 3. (a) Surface temperature as a function of the effective solar flux (that is, the flux normalized to the present value). (b) Planetary albedo as a function of the effective solar flux. Symbols are the same in Fig. 1.

However, the chemical-albedo feedback cannot damp out the changes in the surface temperature when it is higher than 740 K (Fig. 3(a)). Although the planetary albedo should be increased to cool the surface temperature, it is difficult to make the albedo higher than the present (Fig. 2). When

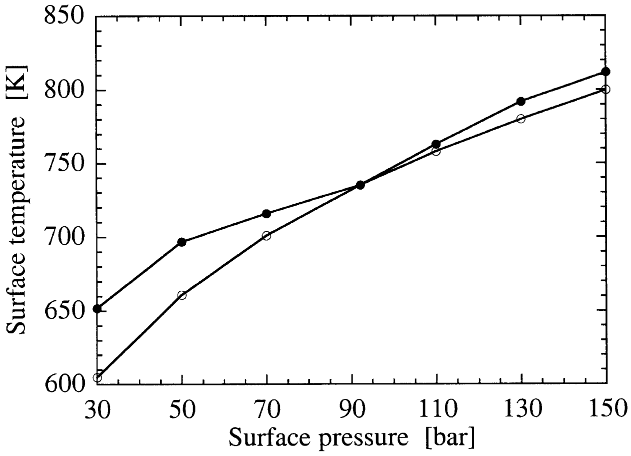

Fig. 4. Surface temperature as a function of the total atmospheric abundance. Effective solar flux is unity. Symbols are the same in Fig. 1.

the surface temperature is higher than 740 K, the mixing ratio of atmospheric SO_2 exceeds 200 ppmv (Fig. 1) and the cloud albedo is independent of the SO_2 abundance (Fig. 3(b)). Therefore, the chemical-albedo feedback cannot act as a thermostat, and the change in the surface temperature is amplified by the chemical-greenhouse feedback (Fig. 3(a)). The warming caused by the chemical-greenhouse feedback depends on the total abundance of the surficial sulfur on Venus, since the atmospheric SO_2 abundance is determined by the total abundance of the surficial sulfur when most of the surficial sulfur is in the atmosphere (Fig. 1).

The total pressure of the atmosphere can vary during the history of Venus due to the change of recycling efficiency of CO_2 between the atmosphere and mantle. The chemical-albedo and chemical-greenhouse feedback also govern the climate at different atmospheric pressure from the present. Figure 4 shows the surface temperature as a function of atmospheric pressure. In doing this calculation, the amount of CO_2 is varied arbitrarily and the mixing ratio of H_2O is fixed. Again, the chemical-albedo feedback stabilizes the surface temperature when the total atmospheric abundance is smaller and the surface temperature is lower than the present. Even if the pressure of the ancient Venus' atmosphere was half of the present, the surface temperature appears to be about 700 K. However, the chemical-greenhouse feedback enhances the increase in the surface temperature when the total atmospheric abundance of CO_2 is larger than the present.

4. Discussion

The cloud albedo depends on the number density, radius, and optical constant of the cloud droplet. In our calculation, the number density and radius of cloud droplets are calculated by the cloud model (Hashimoto and Abe, 1996a, b), though the optical constant of cloud droplet remains constant. The value of the single scattering albedo for solar radiation used in this study is $\varpi = 1 - 1 \times 10^{-7}$, because pure H_2O-H_2SO_4 solution shows small absorption in the solar radiation wavelength (Palmer and Williams, 1975). However, the venusian cloud may be more absorbing than pure H_2O-H_2SO_4 solution due to the impurities in the cloud droplets. If the absorption of cloud is large, thickening of the cloud may not raise the planetary albedo. When the cloud is more absorbing, such as the case of $\varpi = 1 - 1 \times 10^{-3}$, the planetary albedo is 3% smaller than that for $\varpi = 1 - 1 \times 10^{-7}$. A 3% decrease in the planetary albedo would have a large influence on the climate, however, we don't know the variability of the cloud absorption. The effect of the impurities in the cloud droplets should be examined in the future studies.

In this study, the variation of the abundance in the atmospheric H_2O is not considered, though the atmospheric H_2O abundance would have a large effect on the Venus' climate. H_2O is involved in the cloud and greenhouse effect. Atmospheric H_2O of Venus is believed to be lost through the escape of hydrogen to space and supplied by either cometary impacts or volcanic outgassing (e.g., Donahue *et al.*, 1997). The effect of changing H_2O concentration will be discussed elsewhere.

5. Conclusion

If carbonate controls the atmospheric SO_2 abundance, the equilibrium value of SO_2 concentration in the atmosphere should be about 100 times smaller than the observed concentration (e.g., Fegley and Treiman, 1992). Bullock and Grinspoon (1996) argued that the chemical reaction between carbonate and atmospheric SO_2 destabilize the Venus' climate, and the state of the Venus' climate would turn into a completely different one.

On the other hand, if pyrite controls the atmospheric SO_2 abundance, the equilibrium value of SO_2 concentration is similar to the observed value (e.g., Zolotov, 1991; Klose *et al.*, 1992). The chemical-albedo feedback, that is the coupling between the pyrite-magnetite buffer and the cloud albedo, plays an important role in the control of Venus' climate. Our calculation shows that the chemical-albedo feedback overcomes the chemical-greenhouse feedback and stabilizes the Venus' climate against the variation in the solar flux and the atmospheric abundance of CO_2. The chemical-albedo feedback keeps the Venus' climate around the present condition.

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References

Bertaux, J.-L., T. Widemann, A. Hauchecorne, V. I. Moroz, and A. P. Ekonomov, VEGA 1 and VEGA 2 entry probes: An investigation of local UV absorption (220–400 nm) in the atmosphere of Venus (SO_2, aerosols, cloud structure), *J. Geophys. Res.*, **101**, 12709–12745, 1996.

Bézard, B., C. de Bergh, B. Fegley, J.-P. Maillard, D. Crisp, T. Owen, J. B. Pollack, and D. Grinspoon, The Abundance of Sulfur Dioxide Below the Clouds of Venus, *Geophys. Res. Lett.*, **20**, 1587–1590, 1993.

Bohren, C. R. and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, New York, 1983.

Bullock, M. A. and D. H. Grinspoon, The stability of climate on Venus, *J. Geophys. Res.*, **101**, 7521–7529, 1996.

Bullock, M. A. and D. H. Grinspoon, Geological forcing of surface temperatures on Venus, *Lunar Planet. Sci.*, **29**, 1542, 1998.

Chase, M. W., Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, Am.

Chem. Soc. and Am. Inst. of Physics, 1985.

DeBergh, C., B. Bézard, T. Owen, D. Crisp, J.-P. Maillard, and B. L. Lutz, Deutrium on Venus: Observations from Earth, *Science*, **251**, 547–549, 1991.

Donahue, T. M. and R. R. Hodges, Jr., Venus methane and water, *Geophys. Res. Lett.*, **20**, 591–594, 1993.

Donahue, T. M., D. H. Grinspoon, R. E. Hartle, and R. R. Hodges, Jr., Ion/neutral escape of hydrogen and deuterium: Evolution of water, in *Venus II*, edited by S. W. Bougher, D. M. Hunten, and R. J. Phillips, pp. 385–414, Univ. Arizona Press, Tucson, AZ, 1997.

Eberstein, I. J., B. N. Khare, and J. B. Pollack, Infrared Transmission Properties of CO, HCl, and SO_2 and Their Significance for the Greenhouse Effect on Venus, *Icarus*, **11**, 159–170, 1969.

Fegley, B., Jr. and R. G. Prinn, Estimation of the rate of volcanism on Venus from reaction rate measurements, *Nature*, **337**, 55–58, 1989.

Fegley, B., Jr., and A. H. Treiman, Chemistry of Atmosphere-Surface Interactions on Venus and Mars, in *Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions*, edited by J. G. Luhmann, M. Tatrallyay, and R. O. Pepin, pp. 7–71, American Geophysical Union, Washington D.C., 1992.

Fegley, B., Jr., K. Lodders, A. H. Treiman, and G. Klingelhöfer, The rate of pyrite decomposition on the surface of Venus, *Icarus*, **115**, 159–180, 1995.

Ford, P. G. and G. H. Pettengill, Venus: Global surface radio emissivity, *Science*, **220**, 1379–1381, 1983.

Gilliland, R. L., Solar Evolution, *Global and Planet. Change*, **1**, 35–55, 1989.

Hashimoto, G. L. and Y. Abe, Albedo on Venus: I Cloud Model, *Proc. 29th ISAS Lunar Planet. Symp.*, 87–90, 1996a.

Hashimoto, G. L. and Y. Abe, Albedo on Venus: I Cloud Model and Present State, *Bull. Am. Astron. Soc.*, **28**, 1117, 1996b.

Hashimoto, G. L., Y. Abe, and S. Sasaki, CO_2 amount on Venus constrained by a criterion of topographic-greenhouse instability, *Geophys. Res. Lett.*, **24**, 289–292, 1997.

Klose, K. B., J. A. Wood, and A. Hashimoto, Mineral Equilibria and the High Radar Reflectivity of Venus Mountaintops, *J. Geophys. Res.*, **97**, 16353–16369, 1992.

Masursky, H., E. Eliason, P. G. Ford, G. E. McGill, G. H. Pettengill, G. G. Schaber, and G. Schubert, Pioneer Venus Radar Results: Geology from Images and Altimetry, *J. Geophys. Res.*, **85**, 8232–8260, 1980.

Nakajima, S., Y.-Y. Hayashi, and Y. Abe, A Study on the "Runaway Greenhouse Effect" with a One-Dimensional Radiative-Convective Equilibrium Model, *J. Atmos. Sci.*, **23**, 2256–2266, 1992.

Palmer, K. F. and D. Williams, Optical constants of sulfuric acid; Application to the clouds of Venus?, *Appl. Opt.*, **14**, 208–219, 1975.

Pettengill, G. H., P. G. Ford, and S. Nozette, Venus: Global surface radar reflectivity, *Science*, **217**, 640–642, 1982.

Pettengill, G. H., P. G. Ford, and B. D. Chapman, Venus: Surface Electromagnetic Properties, *J. Geophys. Res.*, **93**, 14881–14892, 1988.

Pettengill, G. H., P. G. Ford, and R. A. Simpson, Electrical properties of the Venus surface from bistatic radar observations, *Science*, **272**, 1628–1631, 1996.

Pollack, J. B., O. B. Toon, and R. Boese, Greenhouse Models of Venus' High Surface Temperature, as Constrained by Pioneer Venus Measurements, *J. Geophys. Res.*, **85**, 8223–8231, 1980.

Pollack, J. B., J. B. Dalton, D. Grinspoon, R. B. Wattson, R. Freedman, D. Crisp, D. A. Allen, B. Bezard, C. DeBergh, L.P. Giver, Q. Ma, and R. Tipping, Near-Infrared Light from Venus' Nightside: A Spectroscopic Analysis, *Icarus*, **103**, 1–42, 1993.

Robie, R. A., B. S. Hemingway, and J. R. Fisher, Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10^5 Pascals) Pressures and at Higher Temperatures, *U. S. Geol. Surv. Bull. No. 1452*, 1979.

Ronov, A. B. and A. A. Yaroshevskiy, Chemical Structure of the Earth's Crust, *Geochem. Intl.*, **13**, 1041–1066, 1967.

Suleiman, S. H., M. A. Kolodner, and P. G. Steffes, Laboratory measurement of the temperature dependence of gaseous sulfur dioxide (SO_2) microwave absorption with application to the Venus atmosphere, *J. Geophys. Res.*, **101**, 4623–4635, 1996.

Yung, Y. L. and W. B. DeMore, Photochemistry of the stratosphere of Venus: Implications for atmospheric evolution, *Icarus*, **51**, 119–247, 1982.

Zolotov, M. Y., Pyrite stability on the surface of Venus, *Lunar Planet. Sci.*, **22**, 1569–1570, 1991.

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