Chemistry Of Atmosphere–Surface Interactions On Venus And Mars

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We give a comprehensive review of the chemical interactions between the atmosphere and surface of Venus. Earth-based, Earth-orbital, and spacecraft data on the composition of the atmosphere and surface of Venus are presented and applied to quantitative discussions of the chemical interactions between carbon, hydrogen, sulfur, chlorine, fluorine, and nitrogen gases and plausible minerals on the surface of Venus. The results of our calculations are used to predict stable minerals and mineral asemblages on the surface of Venus, to determine which, if any, atmospheric gases are buffered by mineral assemblages on the surface, and to critically review and assess the prior work on atmosphere–surface chemistry on Venus. We then briefly contrast Martian atmosphere–surface chemistry with that on Venus. Several specific conclusions are presented. Some of these conclusions have been reached previously by other authors, while others are new to this work. These include the following: (1) The CO_2 pressure on Venus is identical within the uncertainties in the thermodynamic data to the CO_2 equilibrium partial pressure developed by the calcite + wollastonite + quartz assemblage at the mean Venus surface temperature of 740 K. However, the rate of this reaction under Venusian surface conditions is not known and needs to be measured experimentally to determine if this important reaction is capable of buffering CO_2 on Venus. (2) Chemical equilibrium calculations using the published thermodynamic data on scapolite minerals predict that meionite (carbonate–bearing scapolite) and sulfate meionite are unstable on the surface of Venus but that marialite (chloride–bearing scapolite) is stable on the surface. (3) The f_{O_2} of the Venusian lower atmosphere and surface is controlled by the CO/CO_2 ratio. It is too reducing for hematite to exist on the surface of Venus, as implied by spectral reflectance measurements made by Venera spacecraft. This apparent inconsistency may reflect kinetic inhibition of the hematite to magnetite conversion or the existence of a stable ferric iron–bearing mineral on the surface of Venus. (4) No pure hydrated silicates are thermodynamically stable on the Venusian surface with the possible exceptions of tremolite and phlogopite which may be stable at high altitudes. However, in any case, the formation of hydrated silicates apparently cannot explain the decreasing water vapor abundance near the surface of Venus. The least objectionable explanation is the formation of H_2CO_3 gas. (5) Atmospheric sulfur gases are not in chemical equilibrium with the Venusian surface. Laboratory reaction rate measurements show that SO_2 is the dominant sulfur gas on Venus because anhydrite formation, the thermodynamically favorable loss process, is too slow to reduce the SO_2 abundance down to the chemical equilibrium value. (6) The abundances of HCl and HF in the Venusian atmosphere are buffered by mineral assemblages on the Venusian surface, although the assemblages

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suggested previously in the literature are incorrect. (7) No pure nitrogen–bearing minerals are thermodynamically stable on the Venusian surface although small amounts of nitrogen dissolved in silicates may constitute a significant fraction of the total nitrogen inventory on Venus. (8) Observational evidence shows that the major carbon and oxygen bearing gases in the Martian atmosphere are not in thermochemical equilibrium with each other. Furthermore, the dominant gas CO_2 is not in thermochemical equilibrium with pyroxene minerals believed to be present on the Martian surface. If this were the case CO_2 would be totally present in the crust as carbonate minerals and N_2 and Ar would be the dominant gases in the atmosphere. (9) Extrapolations of high temperature reaction rate data to Martian surface conditions indicate that at least some thermochemical weathering reactions may be kinetically inhibited on Mars. However, studies of chemical weathering reactions in Antarctic soils and of terrestrial weathering products found on the surfaces of Antarctic meteorites suggest that some thermochemical weathering reactions may proceed on the Martian surface. (10) Thermodynamic calculations predict that goethite [α-FeO(OH)] is unstable on the Martian surface, but its presence is apparently indicated by reflection spectroscopy. This may be due to the kinetic inhibition of goethite dehydration. However, the available kinetic data are inadequate for determining if this is actually the case. (11) Other thermodynamically favorable reactions include the formation of CO_2 clathrate hydrate at the Martian polar caps, oxidation of siderite $FeCO_3$ and rhodochrosite $MnCO_3$ to hematite and pyrolusite, and the formation of hydrated magnesium sulfates and chlorides and calcium chlorides. However with the possible exception of CO_2 clathrate formation, many of these reactions may be kinetically inhibited due to the low temperatures on the Martian surface. (12) Theoretical models of Martian atmospheric photochemistry predict the presence of many highly reactive species such as H_2O_2, HO_2, OH, O_3, etc. at the Martian surface. The predicted abundance of H_2O_2 is slightly below the spectroscopic upper limit. (13) Experimental studies of photochemically driven weathering reactions such as the putative photo-oxidation of magnetite have yielded conflicting and contradictory experimental results. In some cases these suggest that photo-oxidation is a viable process while in other cases no reaction is observed.

INTRODUCTION

Venus and Mars provide two different natural laboratories for studying chemical interactions between planetary surfaces and the overlying atmospheres. The global mean surface temperature on Venus is about 740 K and the global mean surface pressure is about 95 bars. Only a few percent of the solar flux incident on Venus manages to penetrate to the lower atmosphere below the clouds and the short wavelength solar UV radiation capable of photolyzing CO_2, the dominant atmospheric gas, is stopped at high altitudes above the clouds. In contrast, the Martian global mean surface temperature is about 215 K and the global mean surface pressure is about 6 millibars. In other words, the Martian surface is about 530° colder than that of Venus and the Martian surface pressure is about 15,000 times smaller than the pressure at the surface of Venus. Furthermore, photodissociation of CO_2, which is also the dominant atmospheric gas on Mars, occurs all the way down to the Martian surface. Venus would therefore appear to be a good natural laboratory for studying thermochemically driven atmosphere–surface reactions while Mars would appear to be a good natural laboratory for studying photochemically driven atmosphere–surface reactions.

In this paper we present a detailed discussion of the chemistry of atmosphere–surface interactions on Venus. Instead of simply reviewing all the previous results, which are sometimes contradictory and often irrelevant because of new observational data, we will present illustrative calculations that update this previous body of work by incorporating the latest observational results and thermodynamic data. We will then discuss how thermodynamic models of atmosphere–surface chemistry on Venus could be improved by laboratory measurements of new thermodynamic data, or augmented by experimental studies of reaction rate kinetics. We will then briefly compare atmosphere–surface interactions on Venus to those on Mars. Finally we will conclude by summarizing the important issues facing us today about atmosphere–surface interactions on these two planets and by suggesting theoretical, experimental, and observational studies which can improve our knowledge of these important questions.

ATMOSPHERE–SURFACE INTERACTIONS ON VENUS

In the late 1950's, radio emission was detected from Venus and it was found that the brightness temperature of the thermal radio emission was 560±73 K at 3.15 cm wavelength [Mayer et al., 1958]. These measurements provided the first observational evidence for the high surface temperature of Venus, which was confirmed by the Mariner 2 encounter with Venus in December 1962 [Barath et al., 1963, 1964]. Shortly afterward, Mueller [1963] pointed out that the deduced surface temperature of $\sim$ 700 K "corresponds with those attained during moderately high degrees of metamorphism on Earth. It is therefore possible that large parts of the atmosphere of Venus are partially equilibrated with the surface rocks. From this assumption, it follows that the composition of the atmosphere should reflect the mineralogical character of the rocks."

Subsequent investigators adopted Mueller's hypothesis of chemical equilibrium between the atmosphere and surface of Venus in order to explore the consequences for atmospheric chemistry and surface mineralogy. Mueller's assumption is probably qualitatively correct for some (although not all)

species. However, it should also be noted that the Venus mean surface pressure of $\sim$ 95 bars is significantly lower than the maximum pressure of $\sim$ 15 kilobars reached in metamorphic reactions in the terrestrial crust and that the H_2O partial pressure of $\leq$ 0.01 bars is significantly lower than H_2O pressures of several kilobars for many metamorphic reactions on Earth [e.g., see Vernon, 1976]. Both the lower total pressure and the lower water vapor partial pressure on Venus suggest that rates of gas–solid reactions at the surface of Venus will probably be more sluggish than the rates of analogous terrestrial metamorphic reactions, although the trace amounts of HCl and HF present in the atmosphere may increase reaction rates in some cases. Zolotov [1986b] has qualitatively discussed other similarities and differences between metamorphic and weathering reactions on the Earth and Venus.

Basic information about the composition of the atmosphere and surface of Venus is given in Tables 1 and 2, and a representative atmospheric (P,T) profile and the surface area distribution with altitude are illustrated in Figures 1 and 2. The atmospheric composition data in Table 1 is based on the comprehensive review by Von Zahn et al. [1983]; however, both references to the original discovery papers and to the more recent literature are given in the table. A list of the minerals discussed in this paper, their ideal chemical formulas, and the thermodynamic data sources used in our chemical equilibrium calculations is given in Table 3. The thermodynamic data for all gases are taken from the JANAF Tables [Chase et al., 1985]. The uncertainties given on equations in this paper were calculated quadratically using the 2σ uncertainties tabulated by Robie et al. [1979] and Hemingway et al. [1982], the uncertainties given in the JANAF Tables, the uncertainties given by different authors for their measured thermodynamic data, and (in a few cases) estimated uncertainties assigned by us. The sensitivity of results to thermodynamic data and to the associated uncertainties are discussed in more detail where it is appropriate to do so.

TABLE 1. Composition of the Atmosphere of Venus*

Gas	Mixing Ratio	Altitude Range	References
CO_2	96.5%±.8%	$\leq$ 100 km	Adams& Dunham 1932
			von Zahn et al. 1983
H_2O	(1-40) ppm	cloud top	Bottema et al. 1965
			Fink et al. 1972
	(20-200) ppm	sub-cloud	see text
HCl	0.6 ppm	cloud top	Connes et al. 1967
	0.4 ppm	cloud top	Young 1972
	0.4 ppm	cloud top	DeBergh et al. 1989
	0.5 ppm	42 km	Bézard et al. 1990
HF	5 ppb	cloud top	Connes et al. 1967
	10 ppb	cloud top	Young 1972
	4.5 ppb	42 km	Bézard et al. 1990
CO	45±10 ppm	cloud top	Connes et al. 1968
	51 ppm	cloud top	Young 1972
	(20-30) ppm	sub-cloud	Oyama et al. 1980
			Gel'man et al. 1979
	45 ppm	42 km	Bézard et al. 1990
N_2	3.5%±.8%	$\leq$ 45 km	von Zahn et al. 1983
	4%±2%	0-22 km	Hoffman et al. 1980a
	4%±.3%	0-22 km	Istomin et al. 1979
	(3.4–4.6%)	sub-cloud	Oyama et al. 1980
	2.5%±.3%	22-42 km	Gel'man et al. 1979
SO_2	(20-600) ppb	cloud top	Barker 1979
			Conway et al. 1979
			Stewart et al. 1979
	185±43 ppm	sub-cloud	Oyama et al. 1980
	130±35 ppm	sub-cloud	Gel'man et al. 1979
	(30-50) ppm	25-40 km	Berto et al. 1987
H_2S	3±2 ppm	<20 km	Hoffman et al. 1980a
S_{1-8}	20 ppb	sub-cloud	Moroz et al. 1980
			San'ko 1980
	(2-10) ppm	25-40 km	Berto et al. 1987
COS	0.3 ppm	sub-cloud	Bézard et al. 1990
SO	20±10 ppb	cloud top	Na et al. 1990
HDO	1.3±0.2 ppm	sub-cloud	DeBergh et al. 1991

*Excluding the noble gases.

TABLE 2. Composition of the Surface of Venus (Surkov et al., 1984, 1986a)

Oxide	Chemical Composition (Mass % $\pm 1\sigma$) Venera 13	Venera 14	Vega 2
MgO	11.4±6.2	8.1±3.3	11.5±3.7
Al_2O_3	15.8±3.0	17.9±2.6	16±1.8
SiO_2	45.1±3.0	48.7±3.6	45.6±3.2
K_2O	4.0±0.63	0.2±0.07	0.1±0.08
CaO	7.1±0.96	10.3±1.2	7.5±0.7
TiO_2	1.59±0.45	1.25±0.41	0.2±0.1
MnO	0.2±0.1	0.16±0.08	0.14±0.12
FeO	9.3±2.2	8.8±1.8	7.7±1.1
SO_3	1.62±1.0	0.88±0.77	4.7±1.5
Na_2O*	2.0±0.5	2.4±0.4	2.0
Total	98.1%	98.7%	95.4%

*Calculated by Surkov et al.

Carbon Dioxide and Carbon Compounds

Carbon dioxide is the most abundant gas in the atmosphere of Venus (Table 1), and is also the most important gas that is reacting with the Venusian surface. Although the atmospheric abundance of CO_2 on Venus is well known, there are no data on the elemental abundance of carbon in the Venus crust nor on the presence and abundance of possible carbon-bearing phases such as carbonates, scapolites, etc. The Venera 13/14 and Vega 2 spacecraft, which analyzed the Venusian surface by X-ray fluorescence spectroscopy, provided only elemental abundances for elements heavier than magnesium and were not able to detect carbon (see Table 2). However, despite our lack of observational data about the mineralogical composition of the surface of Venus, theoretical models of atmosphere–surface interactions on Venus strongly suggest that carbonates are present on the surface and are responsible for regulating the CO_2 pressure in the atmosphere. But before discussing these models we summarize current knowledge of the carbon inventories of Venus and the Earth.

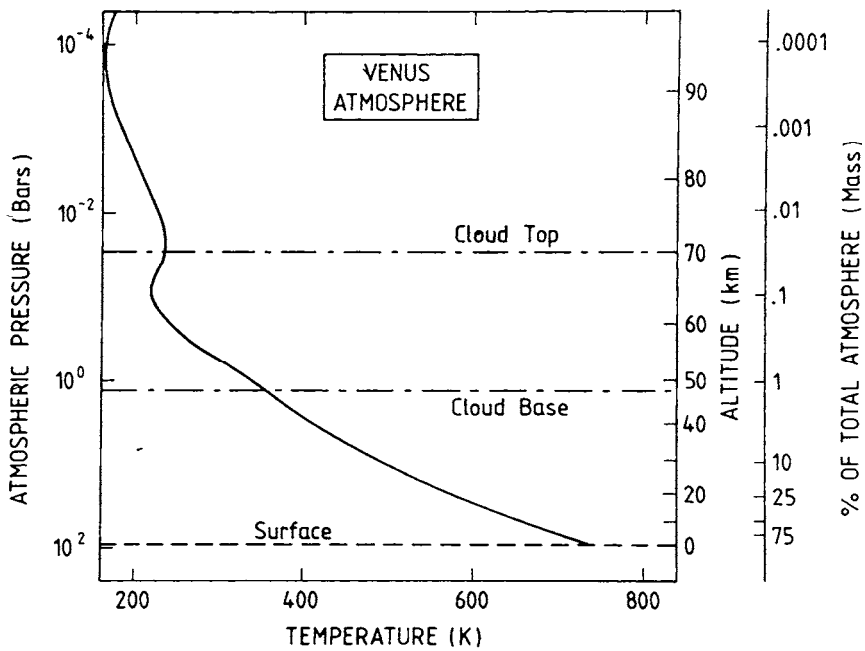

Fig. 1. Pressure–temperature profile for the atmosphere of Venus in the 0 to 90 km altitude region. The 60° latitude model of Seiff [1983] was used to construct this plot.

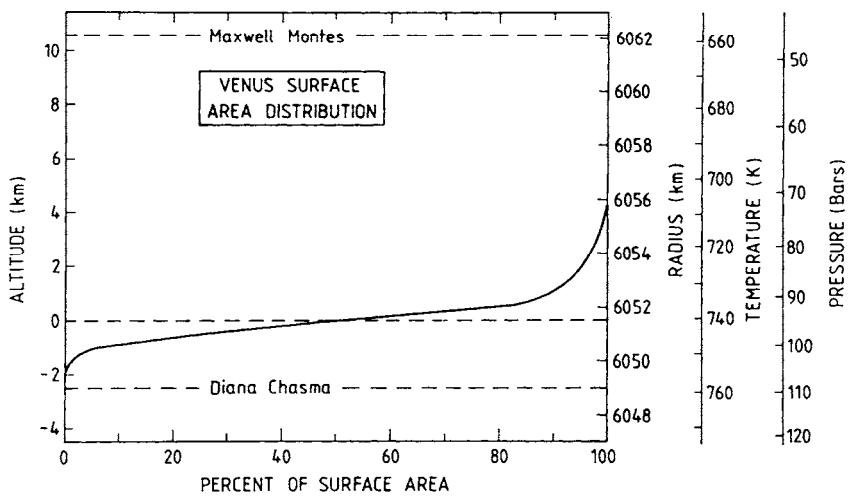

Fig. 2. Surface area distribution on Venus as a function of altitude. The vertical scales indicate the altitude from the median planetary radius of 6051.5 km, and the atmospheric temperature and pressure. The highest (Maxwell Montes) and lowest (Diana Chasma) points observed by Pioneer Venus are also shown. The Pioneer Venus radar altimetry data [Masursky et al., 1980; Pettengill et al., 1980], which cover 93% of the planet, and the 60° latitude (P,T) model of Seiff [1983] were used to construct this plot. Radar mapping of the entire planetary surface at higher resolution is likely to reveal points at both higher and lower altitudes than those found by Pioneer Venus.

CO_2 Abundances on Venus and Earth. The Venusian surface pressure of 95 bars and the CO_2 volume mixing ratio of 0.965±0.008 correspond to a CO_2 column density of 1.4×10^{27} molecules cm^{-2}. For comparison, the CO_2 mixing ratio in the terrestrial troposphere is ~ 340 ppm in nonurban regions and the corresponding column density is ~ 4.8×10^{21} molecules cm^{-2} or about 290,000 times smaller than on Venus. However, according to Berner et al. [1983], the total amount of carbon present as carbonate, organic matter, etc. in the Earth's crust is equal to 7.4×10^{26} CO_2 molecules cm^{-2} (or the equivalent of a global layer of calcite ~ 0.5 km thick). This crustal inventory is similar to

TABLE 3. Thermodynamic Data Sources for Minerals in this Paper

Mineral Name	Ideal Chemical Formula	Source for Data
Acmite	$NaFeSi_2O_6$	Bennington & Brown 1982
Åkermanite	$Ca_2MgSi_2O_7$	Robie et al. 1979
Albite	$NaAlSi_3O_8$	Robie et al. 1979
Andalusite	Al_2SiO_5	Hemingway et al. 1982
Anhydrite	$CaSO_4$	Robie et al. 1979
		Kelley et al. 1941
Anorthite	$CaAl_2Si_2O_8$	Hemingway et al. 1982
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	Helgeson et al. 1978
Antarcticite	$CaCl_2{\cdot}6H_2O$	Glushko et al. 1965-82
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	Berman et al. 1986
Artinite	$Mg_2(OH)_2CO_3{\cdot}3H_2O$	Robie et al. 1979
Bassanite	$CaSO_4 \cdot \frac{1}{2}H_2O$	Kelley et al. 1941
Bischofite	$MgCl_2 \cdot 6H_2O$	Glushko et al. 1965-82
Buddingtonite	$NH_4AlSi_3O_8 \cdot \frac{1}{2}H_2O$	No data available
Calcite	$CaCO_3$	Robie et al. 1979
Calcium Nitrate	$Ca(NO_3)_2$	Parker et al. 1971
Chalcopyrite	$CuFeS_2$	No calculations done
Chlorapatite	$Ca_5(PO_4)_3Cl$	Zhu & Sverjensky 1990
Chloromagnesite	$MgCl_2$	Glushko et al. 1965-82
Chlorphlogopite	$KMg_3AlSi_3O_{10}Cl_2$	No data available
Chrysotile	$Mg_3Si_2O_5(OH)_4$	Robie et al. 1979
Corundum	$\alpha - Al_2O_3$	Robie et al. 1979
Cryolite	Na_3AlF_6	Robie et al. 1979
Diopside	$CaMgSi_2O_6$	Robie et al. 1979
Dolomite	$CaMg(CO_3)_2$	Robie et al. 1979
Enstatite	$MgSiO_3$	Robie et al. 1979
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$	Helgeson et al. 1978
Epsomite	$MgSO_4 \cdot 7H_2O$	DeKock 1986
Fayalite	Fe_2SiO_4	Robie et al. 1979
Feroxyhyte	$\delta - FeO(OH)$	No data available
Ferrosilite	$FeSiO_3$	Helgeson et al. 1978
Fluorapatite	$Ca_5(PO_4)_3F$	Zhu & Sverjensky 1990
Fluor-edenite	$NaCa_2Mg_5Si_7AlO_{22}F_2$	Graham & Navrotsky 1986
Fluorite	CaF_2	Robie et al. 1979
Fluor-pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}F_2$	Westrich 1981
		Westrich & Navrotsky 1981
Fluor-phlogopite	$KMg_3AlSi_3O_{10}F_2$	Robie et al. 1979
		Westrich 1981
Fluor-topaz	Al_2SiO_4F	Barton et al. 1982
Fluor-tremolite	$Ca_2Mg_5Si_8O_{22}F_2$	Graham & Navrotsky 1986
Forsterite	Mg_2SiO_4	Robie et al. 1979
Galena	PbS	Robie et al. 1979
Gehlenite	$Ca_2Al_2SiO_7$	Hemingway et al. 1982
Gibbsite	$Al(OH)_3$	Robie et al. 1979
Glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$	Likhoydov et al. 1982
Goethite	$\alpha - FeO(OH)$	Robie et al. 1979
Grossular	$Ca_3Al_2Si_3O_{12}$	Hemingway et al. 1982
Gypsum	$CaSO_4 \cdot 2H_2O$	DeKock 1986
		Kelley et al. 1941
Halite	$NaCl$	Robie et al. 1979
Hematite	Fe_2O_3	Robie et al. 1979
Hexahydrite	$MgSO_4 \cdot 6H_2O$	DeKock 1986
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	Robie et al. 1979
Hydrophilite	$CaCl_2$	Glushko et al. 1965-82
Hydroxyapatite	$Ca_5(PO_4)_3OH$	Zhu & Sverjensky 1990
Jadeite	$NaAlSi_2O_6$	Robie et al. 1979
Kaolinite	$Al_2Si_2O_5(OH)_4$	Hemingway et al. 1982
Kieserite	$MgSO_4 \cdot H_2O$	DeKock 1986
Laihunite	$Fe^{2+}Fe_2^{3+}Si_2O_8$	No data available
Leonhardtite	$MgSO_4 \cdot 4H_2O$	DeKock 1986
Lepidocrocite	$\gamma - FeO(OH)$	No data available
Leucite	$KAlSi_2O_6$	Robie et al. 1979

Mineral Name	Ideal Chemical Formula	Source for Data
Maghemite	$\gamma - Fe_2O_3$	No data available
Magnesioferrite	$MgFe_2O_4$	Robie et al. 1979
Magnesite	$MgCO_3$	Robie et al. 1979
Magnesium Sulfate	$MgSO_4$	DeKock 1986
Magnetite	Fe_3O_4	Robie et al. 1979
Margarite	$CaAl_4Si_2O_{10}(OH)_2$	Hemingway et al. 1982
Marialite	$Na_4[AlSi_3O_8]_3Cl$	Semenov et al. 1981
Meionite	$Ca_4[AlSiO_4]_6CO_3$	Moecher & Essene 1990
Microcline	$KAlSi_3O_8$	Robie et al. 1979
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	Robie et al. 1979
Monohydrocalcite	$CaCO_3 \cdot H_2O$	Robie et al. 1979
Monticellite	$CaMgSiO_4$	Robie et al. 1979
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	Robie et al. 1979
Nepheline	$NaAlSiO_4$	Robie et al. 1979
Nesquehonite	$MgCO_3 \cdot 3H_2O$	Robie et al. 1979
Paragonite	$NaAl_3Si_3O_{10}(OH)_2$	Robie & Hemingway 1984
Pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	Helgeson et al. 1978
Pentlandite	$(Fe,Ni)_9S_8$	No data available
Periclase	MgO	Robie et al. 1979
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	Berman 1988
		Helgeson et al. 1978
Portlandite	$Ca(OH)_2$	Robie et al. 1979
Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	Hemingway et al. 1982
Pyrite	FeS_2	Robie et al. 1979
Pyrolusite	MnO_2	Robie et al. 1979
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	Hemingway et al. 1982
Pyrrhotite	$Fe_{1-x}S$, $x \sim 0 - 0.125$	Mills 1974
Quartz	SiO_2	Robie et al. 1979
Rhodochrosite	$MnCO_3$	Robie et al. 1979
Rhodonite	$MnSiO_3$	Robie et al. 1979
Sanderite	$MgSO_4 \cdot 2H_2O$	DeKock 1986
Sanidine	$KAlSi_3O_8$	Robie et al. 1979
Sellaite	MgF_2	Robie et al. 1979
Siderite	$FeCO_3$	Robie et al. 1979
Sodalite	$Na_4[AlSiO_4]_3Cl$	Sharp et al. 1989
Sphalerite	ZnS	Robie et al. 1979
Spinel	$MgAl_2O_4$	Robie et al. 1979
Sulfate Meionite	$Ca_4[AlSiO_4]_6SO_4$	Moecher & Essene 1990
Talc	$Mg_3Si_4O_{10}(OH)_2$	Robie et al. 1979
Tephroite	Mn_2SiO_4	Robie et al. 1979
Thenardite	Na_2SO_4	Robie et al. 1979
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	Robie et al. 1979
		Helgeson et al. 1978
Troilite	FeS	Robie et al. 1979
Wollastonite	$CaSiO_3$	Hemingway et al. 1982
Wüstite	$Fe_{.947}O$	Robie et al. 1979

the amount of CO_2 in the atmosphere of Venus, and if all this carbon were released into the Earth's atmosphere the CO_2 pressure would be $\sim$ 53 bars instead of the current $\sim$ 0.3 millibars. (This similarity was probably first noted by Wildt [1942] but both the CO_2 column density on Venus and the terrestrial crustal abundance of carbon accepted at that time have been superseded by better data.) Thus, the CO_2 which is chemically combined in crustal rocks on the Earth is instead found in the atmosphere on Venus because of the high surface temperature. How is this massive CO_2 atmosphere interacting with the surface of Venus today?

Carbonate-Silicate equilibria and atmospheric CO_2. Urey [1952, 1959] originally suggested that reactions such as

$$MgCO_3 + SiO_2 = MgSiO_3 + CO_2 \quad (1)$$

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2 \quad (2)$$

could control or buffer the CO_2 pressure in a planetary atmosphere. However, the low surface temperature accepted at the time for Venus led Urey [1952] to dismiss reactions (1) and (2) as irrelevant to Venus because the equilibrium CO_2 pressures at low temperatures are much lower than the CO_2 pressure in the atmosphere of Venus. He concluded that "Venus owes its large nonequilibrium carbon dioxide atmosphere to the slowness of the chemical reactions and the lack of erosion, both the consequence of the absence of water."

After Mariner 2 confirmed Venus' high surface temperature, theorists began to reconsider carbonate–silicate equilibria as potential CO_2 buffers for the Venusian atmosphere because the equilibrium CO_2 pressures at high temperatures are comparable to that in the Venus atmosphere [e.g., Adamcik and Draper, 1963; Lewis, 1968a, 1970a; Mueller, 1963, 1964a; Vinogradov and Volkov, 1971]. This is illustrated in Figure 3 where the equilibrium CO_2 pressure as a function of temperature for the wollastonite–calcite equilibrium [reaction (2)] is compared to the observed CO_2 pressure in the near-surface atmosphere of Venus. The two curves intersect at $\sim 740\pm30$ K ($\sim 0\pm4$ km) and at the mean Venus surface temperature of $\sim$740 K there is good agreement between the calculated CO_2 pressure of ~ 89 bars and the observed CO_2 pressure of ~ 92 bars. In fact, this agreement is better than that of any other carbonate–silicate buffer and suggests that the wollastonite–calcite equilibrium is buffering the CO_2 pressure in Venus' atmosphere [e.g., Lewis, 1970a]. As we shall discuss later other carbonates may also be stable on the Venusian surface but apparently only in elevated regions of limited areal extent.

Because buffer reactions such as equations (1) and (2) have played a prominent role in chemical models of Venus during the past 3 decades we will briefly review the basic thermodynamic concepts involved in these models before proceeding further. The equilibrium constants for reactions (1) and (2) are given by the expressions:

$$K_1 = [a_{MgSiO_3}/(a_{MgCO_3} \cdot a_{SiO_2})] \cdot f_{CO_2} \quad (3)$$

$$K_2 = [a_{CaSiO_3}/(a_{CaCO_3} \cdot a_{SiO_2})] \cdot f_{CO_2} \quad (4)$$

where a_i is the thermodynamic activity of phase i and f_{CO_2} is the fugacity of CO_2. A pure mineral has unit activity and a mineral which is a component in a solid solution has an activity which is proportional to its molar concentration in the solid solution. Unless stated otherwise, we assume that all the minerals involved in gas–solid reactions are pure phases and have unit activity. However, solid solutions are considered where it is appropriate to do so (e.g., olivine and pyroxene).

Likewise, the CO_2 fugacity is related to the CO_2 partial pressure P_{CO_2} via a multiplicative factor ϕ_i known as the fugacity coefficient. Fugacity coefficients are unity for ideal gases and may be either greater than or less than unity for real gases. They are useful because they allow us to model the thermochemical equilibria involving real gases, such as in the lower atmosphere of Venus by using tables of thermodynamic data for ideal gases (such as the JANAF Tables) combined with fugacity coefficients estimated from the principle of corresponding states [e.g., as described by Hirschfelder et al., 1954].

For the case of CO_2 on Venus, the greatest deviations from ideality would be expected to occur at the highest temperatures and pressures near the surface. However, using the principle of corresponding states we can show that ideality is a good assumption for CO_2 on Venus because the surface temperature is about 2.5 times the CO_2 critical temperature (304 K) and the pressure is about 1.3 times the CO_2 critical pressure (72 bars). Under these conditions the estimated fugacity coefficient for CO_2 is unity to a good first approximation [e.g., see G.N. Lewis and Randall 1961].

We note that ideality is also a good assumption for all other gases in the Venusian atmosphere as long as the G.N. Lewis fugacity rule

$$f_i(\text{mixture}) = y_i f_i(\text{pure}) \quad (5)$$

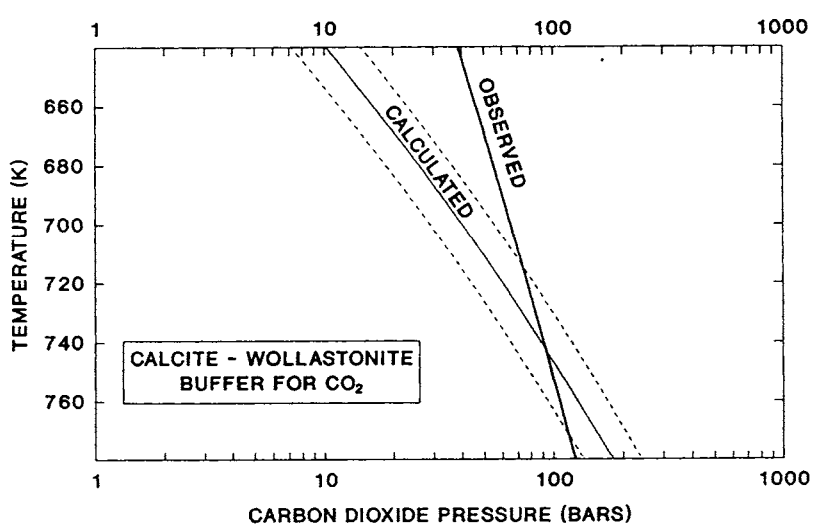

Fig. 3. A comparison of the observed and calculated CO_2 pressures at the surface of Venus. The observed CO_2 partial pressure is simply 0.965 times the total pressure from Seiff [1983]. The calculated CO_2 pressure is for reaction (2). The dashed lines show the range of calculated CO_2 pressures allowed by the uncertainties in the thermodynamic data. The calculated and observed curves intersect at 740 ± 30 K (0 ± 4 km). Refer to Fig. 2 to relate temperatures to altitudes on the surface of Venus.

is valid. The G.N. Lewis fugacity rule relates the fugacity of a pure gas i to its fugacity in a gas mixture where gas i has a mixing ratio y_i. Equation (5) is a good approximation at low pressures where the gas phase is nearly ideal [Prausnitz et al., 1986], as is the case for CO_2 on Venus. Thus, the use of ideal gas chemical equilibrium calculations is justified and introduces significantly less uncertainty into our conclusions than does our imperfect knowledge of the atmospheric and surface composition.

Now, going back to equations (3) and (4), we see that since the thermodynamic activities of all minerals are assumed to be unity, the equilibrium constant is simply the CO_2 pressure. Solving for this as a function of temperature we obtain

$$\log_{10} P_{CO_2}(\text{magnesite}) = 8.62 - 4054(\pm 112)/T \quad (6)$$

$$\log_{10} P_{CO_2}(\text{calcite}) = 7.97 - 4456(\pm 98)/T. \quad (7)$$

Thus, at the Venusian surface temperature of ~ 740 K, the magnesite–enstatite equilibrium develops a CO_2 pressure of $\sim 1,400$ bars while the calcite–wollastonite equilibrium develops a CO_2 pressure of ~ 89 bars. Just what do these CO_2 pressures mean for the stability of magnesite and calcite on Venus?

Basically, the observed CO_2 pressure at the surface of Venus is sufficient for calcite + wollastonite + quartz to coexist but not for magnesite + enstatite + quartz to coexist. In other words, calcite + quartz will react to form wollastonite until either reactant is consumed or the equilibrium CO_2 pressure of 89 bars is generated, while magnesite + quartz will react to form enstatite until either reactant is consumed or the equilibrium CO_2 pressure of 1,400 bars is generated. Conversely, if the assemblage wollastonite + quartz + calcite is exposed to an external CO_2 pressure greater than the equilibrium pressure of 89 bars, wollastonite + CO_2 will react to form calcite + quartz until the CO_2 pressure is reduced to 89 bars or until all wollastonite is exhausted. Thus, the mineral assemblage wollastonite + quartz + calcite buffers the CO_2 pressure because variations in the CO_2 pressure (at constant temperature) are regulated by gas–solid reactions.

At this point it is natural to ask what conditions are required for the calcite–wollastonite equilibrium to take place on the Venusian surface. One of these conditions is that the different solid and volatile phases involved in the reaction are all present. Various authors have argued that calcite is absent on Venus because on the Earth it is formed by sedimentation from water. However, we note that calcite is also found in certain igneous rocks, such as carbonatites, nepheline-syenites [Deer et al., 1963], and kimberlites [Mitchell, 1986]. As discussed later, the observed HCl abundance on Venus can be buffered by other mineral assemblages found in nepheline-syenites. Also, carbonatite magmas have been suggested to explain Magellan radar observations of fluvial-like geologic features on Venus [Kargel et al., 1991]. Kimberlite magmas have been suggested by Head et al. [1991]. Furthermore we also note that the high D/H ratio of ~1.6% on Venus [Donahue et al., 1982; DeBergh et al., 1991] implies the existence of oceans and associated calcite formation via inorganic sedimentation, on Venus at some time in the past. (An alternative steady state model advanced by Grinspoon [1987] to explain the high D/H ratio is very sensitive to poorly constrained input parameters such as the number and size of cometary impacts on Venus over solar system history and is considered by us to be less likely.) Thus, independent arguments suggest that calcite-bearing igneous rocks are indeed present on Venus.

Another condition is that all the solid phases and the CO_2 be in chemical contact. Orville [1974] has interpreted this to mean that all the solid phases must be present in the same igneous rock. In fact, this is the case in nepheline-syenites and related types of alkaline rocks [v. Johannsen, 1938]. However, we note that the calcite + wollastonite + quartz assemblage also could be formed from intimate mixing of different types of fine-grained materials produced by a combination of chemical and physical weathering processes acting on igneous rocks without the necessity for all minerals to have been present initially. For example, thermodynamic calculations by Khodakovsky et al. [1979], which consider the chemical weathering reactions when several major rock types such as andesites, rhyolites, sodium alkaline basalts, and potassium alkaline basalts are exposed to the Venusian atmosphere, predict that significant amounts of calcite will be formed from sodium and potassium alkaline basalts and that significant amounts of quartz will be formed from andesites and rhyolites. In this regard it is interesting to note that the Venera 8 gamma ray spectroscopic analyses for K, U, and Th, and the Venera 13 X-ray fluorescence data for major elements have been interpreted as a high-potassium alkaline basaltic composition [Volkov et al., 1986; Baruskov et al., 1986]. Another route for producing fine-grained calcite by a combination of chemical and physical weathering was proposed by Florensky et al. [1977] and later quantified by Nozette and Lewis [1982]. In this scenario, chemical weathering of rocks at high elevations produces calcite that is then abraded and blown into the hotter lowlands below. In turn, reaction of the calcite + quartz assemblage will yield wollasonite, as occurs in contact metamorphic rocks on the Earth. Thus, several thermodynamically feasible routes lead to the establishment of the calcite–wollastonite equilibrium.

Another important question is the amount of calcite required for buffering the CO_2 pressure in the Venusian atmosphere. Unfortunately this information cannot be derived from equations (2) and (4) because the equilibrium constant for a buffering reaction does not depend on the amount of solid material present; as long as some is present the buffering can take place. However, it is possible to make some mass balance calculations to illustrate how much calcite may be required. The total inventory of atmospheric CO_2 on Venus corresponds to a global calcite layer ~ 0.87 km thick, but the amount of calcite required for buffering is very much smaller because only variations about the CO_2 equilibrium pressure of 89 bars for reaction (2) are involved.

For example, we can consider the effects from adding CO_2 to the Venusian atmosphere by volcanism, which is the most plausible mechanism for perturbing atmosphere–surface chemical equilibria on Venus. As we shall discuss later in connection with SO_2, a geochemical estimate for the current rate of volcanism on Venus is in the range of $\sim 0.4 - 11$ km^3 yr^{-1} with the most plausible value being ~ 1 km^3 yr^{-1}. Assuming that the ratio of CO_2 to total sulfur in the erupted material is the same as the CO_2/SO_2 ratio in the Venusian atmosphere and using published estimates for the amount of sulfur in the erupted material [Fegley and Prinn, 1989], approximately 7.5×10^{20} CO_2 molecules cm^{-2} yr^{-1} will be erupted into the Venusian atmosphere for a total pressure increase of about 0.05 millibars per year. Approximately 0.1 g cm^{-2} of calcite, equivalent to a layer $\sim 440\mu$m thick would have to be formed to bring the CO_2 pressure back to that of the calcite–wollastonite equilibrium. Conversely, a 0.05 millibar CO_2 pressure drop would consume the same amount of calcite, which would be equivalent to about 5 millimeters of Venusian surface material if all the CaO in the Venera and Vega analyses of the surface is present as calcite. Even though all the observed CaO probably is not present as calcite, extreme assumptions about the Venusian volcanism rate and volcanic gas compositions have to be made to change the fact that very small amounts of surface material are sufficient for buffering the likely CO_2 pressure changes on Venus. Furthermore, Lewis [1971a] suggested that materials which are more Ca-rich than average Venus soil are probably responsible for the buffer so the amount of material required is probably quite small.

However, it still remains to be demonstrated that the rate of the calcite–wollastonite reaction is sufficiently rapid for equilibrium to be closely approached on a geologically short timescale. Several kinetic studies [e.g., Jander, 1927; Repa, 1954; Gordon, 1971; Kridelbaugh, 1973; Tanner et al., 1985] have been done on reaction (2), but we cannot quantitatively estimate the rate of the calcite–wollastonite reaction on the Venusian surface because the required kinetic data have not been measured under the appropriate conditions.

For example, none of the studies measured the specific rate (molecules cm^{-2} sec^{-1}), which is required to calculate how fast CO_2 will react with exposed wollastonite on the Venusian surface. Also, the early kinetic studies are either done under conditions that allowed the formation of several other calcium silicates in addition to wollastonite [Jander, 1927] or are only qualitative [Repa, 1954]. Kridelbaugh [1973] studied the rate of decarbonation of calcite + quartz powders in anhydrous CO_2, but Tanner et al. [1985] have pointed out that his data analysis and therefore his rate equation are incorrect. Thus, his data cannot be used to constrain CO_2 production on Venus as Mueller and Kridelbaugh [1973] have attempted to do. Unfortunately the studies of Gordon [1971] and Tanner et al. [1985] are probably also inappropriate to Venus because these workers used binary CO_2-H_2O gas mixtures containing 4% H_2O [Tanner et al., 1985] or 82% H_2O [Gordon, 1971], while the lower atmosphere of Venus contains only $20 - 200$ ppm H_2O.

The work by Gordon [1971], Kridelbaugh [1973], and Tanner et al. [1985] suggests that the mechanism of the decarbonation reaction of calcite + quartz is different under anhydrous and "wet" conditions and the kinetics are also probably different under anhydrous and "wet" conditions. It is not clear if the mechanism for the carbonation reaction of CO_2 + wollastonite is also different under anhydrous and "wet" conditions. However, the careful study of Tanner et al. [1985] shows that the rate limiting step for the carbonation reaction is quartz precipitation from a supercritical CO_2-H_2O fluid. If quartz precipitation remains rate limiting under Venusian surface conditions, the reaction rate is likely to be different than that measured by Tanner et al. [1985] because of the different silica transport and precipitation mechanisms required in the absence of water.

It is also interesting to ask if any other carbonates are likely to be thermodynamically stable on the surface of Venus. A detailed study by Lewis [1970a] of 19 different CO_2 buffer reactions involving carbonates shows that calcite is the only carbonate stable on the Venusian surface at 740 K. This study considered calcite, dolomite, magnesite, and siderite. However, as Figures 4 - 6 illustrate, other carbonate–silicate mineral assemblages may also be stable on the Venusian surface, but probably only at the lower temperatures found in the less extensive, higher elevation areas. The equilibria displayed in Figures 4 - 6 are

$$MgCO_3 + MgSiO_3 = Mg_2SiO_4 + CO_2 \qquad (8)$$

$$\log_{10} P_{CO_2} = 8.85 - 4903(\pm 120)/T \qquad (9)$$

between magnesite + enstatite yielding forsterite + CO_2,

$$CaMg(CO_3)_2 + 4MgSiO_3 = 2Mg_2SiO_4 + CaMgSi_2O_6 + 2CO_2 \qquad (10)$$

$$\log_{10} P_{CO_2} = 8.52 - 4511(\pm 286)/T \qquad (11)$$

between dolomite + enstatite yielding forsterite + diopside + CO_2, and

$$2CaMg(CO_3)_2 + SiO_2 = 2CaCO_3 + Mg_2SiO_4 + 2CO_2 \qquad (12)$$

$$\log_{10} P_{CO_2} = 8.95 - 4735(\pm 122)/T. \qquad (13)$$

between dolomite + quartz yielding calcite + forsterite + CO_2. The CO_2 pressures for these equilibria intersect the observed CO_2 (P,T) profile in the Venusian atmosphere at $\sim 700 \pm 30$ K ($\sim 5 \pm 4$ km), $\sim 660 \pm 70$ K ($\sim 10 \pm 9$ km), and $\sim 645 \pm 25$ K ($\sim 12 \pm 3$ km), respectively.

Thus, for reaction (8), the assemblage forsterite + CO_2 is stable at higher temperatures (lower elevations), the assemblage magnesite + enstatite is stable at lower temperatures (higher elevations), and all phases coexist at $\sim 700 \pm 30$ K ($\sim 5 \pm 4$ km). Likewise, for reaction (10), forsterite +

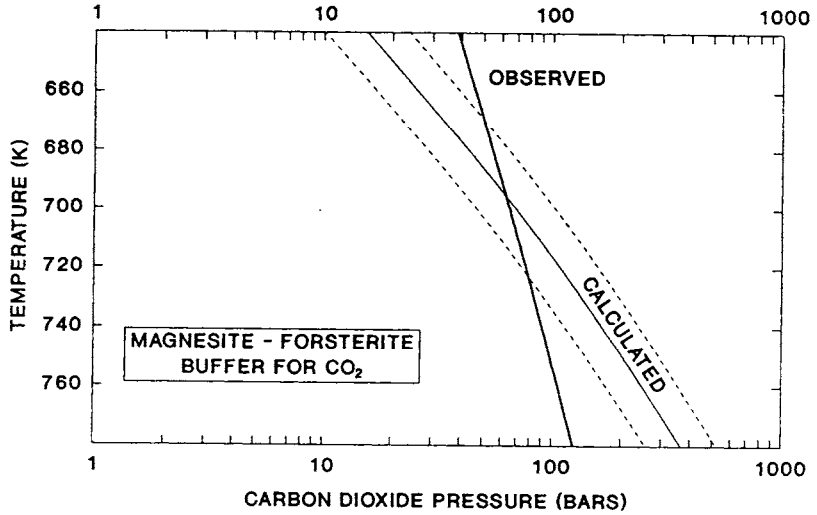

Fig. 4. A comparison of the CO_2 pressure calculated for reaction (8) with the observed CO_2 pressure at the surface of Venus. The dashed lines show the range of calculated CO_2 pressures allowed by the uncertainties in the thermodynamic data. The two curves intersect at 700±30 K (5±4 km). Magnesite is apparently stable only at cooler temperatures (higher altitudes) than calcite, although their stability fields overlap within the formal uncertainties of the thermodynamic data.

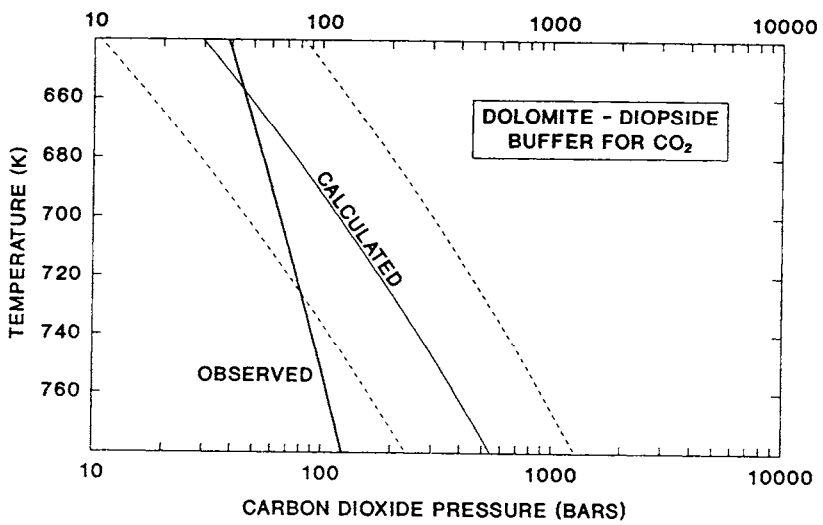

Fig. 5. As in Fig. 4 but for reaction (10). The intersection of the two curves is at 660±70 K (10±9 km).

diopside + CO_2 are stable at lower altitudes, dolomite + enstatite are stable at higher altitudes, and all phases coexist at the ~ 660±70 K (~ 10±9 km) level. A similar interpretation applies to reaction (12). Figures 3 – 6 illustrate that with increasing altitude (i.e., decreasing temperature) on the Venusian surface, first calcite, and then magnesite, and finally dolomite become stable. However, the uncertainties in the thermodynamic data translate into large uncertainties in the altitude ranges within which the carbonates first become stable.

This predicted hypsometric control of carbonate stability on the Venusian surface was first discussed by Florensky et al. [1977] and later studied in more detail by Nozette and Lewis [1982] who suggested that "calcium- and magnesium-rich weathering products are produced at high altitudes by gas–solid reactions with igneous minerals, then removed into the hotter lowlands by surface winds. These fine-grained weathering products may then rereact with the lower atmosphere and buffer the composition of the observed gases carbon dioxide, water vapor, sulfur dioxide, and hydrogen fluoride in some regions of the surface. This process is a plausible mechanism for the establishment in the lowlands of a calcium-rich mineral assemblage, which had previously been found necessary for the buffering of these species." However,

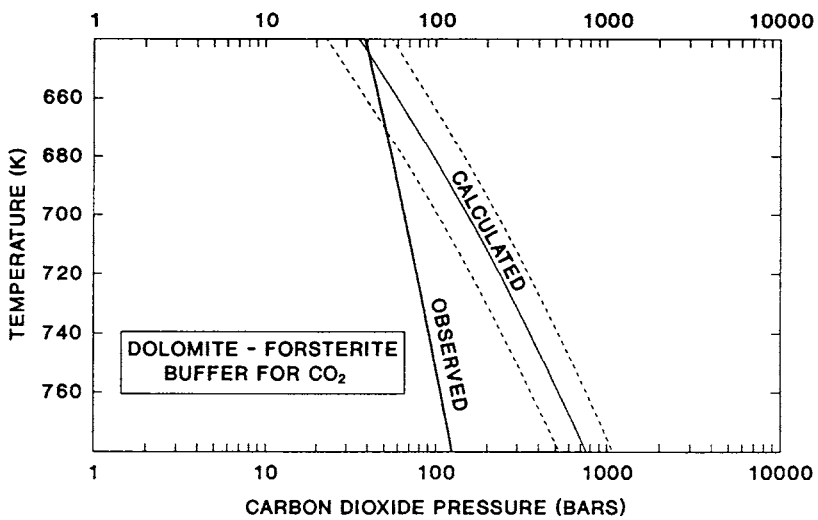

Fig. 6. As in Fig. 4 but for reaction (12). The intersection of the two curves is at 645±25 K (12±3 km). This Fig. and Fig. 5 show that dolomite is probably restricted to only the coolest temperatures (highest altitudes) on Venus.

we must emphasize that the rate of chemical weathering in the cooler highlands will be markedly slower than in the hotter plains regions.

Finally, we note that Zolotov [1991a] recently suggested that rhodochrosite, $MnCO_3$, is stable on Venus and proposed that it is formed by the reaction

$$MnSiO_3 + CO_2 = MnCO_3 + SiO_2 \qquad (14)$$

at all altitudes on the Venusian surface. In support of this suggestion he calculated CO_2 pressures of 60.9 bars at 740 K and 16.3 bars at 675 K. These calculated values are less than the observed CO_2 pressure and if correct would mean that rhodochrosite is stable on Venus.

However, we are unable to confirm Zolotov's results and find instead that the equilibrium CO_2 pressure for reaction (14) is

$$\log_{10} P_{CO_2}(\text{rhodochrosite}) = 8.84 - 4405(\pm 119)/T \qquad (15)$$

which corresponds to pressures of ~770 bars at 740 K and ~210 bars at 675 K. These calculated CO_2 pressures are considerably higher than those observed on Venus and mean that rhodochrosite is unstable. We obtained similar results for two other equilibria involving rhodochrosite

$$2MnCO_3 + SiO_2 = Mn_2SiO_4 + 2CO_2 \qquad (16)$$

$$\log_{10} P_{CO_2} = 8.79 - 4388(\pm 119)/T \qquad (17)$$

$$MnCO_3 + MnSiO_3 = Mn_2SiO_4 + CO_2 \qquad (18)$$

$$\log_{10} P_{CO_2} = 8.74 - 4371(\pm 207)/T \qquad (19)$$

and conclude that $MnCO_3$ is unstable over the entire Venusian surface. It should also be noted that on the Earth $MnSiO_3$ and Mn_2SiO_4 are found as components dissolved in solid solution in low-Ca pyroxene and in olivine [Deer et al., 1963]. If this also occurs on Venus then the equilibrium CO_2 pressures for the reactions above are substantially higher than those calculated for the pure minerals.

Scapolite Minerals. Another carbonate-bearing mineral that may be stable on the surface of Venus is scapolite, which is a three component solid solution commonly found in calcium-rich metamorphic rocks on the Earth [Deer et al., 1963]. The stabilities of the three end-members in the solid solution can be calculated from the decomposition reactions

$$Ca_4[Al_6Si_6O_{24}]CO_3 = 3CaAl_2Si_2O_8 + CaCO_3 \qquad (20)$$

for the decomposition of meionite to anorthite + calcite,

$$Na_4[Al_3Si_9O_{24}]Cl = 3NaAlSi_3O_8 + NaCl \qquad (21)$$

for the decomposition of marialite to albite + halite, and

$$Ca_4[Al_6Si_6O_{24}]SO_4 = 3CaAl_2Si_2O_8 + CaSO_4 \qquad (22)$$

for the decomposition of sulfate meionite to anorthite + anhydrite. The equilibrium constants for reactions (20)–(22) are given by

$$\log_{10} K_{20} = 3.14 - 3468(\pm 569)/T \qquad (23)$$

$$\log_{10} K_{21} = -2.40 + 3082(\pm 575)/T \qquad (24)$$

$$\log_{10} K_{22} = 3.85 - 13976(\pm 612)/T. \qquad (25)$$

These data show that both meionite and sulfate meionite are unstable relative to the assemblages anorthite + calcite and anorthite + anhydrite under all Venusian surface conditions. At 740 K, assuming that anorthite + calcite coexist, the calculated thermodynamic activity for meionite is ~0.03 with a range of $\sim 0.005 - 0.2$ being allowed by the uncertainty in the thermodynamic data. Similarly, assuming that anorthite + anhydrite coexist, the thermodynamic activity for sulfate meionite is $\sim 10^{-15}$ at 740 K. Thus, an isolated grain of meionite on the surface of Venus will spontaneously

decompose to a mixture of anorthite + calcite, and an isolated grain of sulfate meionite on the surface of Venus will spontaneously decompose to a mixture of anorthite + anhydrite. Neither mineral is stable as a pure phase nor is a binary solid solution of the two minerals stable under Venusian surface conditions.

In contrast, the thermodynamic data of Semenov et al. [1981] for marialite show that it is stable on the Venusian surface relative to the assemblage albite + halite. Furthermore, the activity–composition relations for scapolite solid solutions [Moecher and Essene, 1990] suggest that binary solid solutions of meionite + marialite will also be stable on the surface of Venus. Barsukov et al. [1982, 1986] also concluded that meionite–marialite solid solutions are stable on Venus, but Volkov et al. [1986] and Zolotov et al. [1987] reached exactly the opposite conclusion that scapolites are not stable on Venus. However, none of these authors gave the source of their thermodynamic data and their work must therefore be viewed cautiously.

Although the thermodynamic data of Semenov et al. [1981] show marialite to be stable on Venus, we are skeptical of this result for several reasons. First, it is not clear if their data refer to marialite in which Al-Si and anions are totally ordered, totally disordered, or in an intermediate state. The degree of order/disorder affects the configurational entropy and hence the Gibbs free energy of formation for the scapolite sample. For example, Moecher and Essene [1990] show that contributions from Al-Si disorder and anion disorder may potentially comprise up to 12% of the total molar entropy of meionite at 298 K. The resulting uncertainty in ΔG_f° may be ~2 kJ/mole. It is impossible to estimate the importance of similar effects in the samples studied by Semenov et al. [1981]. Second, Orville [1975] concluded that marialite was unstable relative to albite + halite at 750°C and 4 kb. However, the Semenov et al. data show that marialite is stable. Third, the Semenov et al. data also seem to indicate a much greater stability for marialite than implied by terrestrial occurrences [Deer et al., 1963]. Thus, we believe that further thermodynamic studies of well characterized marialite samples are required prior to drawing firm conclusions about its stability on Venus.

The CO/CO_2 Ratio and the Oxygen Fugacity of the Lower Atmosphere. Carbon monoxide was discovered in the atmosphere of Venus by Connes et al. [1968] who derived an abundance of 45 ± 10 ppm at the cloud tops. Young [1972] reanalyzed the Connes spectra and gave a revised CO abundance of 51 ± 1 ppm. Subsequent in-situ measurements by the Pioneer Venus and the Venera 11/12 gas chromatograph experiments of the CO abundance in the lower atmosphere of Venus gave mixing ratios of 32^{+62}_{-22} ppm at 52 km, 30 ± 18 ppm at 42 km, and 20 ± 3 ppm at 22 km [Oyama et al., 1980] and 28 ± 7 ppm in the 36 to 42 km region and 17 ± 1 ppm at 12 km [Gel'man et al., 1979; Marov et al., 1989]. More recent Earth-based spectroscopic observations at $2.3\mu m$ of the night side of Venus give a CO mixing ratio of 45 ppm in the 35 to 45 km altitude region [Bézard et al., 1990]. Within error, this value is the same as that reported by Oyama et al. [1980] for CO in the same altitude range.

Although CO is a trace constituent of the lower atmosphere of Venus it is nevertheless an important gas because the CO/CO_2 ratio in the hot, lower atmosphere probably controls the oxygen fugacity (f_{O_2}) of the atmosphere and probably also controls the oxidation state of the Venusian surface. This point is easily illustrated by considering the thermochemical equilibrium

$$2CO + O_2 = 2CO_2 \tag{26}$$

which has an equilibrium constant K_{26} given by

$$K_{26} = (X_{CO_2}/X_{CO})^2 \cdot (1/f_{O_2}). \tag{27}$$

Substituting the appropriate thermodynamic data and rearranging yields

$$\log_{10} f_{O_2} = 2\log_{10}(X_{CO_2}/X_{CO}) + 9.20 - 29621(\pm 19)/T \tag{28}$$

which gives the f_{O_2} as a function of temperature (and thus altitude) and the CO/CO_2 ratio in the lower atmosphere of Venus. Inserting the CO/CO_2 ratio at 22 km then yields

$$\log_{10} f_{O_2} = 18.57 - 29621(\pm 19)/T \tag{29}$$

which we will assume is valid in the range of 0 to 22 km. We note that the Venera 11/12 gas chromatograph measured a CO mole fraction of 17 ± 1 ppm at 12 km altitude, but within the combined experimental uncertainties, this value is the same as the CO mole fraction of 20 ± 3 ppm measured by the Pioneer Venus gas chromatograph at 22 km.

The calculated oxygen fugacity as a function of temperature in the near surface region of Venus is shown in Figure 7 where it is seen that $f_{O_2} \sim 10^{-21.5}$ bars at ~ 740 K (the temperature at the median planetary radius). However, if the CO mixing ratio at the surface of Venus is actually lower than the value of 20 ppm prevailing at 22 km then the oxygen fugacity will be correspondingly higher. For example, CO mixing ratios of 10 ppm and 5 ppm would lead to oxygen fugacities of $\sim 10^{-20.9}$ bars and $\sim 10^{-20.3}$ bars, respectively. On the other hand, it is difficult to imagine ways to reduce the f_{O_2} below the value of $10^{-21.5}$ bars, which is appropriate for 20 ppm CO, unless we somewhat arbitrarily assume that the oxygen fugacity of the near-surface Venusian atmosphere is not fixed by the CO/CO_2 ratio (and thus not in equilibrium with the dominant atmospheric gas). The results presented by Zolotov [1991d,e] reninforce these conclusions.

Likewise, it is extremely difficult (if not impossible) to find plausible mechanisms to increase the calculated O_2 mixing ratio of $\sim 10^{-23.5}$ predicted at the Venusian surface by approximately 20 orders of magnitude in order to have agreement with the O_2 mixing ratios of 44 ± 25 ppm and 16 ± 7 ppm determined by the Pioneer Venus gas chromatography experiment at altitudes of 52 km and 42 km, respectively [Oyama et al., 1980] or with the O_2 mixing ratio of 18 ± 4

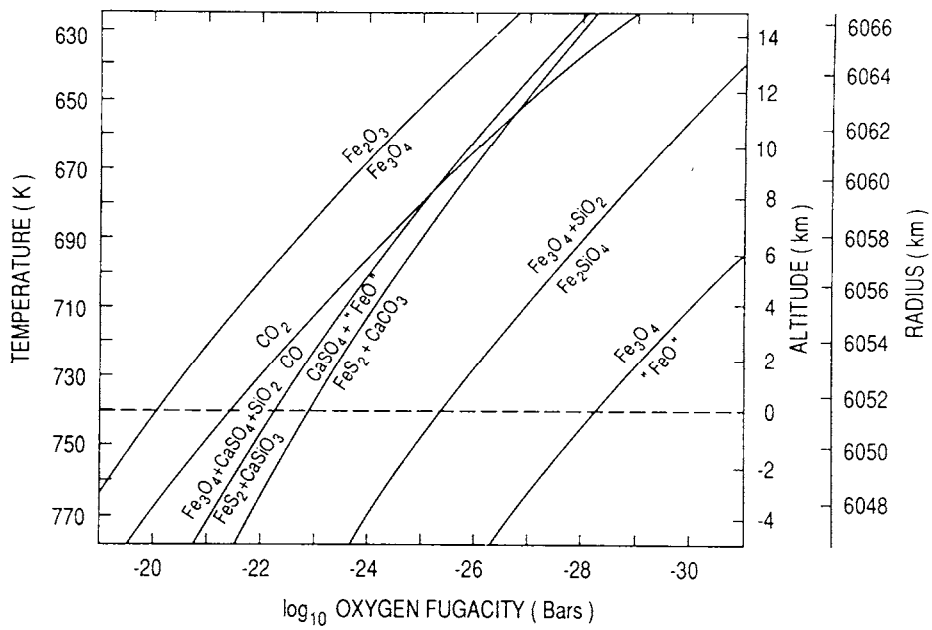

Fig. 7. The temperature dependent oxygen fugacity (CO/CO_2) in the lower atmosphere of Venus is compared to the oxygen fugacities buffered by different iron-bearing mineral assemblages which may exist on the surface of Venus. Mineral assemblages to the right of the Venus atmosphere curve (CO/CO_2) are more reducing; those to the left are more oxidizing. As originally noted by Mueller [1964a], the oxygen fugacity at the surface of Venus is inside the magnetite Fe_3O_4 stability field. Neither wüstite $Fe_{.947}O$ nor hematite Fe_2O_3 is stable under equilibrium conditions on the Venus surface. The two curves involving pyrite FeS_2 are for oxygen fugacity buffers originally proposed by Mueller [1965] for the anhydrite + wollastonite buffer and by Lewis and Kreimendahl [1980] for the anhydrite + calcite buffer. Both reactions are discussed in more detail in connection with sulfide/sulfate equilibria on the surface of Venus.

ppm determined by the Venera 13/14 gas chromatography experiment in the 35 to 58 km altitude region [Mukhin et al., 1983]. However, it is important to note that these measurements are also in conflict with the spectroscopic upper limit of $X_{O_2} < 0.3$ ppm at the cloud tops [Trauger and Lunine, 1983], with the upper limit of $X_{O_2} < 20$ ppm anywhere below 42 km which was determined by the Venera 11/12 gas chromatography experiment [Gel'man et al., 1979], and with the upper limit of $X_{O_2} < 50$ ppm anywhere below 60 km altitude which was determined by the Venera 11/12 spectrophotometer experiment [Moroz, 1981].

It is also important to realize that the large O_2 mixing ratios reported by the Pioneer Venus and Venera 13/14 gas chromatography experiments are incompatible with the observed sulfur chemistry of the atmosphere. As Craig et al. [1983] have shown, the unobserved species SO_3 would be either the dominant or the second most abundant sulfur gas in the lower atmosphere if these large O_2 mixing ratios are correct. In fact, as shown in Table 1, SO_2 is the dominant sulfur gas in the atmosphere of Venus.

Therefore for these reasons we will assume that the reported positive detections of O_2 are in fact incorrect and will not use them as constraints on either the f_{O_2} of the Venusian atmosphere or the oxidation state of the Venusian surface in our subsequent discussion.

Constraints on the Oxidation State of the Venus Surface. Mueller [1963] was probably the first person to suggest that the CO/CO_2 ratio in the hot, lower atmosphere of Venus provided a constraint on the oxidation state and mineralogy of the surface of Venus. This constraint is due to gas–solid reactions exemplified by

$$CO_2(g) + 3\text{“FeO”} = Fe_3O_4 + CO(g) \qquad (30)$$

$$CO_2(g) + 2Fe_3O_4 = 3Fe_2O_3 + CO(g) \qquad (31)$$

which relate the Fe oxidation state in minerals on the Venusian surface to the oxidation state of the near-surface atmosphere. (Both here and elsewhere "FeO" indicates that a fictive component, and the appropriate thermodynamic data, are used to represent wüstite, $Fe_{.947}O$, which is nonstoichiometric.) Despite the fact that CO had not yet been detected on Venus, Mueller [1964a] was able to use Kuiper's [1952] upper limit of $CO/CO_2 \leq 10^{-3}$ to deduce that "$P_{O_2} \geq 10^{-27.1}$ atm at 700°K, which is in the center of the magnetite field."

This conclusion is still valid today and is graphically illustrated in Figure 7 where we see that the CO/CO_2 curve for f_{O_2} is inside the Fe_3O_4 stability field over all temperatures on the Venusian surface. The lower f_{O_2} end of the magnetite field is given by the equilibrium with "FeO"

$$6\text{“FeO”} + O_2 = 2Fe_3O_4 \qquad (32)$$

$$\log_{10} f_{O_2} = 13.055 - 30635(\pm 690)/T. \quad (33)$$

The upper f_{O_2} end of the magnetite field is given by the equilibrium with Fe_2O_3

$$4Fe_3O_4 + O_2 = 6Fe_2O_3 \quad (34)$$

$$\log_{10} f_{O_2} = 14.71 - 25790(\pm 600)/T. \quad (35)$$

Thus, magnetite is predicted to be stable on the Venusian surface while"FeO" (wüstite) is predicted to be absent from the Venusian surface because oxygen fugacities which are $\sim$ 7 orders of magnitude more reducing than CO/CO_2 are needed for wüstite to be stable. Likewise, Fe_2O_3 (hematite) is also predicted to be absent from the surface of Venus because it requires f_{O_2} values about 25 times more oxidizing than CO/CO_2 in order to be stable.

Despite this fact, Zolotov [1987] has predicted that Fe_2O_3 will be stable in the Venus highlands at $\sim$ 3 km altitude. But this assertion is apparently based on the assumption that the gas phase equilibrium (26) between CO and CO_2 will be quenched at the 740 K value, while the gas-solid reaction (34) between Fe_3O_4 and Fe_2O_3 will continue to reach equilibrium. This is an unlikely situation because gas phase reactions are generally more rapid than gas-solid reactions. Thus, if the gas phase reaction is already quenched at a higher temperature it is extremely unlikely that the slower gas–solid reaction will continue to equilibrate. Furthermore, the Fe_3O_4–Fe_2O_3 reaction (34) is noted for being sluggish and slow to attain equilibrium [e.g., see O'Neill, 1988; Hemingway, 1990]. Of course, as discussed in more detail below, the rate of the magnetite $\rightarrow$ hematite conversion and the reverse reaction should be measured under conditions appropriate to the surface of Venus in order to quantitatively assess Zolotov's suggestion. But at the present time we believe that there is very little evidence in favor of the magnetite $\rightarrow$ hematite conversion being a facile reaction and we will base the rest of our discussion on the result shown in Figure 7 that magnetite is the stable Fe oxide over the entire surface of Venus.

However, as Mueller and subsequent investigators have realized [e.g., Lewis, 1970a, 1971b; Lewis and Kreimendahl, 1980; Mueller, 1964a, 1965; Zolotov, 1986a, 1991b], Fe oxides are probably not the only Fe-bearing minerals present on the surface of Venus and it is also interesting to consider the stabilities of FeO-bearing silicates such as olivine $(Mg, Fe)_2SiO_4$ and low-Ca pyroxene $(Mg, Fe)SiO_3$. These minerals can interact with the CO_2 and CO in the Venusian atmosphere via reactions exemplified by

$$2CO_2 + 3Fe_2SiO_4 = 2Fe_3O_4 + 3SiO_2 + 2CO \quad (36)$$

between CO_2 + fayalite yielding magnetite + quartz + CO and by

$$CO_2 + 3FeSiO_3 = Fe_3O_4 + 3SiO_2 + CO \quad (37)$$

between CO_2 + ferrosilite yielding magnetite + quartz + CO.

Actually neither pure fayalite nor pure ferrosilite is expected on the surface of Venus. Ferrosilite, $FeSiO_3$, does not occur in nature and as Figure 7 illustrates, the calculated f_{O_2} at the Venusian surface is $\sim$ 4 orders of magnitude too oxidizing for pure fayalite Fe_2SiO_4 to be thermodynamically stable against oxidation to magnetite + quartz. Instead both fayalite and ferrosilite are probably present dissolved in olivine and low-Ca pyroxene solid solutions formed with the magnesium endmembers Mg_2SiO_4 and $MgSiO_3$. But how much Fe_2SiO_4 or $FeSiO_3$ can be dissolved in olivine or low-Ca pyroxene under Venusian surface conditions?

We can answer this question by first using the equilibrium constants for reactions (36) and (37) to calculate the activites of fayalite and ferrosilite in the two solid solutions and then using activity-composition models to calculate the compositions of the olivines and pyroxenes. Taking thermodynamic data from Robie et al. [1979] and Helgeson et al. [1978] we calculate that

$$\log_{10} a_{Fa} = \frac{2}{3}\log_{10}\frac{X_{CO}}{X_{CO_2}} + 0.364 + 1060(\pm 160)/T \quad (38)$$

$$\log_{10} a_{Fs} = \frac{1}{3}\log_{10}\frac{X_{CO}}{X_{CO_2}} + 0.235 + 496(\pm 146)/T \quad (39)$$

where a_{Fa} and a_{Fs} are the thermochemical activities of fayalite in olivine and ferrosilite in low-Ca pyroxene. Again, assuming a constant CO mixing ratio of 20 ppm we derive

$$\log_{10} a_{Fa} = -2.76 + 1060(\pm 160)/T \quad (40)$$

$$\log_{10} a_{Fs} = -1.326 + 496(\pm 146)/T \quad (41)$$

for Venusian surface conditions. Low-Ca pyroxene shows nearly an ideal one-site solid solution between Fe and Mg [Kern and Weisbrod, 1967] so we may use the a_{Fs} from equation (41) as the ferrosilite mole fraction X_{Fs} in low-Ca pyroxene.

However, olivine is not an ideal Fe-Mg solid solution at Venusian surface temperatures. Instead it is nonideal and is represented as a sub-regular two site solid solution using equations modified from Wood [1987]

$$\log_{10} a_{Fa} = \log_{10} X_{Fa}^2 + (1 - X_{Fa})^2(1 + 2X_{Fa}) \cdot 438/T \quad (42)$$

$$\log_{10} a_{Fo} = \log_{10} X_{Fo}^2 + (1 - X_{Fo})^2(1 - X_{Fo}) \cdot 874/T. \quad (43)$$

The fayalite mole fraction X_{Fa} in olivine is then calculated by solving equations (38) and (42) simultaneously. Table 4 shows the predicted compositions of olivine and low-Ca pyroxene (along with the range of values due to the uncertainties in the thermodynamic data) as a function of altitude.

The results of the thermodynamic calculations show that under equilibrium conditions more Fe_2SiO_4 dissolves in olivine and more $FeSiO_3$ dissolves in low-Ca pyroxene in rocks in the highland regions than in the lowland regions of Venus. In other words, the Fe^{2+} content of olivine and low-Ca pyroxene increases with increasing altitude (and thus with decreasing temperature) on Venus. At $\sim$ 740 K (in the low-

TABLE 4. Predicted Composition of Olivine and Pyroxene on the Venus Surface

Altitude (km)	Temperature (K)	$\log_{10} f_{O_2}$ (bars)	Olivine Mole % Fa	Olivine Range	Pyroxene Mole % Fs	Pyroxene Range
-4	770	-19.9	10.8	(8.4 - 13.9)	20.8	(13.4 - 32.1)
-2	755	-20.7	11.0	(8.5 - 14.3)	21.4	(13.7 - 33.4)
0	740	-21.5	11.2	(8.6 - 14.6)	22.1	(14.0 - 34.7)
2	725	-22.3	11.5	(8.8 - 15.0)	22.8	(14.4 - 36.2)
4	710	-23.2	11.7	(9.0 - 15.5)	23.6	(14.7 - 37.8)
6	695	-24.1	12.0	(9.1 - 16.0)	24.4	(15.1 - 39.5)
8	679	-25.1	12.3	(9.3 - 16.6)	25.4	(15.5 - 41.5)
10	663	-26.1	12.7	(9.5 - 17.2)	26.4	(15.9 - 43.8)
12	648	-27.1	13.0	(9.6 - 17.8)	27.5	(16.4 - 46.1)

lands), olivine containing up to ~ 9-15 mole % Fe_2SiO_4 (Fa_{9-15}) and low-Ca pyroxene containing up to ~ 14-35 mole % $FeSiO_3$ (Fs_{14-35}) are predicted to be stable while more Fe^{2+}-rich olivine and low-Ca pyroxene will be oxidized via reactions such as equations (36) and (37). However, at ~ 10 km altitude (e.g., on Maxwell Montes) where the temperature is ~ 663 K, more Fe^{2+}-rich olivine (Fa_{13-17}) and low-Ca pyroxene (Fs_{16-44}) are stable. For comparison we note that Zolotov [1987] predicted that olivine with $\leq$ 10 mole % Fe_2SiO_4 and pyroxene with $\leq$ 30 mole % $FeSiO_3$ would be resistant to oxidation at ~ 735 K. Zolotov [1991b] revised his prior results slightly and now predicts that only much more magnesian pyroxene with $\leq$ 10 mole % $FeSiO_3$ will be stable at 735 - 745 K.

The thermodynamic predictions can also be compared to the (limited) observational data about the oxidation state of the Venusian surface. Pieters et al. [1986] used a combination of the Venera 9/10 wide angle photometer measurements and the Venera 13/14 color images to derive the spectral reflectance of the Venusian surface in the 0.54μm - 1.0μm range. They found that at visible wavelengths the spectral reflectance of the Venusian surface was not diagnostic about the Fe oxidation state (with either Fe^{2+}- or Fe^{3+}-bearing minerals being acceptable), but that a high reflectance in the near IR region apparently required Fe^{3+}-bearing phases. However, as Pieters et al. [1986] noted and as Figure 7 graphically illustrates, with the exception of magnetite, the presence of Fe^{3+}-bearing minerals (e.g., hematite) is not consistent with thermodynamic equilibrium predictions about the oxidation state of the Venusian surface. How can the apparent discrepancy between the conclusions of Pieters et al. [1986] and the thermodynamic equilibrium predictions be explained?

Obvious explanations such as instrumental artifacts and the presence of minor phases with just the right spectral reflectance properties have been discussed by Pieters et al. [1986] who point out that such explanations are unlikely although they cannot be totally rejected. They then suggested that the two most plausible explanations left are either the existence of a more oxidizing environment at the Venusian surface or incomplete equilibrium between the surface mineralogy and the (more reduced) lower atmosphere.

From our previous discussion, we see that the postulated existence of a more oxidizing environment near the surface of Venus would require a lower CO mixing ratio near the surface than is actually observed in the 12 - 22 km altitude region. In fact, the CO mixing ratio must be decreased to ~ 4 ppm in order to reach the Fe_3O_4-Fe_2O_3 boundary. Higher oxygen fugacities would require even lower CO mixing ratios. However, extrapolating the apparent trend in the Pioneer Venus and Venera 11/12 data for CO downward to the Venusian surface gives a CO mixing ratio of ~ 13 ppm, corresponding to $f_{O_2} \sim 10^{-21.2}$, which is an order of magnitude too reducing for hematite to be stable. We also note that the "Contrast" experiment on Venera 13/14, which qualitatively measured the f_{O_2} from the color change taking place on an indicator plate as a result of the reactions

$$Na_4V_2O_7 + CO_2 + CO = V_2O_4 + 2Na_2CO_3 \qquad (44)$$

$$Na_4V_2O_7 + 2CO = V_2O_3 + 2Na_2CO_3, \qquad (45)$$

indicated $f_{O_2} \leq 10^{-21}$ [Florensky et al., 1983; Volkov et al., 1986], which is inside the magnetite field. Thus, f_{O_2} values $\geq 10^{-20.1}$, which are appropriate for the magnetite-hematite boundary at ~ 740 K, appear unlikely but cannot be definitively ruled out until either the CO mixing ratio or the oxygen fugacity has been measured quantitatively in the 0 - 12 km altitude range on Venus.

The second possibility, that the surface mineralogy may be incompletely equilibrated with the Venusian atmosphere, is certainly plausible but it is impossible to evaluate quantitatively because the required reaction rate measurements have not yet been made. As noted earlier, reaction (34) which converts Fe_3O_4 and Fe_2O_3 is slow at temperatures below 1000 K [e.g., see O'Neill, 1988; Hemingway, 1990], but the kinetics of this reaction have not been measured under Venusian surface conditions. Likewise no kinetic data are available for oxidation - reduction reactions between other Fe^{3+}- and Fe^{2+}-bearing minerals. Thus, it is currently impossible to estimate the timescales for the reduction of any primary Fe^{3+}-bearing minerals which may have been brought to the surface of Venus in basaltic magma.

A third possibility, which was not considered by Pieters et al. [1986], is that a stable Fe^{3+}-bearing mineral may be

produced on the Venusian surface as the result of chemical weathering reactions. We studied this alternative quantitatively for three ferric minerals for which thermodynamic data are available. Acmite [ideally $NaFe^{3+}Si_2O_6$], is a Fe^{3+}-bearing pyroxene commonly found in alkaline rocks on the Earth [Deer et al., 1963]. Acmite stability on the Venusian surface is controlled by redox reactions exemplified by

$$3Al_2SiO_5 + 6NaFeSi_2O_6 + 3SiO_2 + CO = 2Fe_3O_4 + 6NaAlSi_3O_8 + CO_2 \quad (46)$$

which has the equilibrium constant

$$\log_{10}K_{46} = 13.92 + 4321(\pm 1506)/T \quad (47)$$

from 600 to 800 K. Taking 20 ppm CO, equation (47) shows that acmite is unstable under Venusian surface conditions; at equilibrium the acmite thermodynamic activity is $\sim 3 \times 10^{-3}$, which is far too low to be important even as a component in pyroxene solid solution.

Magnesioferrite, $MgFe_2O_4$, is a spinel group mineral which on the Earth is found with Fe^{2+} partially substituting for Mg^{2+} [Deer et al., 1963]. The stability of $MgFe_2O_4$ on the surface of Venus is controlled by redox reactions exemplified by

$$3MgFe_2O_4 + 3SiO_2 + CO = 2Fe_3O_4 + 3MgSiO_3 + CO_2 \quad (48)$$

in felsic rocks and exemplified by

$$3MgFe_2O_4 + 3MgSiO_3 + CO = 2Fe_3O_4 + 3Mg_2SiO_4 + CO_2 \quad (49)$$

in mafic rocks. The corresponding equilibrium constants are

$$\log_{10}K_{48} = 0.91 + 7225(\pm 451)/T \quad (50)$$

$$\log_{10}K_{49} = 1.61 + 4678(\pm 467)/T \quad (51)$$

and the corresponding thermodynamic activities for magnesioferrite are ~0.01 in felsic rocks and ~0.08 in mafic rocks. Thus, magnesioferrite is unstable as a pure phase; however, it may be present as a minor component dissolved in magnetite. But it is unlikely that a magnetite-rich magnesioferrite solid solution would give the spectral signature observed by Pieters et al. [1986].

Finally, Nikolayeva [1989] suggested that chemical weathering reactions could produce epidote [ideally $Ca_2Fe^{3+}Al_2Si_3O_{12}(OH)$], which terrestrially is produced during retrograde metamorphism [Deer *et al.*, 1963]. However, as we show later, epidote is thermodynamically unstable on Venus because the water vapor content of the atmosphere is so small.

Thus, none of the common ferric minerals for which thermodynamic data are available appear capable of explaining the observations of Pieters *et al.* [1986]. No thermodynamic data is available to assess the stabilities of other common ferric minerals such as Fe^{3+}-bearing phlogopite and amphiboles. However, the most interesting candidate mineral is laihunite (ideally $Fe^{2+}Fe_2^{3+}Si_2O_8$) which is a nonstoichiometric distorted olivine-type mineral found in nature and also produced by the oxidation in air of synthetic fayalite [Kitamura et al., 1984; Kondoh et al., 1985]. Laihunite could be produced during olivine oxidation on Venus via reactions exemplified by

$$6Fe_2^{2+}SiO_4 + 4CO_2 = 3Fe^{2+}Fe_2^{3+}Si_2O_8 + Fe_3O_4 + 4CO. \quad (52)$$

Olivine oxidation has been studied by several investigators [e.g., Champness, 1970; Haggerty and Baker, 1967; Wu and Kohlstedt, 1988, and references therein]. However, all these studies have been done in air and no information is available on the analogous reaction in CO/CO_2 gas mixtures.

Water and Hydrogen Compounds

The Abundance of Atmospheric Water Vapor. The atmosphere of Venus is extremely dry. Earth-based spectroscopic observations from ground-based telescopes [e.g., Barker, 1975] and from high flying aircraft [Fink et al., 1972; Kuiper et al., 1969] show that the atmosphere above the clouds contains $\sim 1 - 40$ ppm water vapor and that the amounts are variable. A variety of in situ spacecraft measurements [e.g., see the reviews by von Zahn et al., 1983 and Krasnopolsky, 1986] and recent Earth-based spectroscopic observations [Bézard et al., 1990; Bell et al., 1991] show that the atmosphere below the clouds contains $\sim 20 - 200$ ppm water vapor and that the amount is spatially and temporally variable. For comparison, the terrestrial troposphere contains $\sim 1 - 4\%$ water vapor.

It is difficult to measure the small amounts of water vapor present in the atmosphere of Venus. Ground-based spectroscopic observations have to contend with interference from the telluric water lines which are stronger than the water lines in the atmosphere of Venus. In situ spacecraft experiments, such as mass spectrometers, have to avoid (or be corrected for) contamination from residual terrestrial water in the instrument. Other spacecraft experiments, such as gas chromatographs and water vapor detectors based on conductivity measurements, have to avoid contamination by the strong acids (e.g., HF, HCl, and H_2SO_4) in the Venusian atmosphere. In fact, many of the early ground-based spectroscopic observations and many of the in situ measurements were affected by such problems and incorrectly indicated higher water vapor abundances than are actually present on Venus.

For example, water vapor detectors using chemical absorbents such as P_2O_5, LiCl, and $CaCl_2$ were flown on several Venera spacecraft and on the Vega 1/2 spacecraft [Vinogradov et al., 1971; Surkov et al., 1983, 1986b]. However, these devices are susceptible to errors because of the presence of strong electrolytes such as HF, HCl, and H_2SO_4 on Venus and generally indicated significantly higher H_2O con-

tents than implied by Earth-based microwave observations of sub-cloud water vapor [e.g., Janssen and Klein, 1981] or than measured by other instruments on the same spacecraft. Likewise, the Pioneer Venus (PV) gas chromatography experiment [Oyama et al., 1980] reported significantly higher H_2O contents (of 5200 ppm at 42 km and 1350 ppm at 22 km) than either the PV mass spectrometer [see Fig. 8 in Hunten et al., 1989; Hoffman et al., 1980b] or the scanning spectrophotometer experiment on the Venera 11/12 and Venera 13/14 spacecraft [Moroz, 1983; Moroz et al., 1979, 1983].

These apparent discrepancies have led to much debate and theorizing about the water vapor content of the Venusian atmosphere below the clouds. For example, Grinspoon [1987] and Grinspoon and Lewis [1988] take the global mean water vapor abundance on Venus as 20 ppm, Lewis and Grinspoon [1990] estimate a slightly higher global mean abundance of 50±20 ppm, and Donahue in Hunten et al. [1989] suggests that the global mean water vapor abundance is probably 200±100 ppm. Furthermore data from the net flux radiometers on the 3 Pioneer Venus small probes suggest that below the clouds, the water vapor abundance is spatially variable with mixing ratios of 20–50 ppm near 60° N latitude, 200–500 ppm near 30° S latitude, and >500 ppm near the equator [Revercomb et al., 1985].

However several recent developments have probably resolved this issue in favor of the lower water vapor contents determined by optical spectroscopy and mass spectroscopy. The first development is that an independent analysis of the Venera 11/12 scanning spectrophotometer data by Young et al. [1984] confirms the conclusions of Moroz et al. [1979] that the water vapor content below the clouds is $\leq$ 200 ppm and decreases to a value of $\sim$ 20 ppm near the surface of Venus. The second development is that the scanning spectrophotometer experiment on the Venera 13/14 spacecraft also confirms the results of the earlier measurements made on the Venera 11/12 spacecraft [Moroz, 1983; results of Moroz et al. reviewed in Krasnopolsky 1986]. The third development is that Donahue has been able to deconvolve the contributions of terrestrial and Venusian water to peaks in the PV mass spectrometer by virtue of the dramatically different D/H ratios for water on the two planets. This deconvolution leads to a water vapor profile similar to that determined by Moroz and his colleagues. Finally, recent Earth-based spectroscopic observations at 2.3μm of the night side of Venus give a H_2O mixing ratio of 40 ppm in the 35 to 45 km altitude region [Bézard et al., 1990].

Taken together these results suggest that on average the water vapor content of the lower Venusian atmosphere is $\sim$ 200 ppm at $\sim$ 52 km and decreases to $\sim$ 20 ppm near the surface. However this water vapor profile is difficult to explain. As shown in Figure 8, the water vapor profile on Venus apparently reaches a maximum at $\sim$ 50 to 60 km and decreases at higher and lower altitudes. The decrease

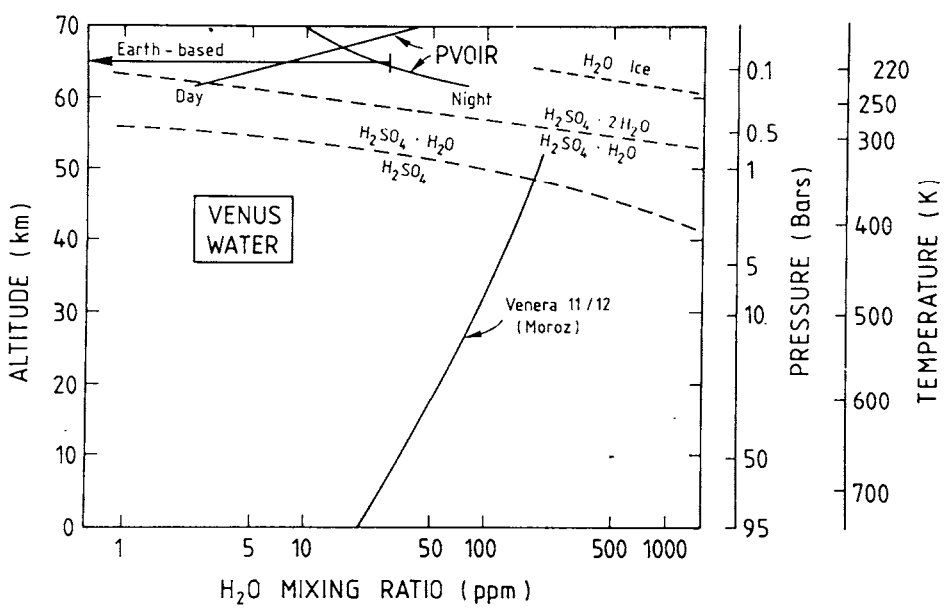

Fig. 8. The vertical distribution of water vapor in the atmosphere of Venus. The three different sets of measurements shown are (1) Earth-based spectroscopic data [Barker, 1975; Fink et al., 1972; Kuiper et al., 1969), (2) Pioneer Venus Orbiting Infrared Radiometer (PVOIR) data [Schofield et al., 1982], and (3) scanning spectrophotometer data from Venera spacecraft [Moroz, 1983; Moroz et al., 1979, 1983]. Dashed lines showing the water vapor pressures over water ice and over concentrated sulfuric acid solutions (calculated from JANAF data) are also shown. As originally noted by Young [1973], the decreasing water vapor concentration near the cloud tops (60–70 km) is consistent with the low water vapor pressures over concentrated sulfuric acid solutions. However, the dropoff in water vapor in the lower atmosphere of Venus is still unexplained although several possible mechanisms have been suggested.

at higher altitudes is consistent with the decreasing water vapor pressure over the concentrated sulfuric acid droplets that make up the clouds of Venus [e.g., see Young, 1973]. Concentrated sulfuric acid is a powerful dessicating agent because of reactions exemplified by

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad (53)$$

which lead to very low concentrations of unbound H_2O in concentrated sulfuric acid solutions and thus to very low water vapor pressures over these solutions. Thermodynamic data (e.g., from the JANAF Tables [Chase et al., 1985]) shows that the resulting water vapor pressures over aqueous sulfuric acid solutions containing $73 - 84$ mass % H_2SO_4, which make up the clouds of Venus [Young, 1973; Hansen and Hovenier, 1974; Esposito et al., 1983], are low enough to explain the observed water vapor mixing ratios at the cloud tops of Venus. However, this mechanism cannot also explain the decreasing water vapor abundance in the lower atmosphere of Venus because the sulfuric acid solutions evaporate via reactions exemplified by

$$H_2SO_4(\text{aqueous}) = H_2O(g) + SO_3(g) \quad (54)$$

$$H_2SO_4(\text{aqueous}) = H_2SO_4(g) \quad (55)$$

at the cloud base (~48 km) and are not present below this level.

We note that the vertical and meridional distribution and the temporal variation of water vapor in the lower atmosphere of Venus can be probed using the newly discovered infrared windows at 2.3μm, 1.7μm, and shorter wavelengths [e.g., Kamb et al., 1988; Crisp et al., 1989; Bézard et al., 1990; Bell et al., 1991]. Thus, we anticipate that in the near future, Earth-based and Galileo NIMS observations will greatly increase our knowledge of the abundance, distribution, and variability of water vapor in the lower atmosphere of Venus. However, at present we are still left with a question about the cause of the observed decrease in water vapor at lower altitudes. Possible answers to this question will be discussed in the next sections.

Hydrated Silicates. One possibility to explain the low water vapor abundance in the near-surface atmosphere is the presence of hydrated minerals on the surface of Venus. If these were stable on the Venusian surface they could provide a sink for atmospheric H_2O by reaction of anhydrous silicates with water vapor to form hydrated silicates. In addition, the presence of hydrated minerals would have important consequences for the geochemistry, geology, and geophysics of the interior of Venus. Small amounts of water markedly decrease the melting point of rocks, with as little as 0.5% (by mass) decreasing the melting point by 200°. In addition to decreasing the melting point, water also affects the composition of the melt which is formed. Finally, other physical properties such as the creep behavior of rocks are dramatically affected by the presence of small amounts of water.

The presence of hydrated silicates on the Venusian surface was probably first suggested by Mueller [1964a,b]. He assumed that the water vapor mixing ratio above the clouds was indicative of that at the surface and then used the spectroscopic data of Bottema et al. [1964] to set a limit of $P_{H_2O} \leq 10^{-3}$ to 10^{-2} bars at the surface. Mueller [1964a] noted that "at 700°K such small quantities of water require that it must almost all be bound as structural water in hydrous phases. The most likely phases to consider are the hydrous silicates such as the amphiboles and micas." In particular Mueller [1964a] first suggested that a mica mineral, phlogopite might be stable under Venusian surface conditions. However, the lack of thermodynamic data for many hydrated minerals combined with the lack of knowledge about the actual water vapor partial pressure at the Venusian surface prevented Mueller from making any definitive predictions about hydrated silicate stability on Venus.

Problems with unavailable or unreliable thermodynamic data and uncertainty about the actual water vapor content of the lower atmosphere of Venus also plagued the work of subsequent investigators [e.g., Lewis, 1968a,1970a; Lewis and Kreimendahl, 1980; Khodakovsky et al., 1979; Barsukov et al., 1980; Volkov et al., 1986]. Thus, the literature is full of conflicting predictions. For example, Lewis [1968a] predicted that muscovite and phlogopite would be present on the surface while Lewis [1970a], Lewis and Kreimendahl [1980], and Nozette and Lewis [1982] calculated that muscovite and phlogopite were unstable and that the amphibole tremolite would be present. Likewise, Khodakovsky et al. [1979] predicted the presence of several hydrated minerals (epidote, glaucophane, tremolite, phlogopite, annite) but Khodakovsky [1982], Barsukov et al. [1980] and Volkov et al. [1986] later claimed that none of these phases were stable on Venus. However, the Soviet work is contradicted by the prediction of Nozette and Lewis [1982] that tremolite will be stable at high altitudes on the Venusian surface even with only 20 ppm water in the atmosphere. What hydrated silicates (if any) are stable on Venus?

Tremolite[$Ca_2Mg_5Si_8O_{22}(OH)_2$]. Tremolite is an amphibole and is probably the most frequently suggested hydrated silicate on Venus. In order for tremolite to be stable on Venus, the equilibrium H_2O vapor pressure for the dehydration reaction

$$Ca_2Mg_5Si_8O_{22}(OH)_2 = H_2O + SiO_2 + 2CaMgSi_2O_6 + 3MgSiO_3 \quad (56)$$

must be less than or equal to the H_2O partial pressure in the atmosphere. This critical value is ~ 0.002 bars at the surface of Venus.

Taking thermodynamic data from Robie et al. [1979], the equilibrium H_2O vapor pressure for reaction (56) is

$$\log_{10} P_{H_2O} = 8.05 - 6742(\pm 1334)/T \quad (57)$$

from 600 to 800 K. The corresponding water vapor mixing ratios are tabulated as a function of altitude from 0 to 12 km in Table 5. Over this entire range, tremolite is thermodynamically unstable on the Venusian surface because the

TABLE 5. Minimum Water Concentrations for Tremolite Stability on Venus

Altitude (km)	Temperature (K)	Water Vapor Mixing Ratios and the Range of Values			
0	740	915 ppm	(15 ppm	–	5.8%)
2	725	670 ppm	(10 ppm	–	4.6%)
4	710	490 ppm	(6 ppm	–	3.7%)
6	695	340 ppm	(4 ppm	–	2.9%)
8	679	230 ppm	(2.5 ppm	–	2.2%)
10	663	150 ppm	(1.5 ppm	–	1.6%)
12	648	100 ppm	(0.9 ppm	–	1.2%)

amount of water vapor in the atmosphere is several times less than the amount needed for tremolite to be stable. Within the rather large uncertainties in the thermochemical data, one could conclude that tremolite may be stable over this entire altitude range. However, this conclusion is probably incorrect.

Most of the uncertainty in the calculated equilibrium water vapor pressure arises from the uncertainty in the determination by HF acid solution calorimetry of the heat of formation of tremolite [Weeks, 1956]. Robie et al. [1979] used these data in their compilation. An independent assessment of the thermodynamic properties for tremolite by Helgeson et al. [1978], who used the results of high pressure phase equilibria experiments [Boyd, 1959] instead of the HF acid solution calorimetry work, also indicates that tremolite is unstable on the surface of Venus. In this case, the calculated water vapor mixing ratio needed for tremolite stability is $\sim$ 2.7% at 740 K and decreases to $\sim$ 0.4% at 648 K (at 12 km altitude).

Extrapolation of the water vapor mixing ratios in Table 5 to lower temperatures (and thus to higher altitudes) indicates that tremolite could be thermodynamically stable at $\sim$ 14 km and above. For comparison, Nozette and Lewis [1982] concluded that tremolite would be stable at altitudes of 16.3 km and higher. In this regard it is important to remember that the highest point measured on Venus by the Pioneer Venus radar altimeter is $\sim$ 11 km high [Masursky et al., 1980]. However higher elevations are not excluded by the PV radar altimetry which covered only 93% of the planet at low resolution. But in any case from our calculations we can conclude that tremolite is probably unstable on the extensive low-lying regions of the Venusian surface, and if present at all could be found only in higher elevation regions of limited areal extent.

This conclusion is tentative because of the disagreement between the phase equilibrium data [Boyd, 1959] and the calorimetric data [Weeks, 1956]. However, the recent data of Jenkins et al. [1991] on the thermodynamic properties of synthetic tremolite, which were published after our calculations were completed, show that tremolite is even less stable than indicated by either Robie et al. [1979] or by Helgeson et al. [1978]. If this is the case, then it is unlikely that tremolite is thermodynamically stable anywhere on the Venusian surface.

Phlogopite[$KMg_3AlSi_3O_{10}(OH)_2$]. Phlogopite is a mica, an end-member of a solid solution series involving F-OH-Cl and Fe-Mg exchange. Here, we consider only the Mg-OH end-member, which has often been suggested to be present on the surface of Venus. The stability of an isolated phlogopite grain on the Venusian surface is governed by the dehydration reaction

$$2KMg_3AlSi_3O_{10}(OH)_2 = 2H_2O + 3Mg_2SiO_4 + KAlSi_2O_6 + KAlSiO_4 \quad (58)$$

and the equilibrium water vapor pressure in the 600 to 800 K range is

$$\log_{10} P_{H_2O} = 9.50 - 7765(\pm 240)/T. \quad (59)$$

This equation is calculated using thermodynamic data from Helgeson et al. [1978] for phlogopite and data from Robie et al. [1979] for the other phases.

The corresponding water vapor mixing ratios that are required for the stability of isolated phlogopite grains are tabulated in Table 6. We can see that phlogopite, like tremolite, apparently requires water vapor mixing ratios of $\sim$ 100 – 1000 ppm to be stable. These values are 5 to 50 times higher than the water vapor content measured by Venera 11/12 and 13/14 near the surface of Venus. Within the formal uncertainties in the thermodynamic data, isolated phlogopite grains apparently could be stable at $\sim$12 km and above on Venus.

However, a more recent assessment of the thermodynamic properties of phlogopite by Berman [1988] leads to less negative ΔG_f° values and thus to higher equilibrium water vapor pressures for reaction (58). Using Berman's [1988] phlogopite data instead of the Helgeson et al. [1978] data, the equilibrium expression for reaction (58) is

$$\log_{10} P_{H_2O} = 8.58 - 6774(\pm 294)/T. \quad (60)$$

At 740 K, the calculated water vapor pressure is $\sim$0.27 bars, or about 140 times higher than the Venera measurements indicate. At lower temperatures (i.e., higher altitudes) the equilibrium water vapor pressures calculated from Berman's data are significantly higher than the observed water vapor abundances and than the equilibrium water vapor pressures calculated from Helgeson's data.

If solid-solid reactions are sufficiently rapid, the stability of phlogopite will probably be influenced by reactions with

TABLE 6. Minimum Water Concentrations for Phlogopite Stability on Venus

Altitude (km)	Temperature (K)	Water Vapor Mixing Ratios and the Range of Values			
0	740	1060 ppm	(500 ppm	–	2200 ppm)
2	725	730 ppm	(340 ppm	–	1570 ppm)
4	710	490 ppm	(230 ppm	–	1070 ppm)
6	695	325 ppm	(150 ppm	–	720 ppm)
8	679	200 ppm	(90 ppm	–	460 ppm)
10	663	125 ppm	(55 ppm	–	280 ppm)
12	648	75 ppm	(30 ppm	–	180 ppm)

other minerals in the surrounding rock. Phlogopite stability in mafic (basaltic) rocks is controlled by the reaction

$$3MgSiO_3 + KMg_3AlSi_3O_{10}(OH)_2 = KAlSi_3O_8 + 3Mg_2SiO_4 + H_2O \quad (61)$$

while phlogopite stability in felsic (granitic) rocks is governed by the reaction

$$3SiO_2 + KMg_3AlSi_3O_{10}(OH)_2 = KAlSi_3O_8 + 3MgSiO_3 + H_2O. \quad (62)$$

Taking thermodynamic data for phlogopite from Helgeson et al. [1978] and from Robie et al. [1979] for the other phases, the equilibrium water vapor pressures for reactions (61) and (62) are given by

$$\log_{10} P_{H_2O} = 8.68 - 6685(\pm 425)/T \quad (63)$$

$$\log_{10} P_{H_2O} = 8.48 - 5506(\pm 408)/T \quad (64)$$

respectively. Although the equilibrium expressions show that phlogopite is more stable in mafic rocks than in felsic rocks, the equilibrium water vapor pressures required for phlogopite stability in both rock types are significantly higher than the values near the surface of Venus. Recalculating equations (63) and (64) using Berman's phlogopite data leads to the same conclusion.

We conclude that although phlogopite thermodynamic data from different compilations show surprisingly large differences, phlogopite, like tremolite, cannot exist in low-lying regions on the Venusian surface and if present at all, could only be found in elevated terrain. But we should realize that at these high altitudes (and low temperatures) the kinetics of phlogopite formation by the vapor phase hydration of anhydrous silicates may inhibit phlogopite formation in geologically reasonable times.

Talc, Epidote, Pargasite, and Muscovite. Talc is a hydrated magnesium silicate, epidote is a hydrated Fe^{3+}-bearing orthosilicate, pargasite is a hornblende in the amphibole group , and muscovite is a mica. These are the only other hydrated silicates (for which thermodynamic data are available) that have equilibrium water vapor pressures less than the total pressure at the Venusian surface. Talc dehydration occurs via the reaction

$$Mg_3Si_4O_{10}(OH)_2 = H_2O + SiO_2 + 3MgSiO_3 \quad (65)$$

which has an equilibrium water vapor pressure given by

$$\log_{10} P_{H_2O} = 8.58 - 6088(\pm 302)/T \quad (66)$$

from 600 to 800 K. Epidote dehydration occurs via the reaction

$$2Ca_2FeAl_2Si_3O_{12}(OH) = H_2O + Ca_3Al_2Si_3O_{12} + CaAl_2Si_2O_8 + SiO_2 + \frac{2}{3}Fe_3O_4 + \frac{1}{6}O_2 \quad (67)$$

which has an equilibrium constant given by

$$\log_{10} K_{67} = 10.01 - 9634(\pm 437)/T \quad (68)$$

from 600 to 800 K. Pargasite dehydration occurs via the reaction

$$2NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2 = 2H_2O + CaAl_2Si_2O_8 + 2NaAlSiO_4 + 3CaMgSi_2O_6 + 2Mg_2SiO_4 + MgAl_2O_4 \quad (69)$$

which has an equilibrium water vapor pressure given by

$$\log_{10} P_{H_2O} = 5.04 - 2911(\pm 1728)/T \quad (70)$$

from 600 to 800 K. Muscovite dehydration occurs via the reaction

$$KAl_3Si_3O_{10}(OH)_2 = H_2O + Al_2O_3 + KAlSi_3O_8 \quad (71)$$

which has an equilibrium water vapor pressure given by

$$\log_{10} P_{H_2O} = 7.80 - 4765(\pm 254)/T \quad (72)$$

from 600 to 800 K. Thermodynamic data from Helgeson et al. [1978] and Robie et al. [1979] were used to calculate the equilibrium constants for the dehydration reactions.

In all cases, the water vapor mixing ratios needed for these hydrated silicates to be stable far exceed the observed values. Talc requires $\sim$ 2% H_2O, pargasite requires $\sim$ 13% H_2O, and muscovite requires $\sim$ 24% H_2O to be stable at 740 K. Because it contains Fe^{3+}, epidote stability depends on both the oxygen fugacity and the water vapor partial pressure. At 740 K, the equilibrium constant K_{67} for epidote dehydration is

$$K_{67} = 10^{-3.009} = P_{H_2O} \cdot f_{O_2}^{1/6} \quad (73)$$

and the corresponding water vapor mixing ratio is $\sim$ 4% for an oxygen fugacity of $10^{-21.5}$ bars. None of these four minerals are stable at any point on the Venusian surface, even when the uncertainties in the thermodynamic data are taken into account.

Other Hydrated Silicates. The other hydrated silicates for which thermodynamic data are available are paragonite, glaucophane, margarite, chrysotile serpentine, anthophyllite, prehnite, pyrophyllite, and kaolinite clay. Their equilibrium water vapor pressures at the surface of Venus were calculated using thermodynamic data from literature compilations and the original experimental papers (see Table 3 for sources). The results of these calculations, which are summarized in Table 7, show that none of these hydrated silicates can be stable anywhere on the Venusian surface because the equilibrium water vapor pressures exceed the total atmospheric pressure. In this regard we note that anthophyllite, which Mueller [1970] had suggested would be stable, requires $P_{H_2O} \geq 510$ bars to be stable at 740 K on the Venusian surface.

Amphibole and Mica Solid Solutions. Thus, our calculations show that no pure hydrated silicates are stable in the extensive low-lying regions on Venus and that only tremolite and phlogopite are possibly stable at elevations exceed-

TABLE 7. Equilibrium Water Vapor Pressures for Hydrated Silicates on the Venus Surface (740 K)

Mineral Name	Ideal Formula	Water Vapor Pressure
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	0.09 bars
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	0.1 bars
Talc	$Mg_3Si_4O_{10}(OH)_2$	2 bars
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$	4 bars
Pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	13 bars
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	23 bars
Paragonite	$NaAl_3Si_3O_{10}(OH)_2$	110 bars
Glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$	230 bars
Margarite	$CaAl_4Si_2O_{10}(OH)_2$	240 bars
Chrysotile	$Mg_3Si_2O_5(OH)_4$	310 bars
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	510 bars
Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	610 bars
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	620 bars
Kaolinite	$Al_2Si_2O_5(OH)_4$	890 bars
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	12,600 bars

ing those observed by the PV radar altimeter. However on the Earth amphiboles and micas frequently have complex compositions [Deer et al., 1963]. Two of the observed substitutions that are important here are Fe^{2+} substituting for Mg^{2+} and F^- substituting for OH^-. What are the effects of these substitutions on amphibole and mica stabilities? Unfortunately, this question is difficult to answer because very few data are available on the thermodynamic properties of the Fe-bearing and F-bearing endmember minerals or for the relevant solid solutions.

Annite, which is the Fe-bearing analog of phlogopite, is one mineral for which the necessary data are available. Annite dehydration occurs via the reaction

$$2KFe_3AlSi_3O_{10}(OH)_2 + O_2 = 2H_2O + 2Fe_3O_4 + 2KAlSi_3O_8 \quad (74)$$

which has an equilibrium constant

$$K_{74} = P^2_{H_2O}/f_{O_2} \quad (75)$$

dependent on both the water vapor pressure and the oxygen fugacity. Thermodynamic data from Helgeson et al. [1978] give the equation

$$\log_{10}K_{74} = 6.45 + 17217(\pm 580)/T \quad (76)$$

and taking $f_{O_2} \sim 10^{-21.5}$ bars yields $P_{H_2O} \sim 10^{4.1}$ bars at 740 K. (Water vapor is certainly non-ideal at these pressures, but inclusion of the proper non-ideality corrections will not alter the conclusion that annite is thermodynamically unstable on the Venusian surface.) Thus, annite is much less stable than phlogopite on Venus and any Fe substitution for Mg in phlogopite will actually increase the amount of water vapor required for phlogopite stability on Venus. Likewise, phase diagrams for ferro-actinolite, the Fe^{2+}-bearing analog of tremolite, show that it is less stable than tremolite and decomposes at temperatures about 300° lower than tremolite does at an oxygen fugacity defined by the fayalite–magnetite–quartz buffer [Gilbert et al., 1982]. These phase diagrams indicate that Fe substitution for Mg in tremolite will also decrease tremolite stability on Venus.

However F substitution for OH in amphiboles has the opposite effect and increases amphibole stabilities [e.g.,Gilbert et al., 1982; Grigoriev and Isküll, 1937; Comeforo and Kohn, 1954; Valley et al., 1982; Graham and Navrotsky, 1986]. For example, the equilibrium temperature ($\Delta G = 0$) for fluor-tremolite decomposition via the reaction

$$Ca_2Mg_5Si_8O_{22}F_2 = CaF_2 + 2SiO_2 + CaMgSi_2O_6 + 4MgSiO_3 \quad (77)$$

is $1136 \pm 3°C$ at 1 bar versus an equilibrium temperature of only 552°C at $P_{H_2O} = 1$ bar for the analogous tremolite decomposition reaction [Gilbert et al., 1982].

Fluor-amphibole and fluor-phlogopite stability is considered later in connection with HCl and HF buffers; these results show that fluor-tremolite, fluor-edenite, and fluor-phlogopite are stable (within the uncertainties in the thermodynamic data) over a wide range of altitudes on the Venusian surface. Thus, OH may be present in amphiboles and phlogopite in solid solution with F, but, as shown above, not as hydroxyl end-member minerals. Assuming ideal solid solution of OH- and F-endmembers, we attempted to calculate the mole fractions of dissolved tremolite and phlogopite using the exchange reactions

$$2H_2O + Ca_2Mg_5Si_8O_{22}F_2 = Ca_2Mg_5Si_8O_{22}(OH)_2 + 2HF \quad (78)$$

$$2H_2O + KMg_3AlSi_3O_{10}F_2 + KMg_3AlSi_3O_{10}(OH)_2 + 2HF \quad (79)$$

which have the equilibrium constants

$$\log_{10}K_{78} = -1.46 - 3915(\pm 1167)/T \quad (80)$$

$$\log_{10}K_{79} = -2.44 - 2900(\pm 1840)/T. \quad (81)$$

However, the uncertainties in the thermodynamic data for the tremolite and phlogopite exchange reactions are so large that a wide range of tremolite and phlogopite mole fractions up to unity are derived. The calculated minimum mole fractions at 740 K are ~0.08 for tremolite and ~0.02 for phlogopite. The analogous exchange reaction involving fluor-edenite is not considered because no thermodynamic data are available for edenite.

To summarize, no pure hydrated silicates are thermodynamically stable on the Venusian surface with the possible exceptions of tremolite and phlogopite which may be stable at high altitudes. Although stability of tremolite and phlogopite is possible within the formal uncertainties in the thermodynamic data, it is unlikely. The recently published data on the thermodynamic properties of synthetic tremolite [Jenkins et al., 1991] strengthen this con-

clusion. Solid solutions of hydroxy- and fluor-amphiboles, and of hydroxy- and fluor-micas such as tremolite solid solutions with fluor-tremolite and phlogopite solid solutions with fluor-phlogopite may be stable on the Venusian surface, but the uncertainties in the relevant thermodynamic data are too large to permit any definitive predictions from being made at present. High pressure phase equilibrium experiments conducted by experimental petrologists show that some amphibole and hornblende minerals are more stable than those considered here; however, these phases could not be considered because of a lack of thermodynamic data. These minerals include edenite [$NaCa_2Mg_5Si_7\ AlO_{22}(OH)_2$], some members of the richterite family, and some alkali amphiboles; they are discussed by Gilbert et al. [1982]. Furthermore, as noted above, the existing thermodynamic data for phlogopite need to be measured with greater precision to better constrain the stability of this mineral on the surface of Venus. Thus, further work on basic thermodynamic data for several amphibole, hornblende, and mica minerals is needed before firm conclusions can be drawn about the stabilities of hydrated silicates on the surface of Venus and their potential as a sink for water vapor.

Molecular Hydrogen. Another proposed sink for water vapor in the lower atmosphere of Venus is the formation of molecular H_2 by the oxidation of Fe-bearing minerals on the surface of Venus. These reactions are exemplified by

$$2H_2O + 3Fe_2SiO_4 = 2Fe_3O_4 + 3SiO_2 + 2H_2 \quad (82)$$

$$\log_{10}K_{82} = -4.80 + 791(\pm 480)/T \quad (83)$$

between H_2O + fayalite yielding magnetite + quartz + H_2 and by

$$H_2O + 3FeSiO_3 = Fe_3O_4 + 3SiO_2 + H_2 \quad (84)$$

$$\log_{10}K_{84} = -2.56 + 499(\pm 438)/T \quad (85)$$

between H_2O + ferrosilite yielding magnetite + quartz + H_2.

Combining these equilibrium constants with the fayalite and ferrosilite activities calculated earlier, we find that at 740 K the equilibrium H_2 mixing ratio at the Venus surface is only ~3 ppb. This is approximately 7200 times lower than the observed H_2O mixing ratio.

In this regard, we also note that two different spacecraft experiments have reported molecular hydrogen on Venus. The first report was by Taylor et al. [1980] who interpreted the mass 2 peak observed by the Pioneer Venus Orbiter Ion Mass Spectrometer (PV OIMS) as H_2^+. Kumar et al. [1981] analyzed these data and derived an H_2 mixing ratio of 10 ppm at altitudes below 140 km. However, Hartle and Taylor [1983] and Kumar and Taylor [1985] later examined and modelled the PV data in more detail and concluded that the mass 2 peak is due mainly to D^+ with <0.1 ppm H_2^+ (at the 130 km level). The second report was by the Venera 13/14 gas chromatography experiment which supposedly detected 25±10 ppm H_2 in the 49–58 km altitude range [Mukhin et al., 1983]. However, as described earlier, this experiment also detected a similar amount of O_2 in approximately the same altitude range. The similar H_2 and O_2 mixing ratios are thermodynamically inconsistent; one or both must be incorrect. The problems with the carrier gas flow in the Venera 13/14 gas chromatography experiment [Krasnopolsky, 1986] lead us to believe that none of the peaks were identified properly. Thus, we also discount the H_2 identification of Mukhin et al. [1983]. However, even the upper limit of <0.1 ppm H_2 deduced by Kumar and Taylor [1985], which is still significantly higher than the thermodynamic equilibrium value, is too low to provide a sink of the required magnitude for water vapor.

Gas Phase Sinks. Hydrogen sulfide. The formation of H_2S via reactions exemplified by

$$H_2O + COS = CO_2 + H_2S \quad (86)$$

has also been suggested as a sink for water vapor, and apparently received observational support with the reported detection of 80±40 ppm H_2S and 40±20 ppm COS in the 29–37 km altitude range by the Venera 13/14 gas chromatography experiment [Mukhin et al., 1983]. However, as noted above, problems with the carrier gas flow [Krasnopolsky, 1986] during these measurements apparently caused problems with peak identifications for almost all compounds. Thus, the derived COS and H_2S abundances are suspect. Furthermore, Bézard et al. [1990] have detected COS at a much lower level of ~0.3 ppm in the 35–45 km altitude range. Assuming that the COS mixing ratio is constant down to the surface, and using the equilibrium constant

$$\log_{10}K_{86} = -0.15 + 1810(\pm 69)/T \quad (87)$$

for reaction (86), we find that the predicted H_2S mixing ratio is ~1 ppb at the surface (740 K). The equilibrium H_2S mixing ratio increases only very slightly with decreasing temperature to ~5 ppb at 600 K and is clearly insufficient to serve as a water vapor sink.

Carbonic acid gas. Recently, Lewis and Grinspoon [1990] have suggested that formation of carbonic acid gas via the reaction

$$H_2O + CO_2 = H_2CO_3 \quad (88)$$

serves as a water vapor sink in the lower atmosphere of Venus. On the basis of estimated thermodynamic data, they calculate the equilibrium constant for reaction (88) as

$$\log_{10}K_{88} = 0.43 - 1310/T \quad (89)$$

with an uncertainty of a factor of 2 to 3. Assuming conservation of hydrogen atoms between water vapor and carbonic acid gas, Lewis and Grinspoon then calculate vertical profiles for these species. Figure 9, modified from their paper, shows a representative calculation including H_2SO_4 gas which is also included in their modelling.

The high CO_2 pressure in the lower atmosphere of Venus drives reaction (88) to the right and produces significant amounts of H_2CO_3 gas (~80% of total hydrogen) at the

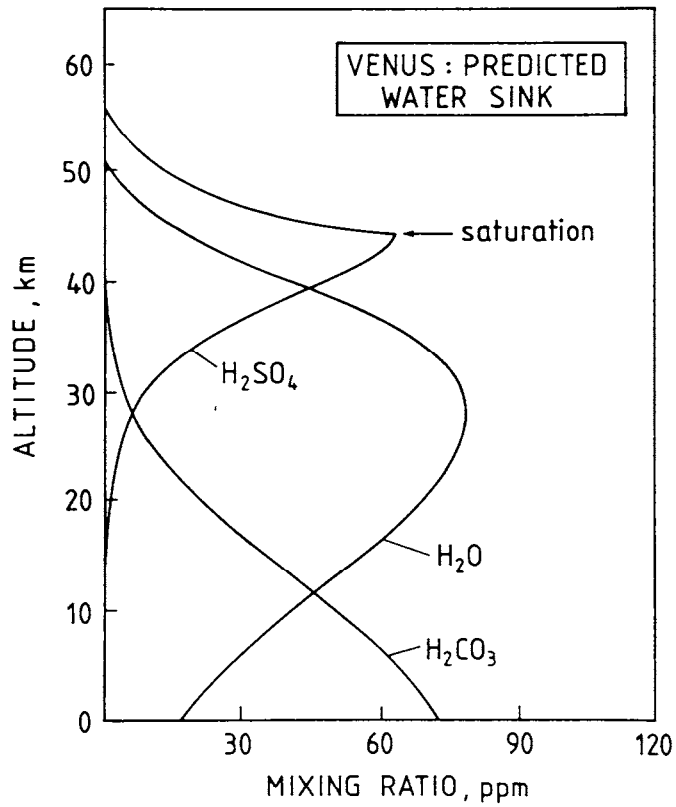

Fig. 9. Predicted vertical profiles for H_2O, H_2SO_4, and H_2CO_3 in the lower atmosphere of Venus [modified from Fig. 1 of Lewis and Grinspoon 1990]. Their calculations, based on estimated thermochemical data, predict that the reaction $H_2O(g) + CO_2(g) = H_2CO_3(g)$ is driven to the right at the high pressures in the lower atmosphere of Venus and that carbonic acid gas is a sink for water vapor.

surface of Venus. The equilibrium H_2O mixing ratio of $\sim 10 \pm 4$ ppm is consistent with the observed value of ~ 20 ppm.

However, we feel that there are two potential problems with this explanation. One is that H_2CO_3 gas has not been isolated or characterized spectroscopically, but has only been proposed on the basis of a peak in the mass spectrum of decomposing NH_4HCO_3 solid [Terlouw et al., 1987]. A second problem is that the formation of significant amounts of H_2CO_3 gas implies fugacity coefficients less than unity in H_2O-CO_2 gas mixtures and negative deviations from ideality for the molar volumes of mixing (ΔV_M) in H_2O-CO_2 gas mixtures. However, these mixtures display positive deviations from ideality [e.g., Kerrick and Jacobs, 1981], which indicates a tendency for unmixing instead of a tendency for compound formation. Thus, before the Lewis and Grinspoon model can be accepted, it is clearly necessary to verify the existence of the postulated carbonic acid gas and to quantitatively determine its thermodynamic properties.

Deuterium. Measurements made by the Pioneer Venus ion and neutral mass spectrometers provided the first evidence for deuterated species in the atmosphere of Venus. McElroy et al. [1982] interpreted the mass 2 peak observed by the Pioneer Venus Orbiter Ion Mass Spectrometer as D^+ and derived a D/H ratio $\sim 10^{-2}$. Subsequently, Hartle and Taylor [1983] derived a D/H ratio of $2.2(\pm 0.6) \times 10^{-2}$ from the same data. Kumar and Taylor [1985] later derived D/H ratios of 1.4% and 2.5% from analyzing PV OIMS data from two orbits. Within the uncertainties, all values are probably consistent and are $\sim 100 - 160$ times higher than the terrestrial value of $\sim 1.6 \times 10^{-4}$ [Craig, 1961]. However, as mentioned earlier, the identification of the mass 2 peak as D^+ is not unique and Taylor et al. [1980] and Kumar et al. [1981] identified the same peak as H_2^+.

Donahue et al. [1982] showed that the data obtained by the PV Large Probe Neutral Mass Spectrometer during the time the inlet was clogged (presumably by sulfuric acid cloud droplets) are consistent with a Venusian D/H ratio $\sim 1.6 \times 10^{-2}$. However, this analysis was questioned by Bertaux and Clarke [1989] who used an upper limit on the Venusian deuterium Lyman-α emission obtained from observations by the International Ultraviolet Explorer satellite to derive $D/H < 5 \times 10^{-3}$ for Venus.

Deuterated water vapor HDO was detected by infrared spectroscopy (at 3.6 μm) in the Venusian atmosphere by DeBergh et al. [1989] who found a HDO mixing ratio of ~ 0.1 ppm above the clouds. When combined with previous H_2O observations [e.g., Barker, 1975; Fink et al., 1972] a D/H value at least 3 times greater than the terrestrial value was implied.

More recently, DeBergh et al. [1991] have observed HDO and H_2O on the night side of Venus at 2.3 μm, which probes the Venusian atmosphere in the 35 to 45 km altitude region [Bézard et al., 1990]. They find an HDO mixing ratio of 1.3 ± 0.2 ppm and an H_2O mixing ratio of 34 ± 10 ppm, corresponding to $D/H = (1.9 \pm 0.6) \times 10^{-2}$, or 120 ± 40 times the terrestrial value, in agreement with the determination by Donahue et al. [1982].

Deuterated water HDO is the major deuterium reservoir in the atmosphere of Venus. However, exchange of deuterium in this reservoir with hydrogen combined in other gases via equilibria such as

$$H_2 + HDO = HD + H_2O \quad (90)$$

$$HCl + HDO = DCl + H_2O \quad (91)$$

$$HF + HDO = DF + H_2O \quad (92)$$

$$H_2S + HDO = HDS + H_2O \quad (93)$$

$$H_2SO_4 + HDO = HDSO_4 + H_2O \quad (94)$$

leads to the production of other, less abundant deuterium-bearing gases.

Fegley [1989] calculated the deuterium fractionation factors for several gases (DF, DCl, HDS, HD) as a function

of temperature and altitude by using thermodynamic data tabulated by Richet et al. [1977]. The results of these calculations are displayed in Figures 10–13. The deuterium fractionation factor α is defined as

$$\alpha_{gas} = [(D/H)_{gas}]/[(D/H)_{H_2O}] \quad (95)$$

and is related to the abundances of the different deuterated gases by equations such as

$$HD/H_2 = HDO/H_2O \cdot \alpha_{H_2} \quad (96)$$

$$DCl/HCl = HDO/H_2O \cdot 2\alpha_{HCl} \quad (97)$$

$$DF/HF = HDO/H_2O \cdot 2\alpha_{HF} \quad (98)$$

$$HDS/H_2S = HDO/H_2O \cdot \alpha_{H_2S}. \quad (99)$$

The equilibrium abundances of these deuterated species calculated from the α values in Figures 10–13 are predicted to be substantial, especially if the deuterium exchange equilibria are established at the Venusian surface where the gas phase reactions may be catalyzed by Fe-bearing minerals. For example, the predicted DCl/HCl ratio is $\sim$ 3% if reaction (91) is quenched at the surface (740 K) and DCl/HCl is $\sim$ 1% if reaction (91) is quenched at the cloudtops (250 K).

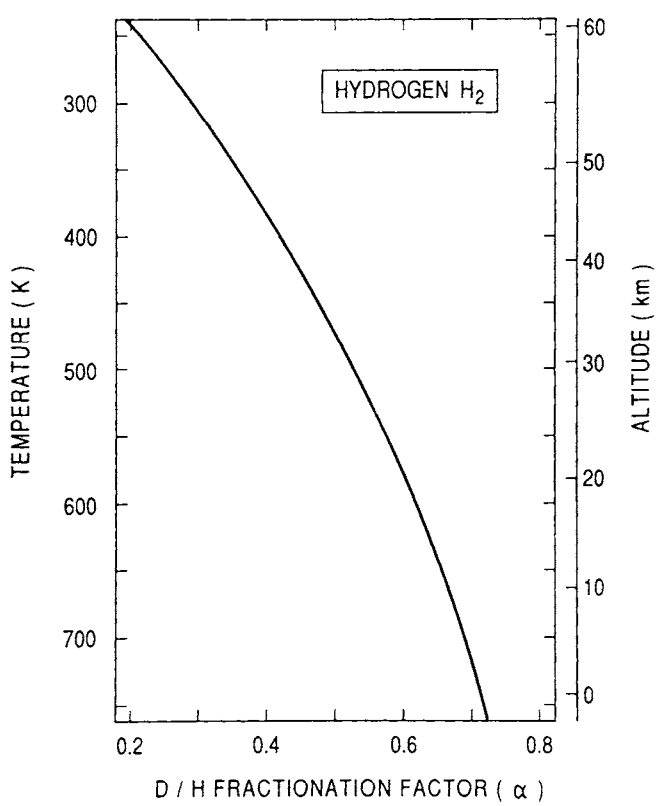

Fig. 10. Predicted thermochemical fractionation factors (α) for deuterium exchange between H_2 + H_2O in the atmosphere of Venus. The fractionation factor is defined as the D/H atom ratio in H_2 relative to the D/H atom ratio in H_2O and is tabulated as a function of temperature by Richet et al. [1977]. The HD/H_2 molar ratio is equal to α times the HDO/H_2O molar ratio.

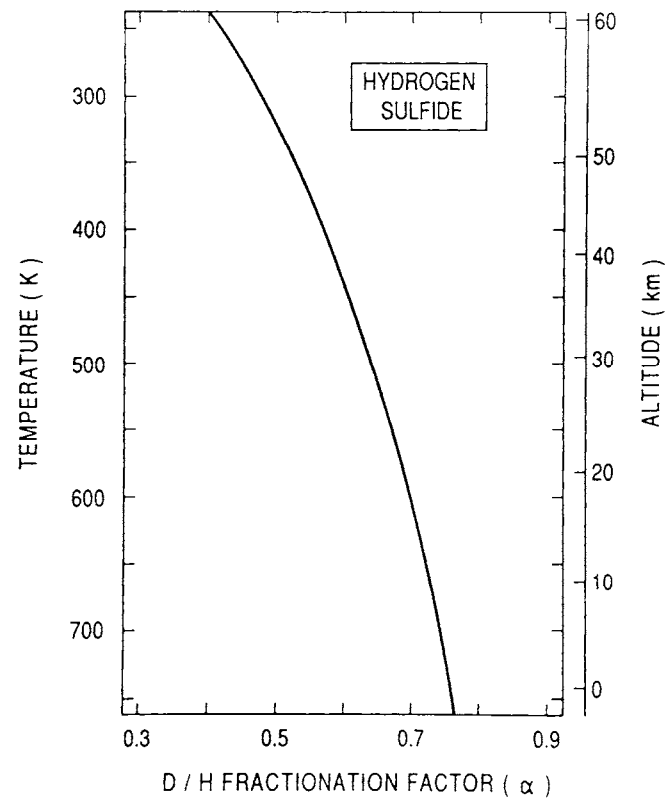

Fig. 11. Predicted thermochemical fractionation factors (α) for deuterium exchange between H_2S + H_2O in the atmosphere of Venus. The HDS/H_2S molar ratio is equal to α times the HDO/H_2O molar ratio.

The upper limit of <8% for DCl/HCl reported by Buie et al. [1982] is consistent with these predictions and suggests that more sensitive observations of DCl, DF, etc. are worth pursuing in order to obtain independent estimates of D/H on Venus.

Sulfur-Bearing Gases and Minerals

Atmospheric Abundances of Sulfur Gases. Sulfur dioxide was discovered on Venus by three different groups at about the same time [Barker, 1979; Conway et al., 1979; Stewart et al., 1979]. Their ultraviolet spectra of the region above the clouds showed SO_2 mixing ratios of <20 ppb to $\sim$600 ppb with higher values being observed for longer path lengths in the Venusian atmosphere. As noted by Barker [1979] this behavior is consistent with photochemical destruction of SO_2 in the upper atmosphere of Venus [e.g.,as modelled by Winick and Stewart, 1980]. Subsequent long-term observations of SO_2 by Esposito and colleagues [Esposito, 1984; Esposito et al., 1988; Na et al., 1990] show a decline in SO_2 mixing ratios above the clouds from 380±80 ppb in 1978 to 50±20 ppb in 1986. This decrease is also consistent with the photochemical destruction of SO_2 to form H_2SO_4 cloud particles. The higher SO_2 mixing ratios observed in 1978-79 can be interpreted as evidence for an injection of SO_2 into

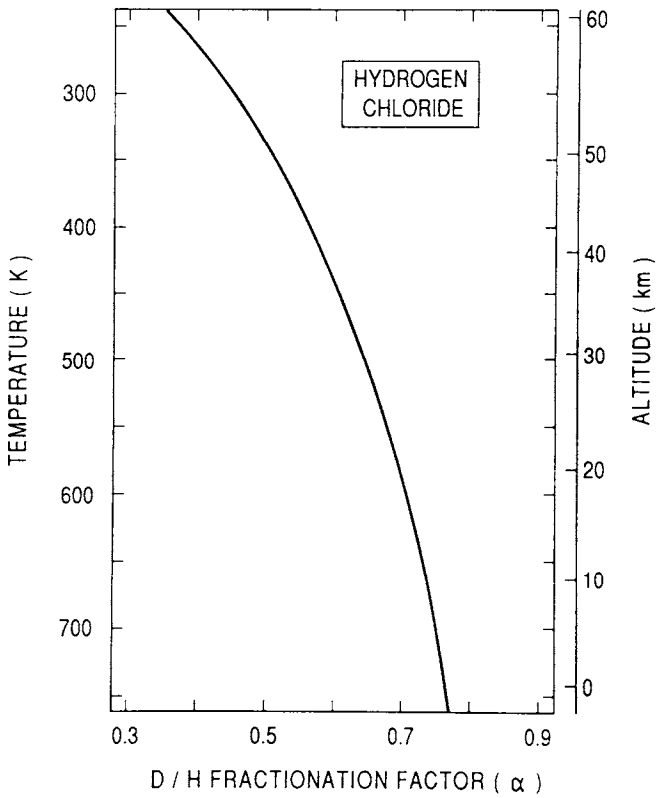

Fig. 12. Predicted thermochemical fractionation factors (α) for deuterium exchange between HCl + H_2O in the atmosphere of Venus. The DCl/HCl molar ratio is equal to 2α times the HDO/H_2O molar ratio.

the Venus upper atmosphere by active volcanism [Esposito, 1984].

The first observations of SO_2 below the clouds were made by Pioneer Venus and Venera 11/12. The Pioneer Venus gas chromatography experiment observed 185±43 ppm SO_2 at 22 km altitude [Oyama et al., 1980]. The Venera 11/12 gas chromatography experiment reported 130±35 ppm SO_2 in the 0-42 km altitude range [Gel'man et al., 1979]. The only subsequent measurement of SO_2 below the clouds is that of Berto et al., [1987] who reported 30–50 ppm SO_2 in the 25-40 km altitude range from the scanning spectrophotometer experiment on the Vega 1/2 spacecraft. However, the results of Berto et al., [1987] also indicate significant supersaturation of elemental sulfur vapor and must be interpreted with caution. Finally, Steffes et al. [1990] used Earth-based microwave observations to derive model-dependent upper limits on the SO_2 abundance below the clouds. This is done by analyzing the continuum absorption in the microwave spectra. Steffes et al. [1990] interpreted their upper limits as showing a decrease in SO_2 below the values measured earlier, but in fact their upper limits are generally consistent (within the uncertainties) with the earlier Pioneer Venus and Venera 11/12 observations.

The other sulfur-bearing gases which have been reported in the atmosphere of Venus are SO, COS, H_2S, H_2SO_4, and elemental sulfur S_x. Na et al. [1990] discovered SO on Venus. Their ultraviolet observations yield 20±10 ppb SO above the clouds. Carbonyl sulfide COS was first unambiguously observed by Bézard et al. [1990] in their 2.3μm observations of the night side of Venus. They found ~0.3 ppm COS in the 35-45 km altitude region. A preliminary detection of 3±2 ppm H_2S below 20 km altitude was reported by Hoffman et al. [1980a] and an upper limit of 2 ppm H_2S was reported by the Pioneer Venus gas chromatography experiment at 22 km altitude [Oyama et al., 1980]. Sulfuric acid vapor has not been observed spectroscopically, but Steffes et al. [1990] have interpreted the continuum absorption in their microwave spectra as requiring a few ppm gaseous H_2SO_4. This is consistent with the extensive evidence showing that aqueous sulfuric acid droplets constitute the cloud particles [Esposito et al., 1983]. Elemental sulfur vapor is interpreted to be the source of the strong absorptions observed in the 450 to 600 nm wavelength region by the scanning spectrophotometer experiment on the Venera 11/12 spacecraft [Moroz et al., 1979, 1980]. San'ko [1980] analyzed these observations and calculated the abundance

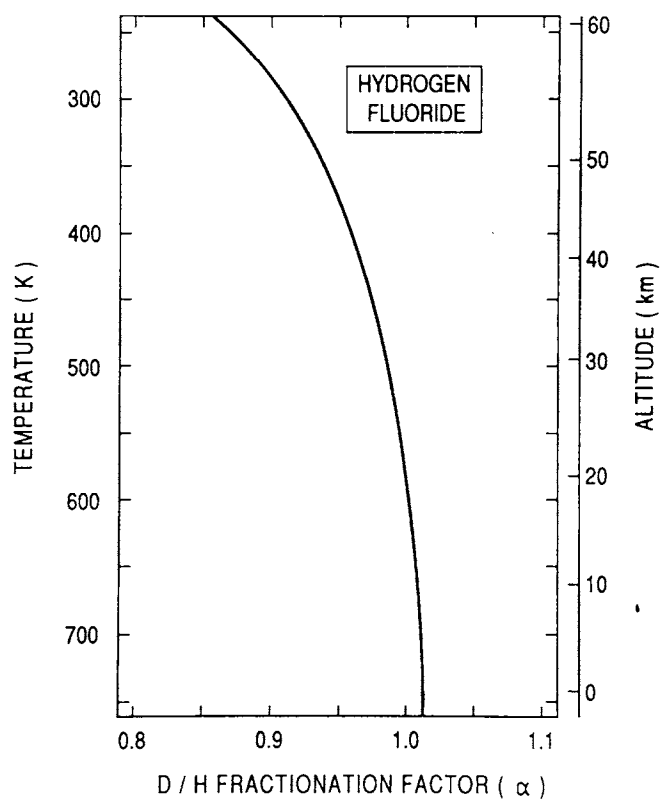

Fig. 13. Predicted thermochemical fractionation factors (α) for deuterium exchange between HF + H_2O in the atmosphere of Venus. The DF/HF molar ratio is equal to 2α times the HDO/H_2O molar ratio.

of the different elemental sulfur vapor species assuming gas phase thermodynamic equilibrium between them. He found a total elemental sulfur mixing ratio (S_x, x = 1-8) of ~20 ppb in the 0-50 km altitude region with S_2 being dominant below ~30 km. Zolotov [1985] redid these calculations and obtained generally similar results to those of San'ko [1980]. The Moroz et al. [1979, 1980] data and the models of San'ko [1980] and Zolotov [1985] rule out the much higher (~0.6%) elemental sulfur mixing ratios proposed by Young [1979] to explain earlier Venera photometer data. As noted above, Berto et al. [1987] attributed absorption in the 220 to 370 nm wavelength region to elemental sulfur vapor. They obtained much higher mixing ratios of 2-10 ppm for sulfur vapor in the 25-40 km altitude range. This is 200-500 times greater than the total sulfur mixing ratio derived by San'ko [1980]. The reasons for these differences, which may represent temporal and/or spatial variations in sulfur chemistry or simply data analysis problems, are unclear.

Finally, the Venera 13/14 gas chromatograph experiment also claimed the detection of 80±40 ppm H_2S and 40±20 ppm COS in the 29-37 km altitude region and 0.2 ppm SF_6 in the 35-58 km altitude region [Mukhin et al., 1983]. However, as noted earlier, problems with the carrier gas flow during the measurements [Krasnopolsky, 1986] apparently caused problems with peak identifications for many compounds. Furthermore, the COS measurement conflicts with the much lower COS mixing ratio observed by Bézard et al. [1990] in the same altitude region and the H_2S measurement conflicts with the earlier Pioneer Venus results. If, as discussed later, COS is produced by pyrite weathering, the fast rate of this reaction [Fegley and Treiman, 1990] is predicted to lead to short-term variations in the spatial and temporal abundances of COS in the lower atmosphere of Venus. Likewise, pyrrhotite oxidation is also relatively rapid [Treiman and Fegley 1991] and short-term variations in COS may also occur as a result of this process. However, the apparent instrumental problems with the Venera 13/14 gas chromatography experiment lead us to conclude that the Venera 13/14 results for H_2S and COS are incorrect and we will not use them as constraints on Venus sulfur chemistry. Also, we note that the SF_6 measurement is apparently inconsistent with observed abundances of HF, H_2O, and SO_2 and we discuss it later in connection with halogen-bearing gases.

To summarize this section, we interpret the Earth-based and spacecraft observations of sulfur gases in the lower atmosphere of Venus as showing that SO_2 is the dominant sulfur-bearing gas and that reduced sulfur gases such as COS, H_2S, and elemental sulfur vapor are minor species that constitute $\leq$2% of total gaseous sulfur. However, we also note that if all Earth-based and spacecraft observations are taken at face value, a different picture emerges in which the sulfur chemistry of the lower atmosphere is rapidly cycling between dominance by oxidized and reduced sulfur gases. In this picture, which we do not endorse, the Pioneer Venus and Venera 11/12 observations indicate dominance by SO_2 (1978), the Venera 13/14 observations indicate dominance by COS + H_2S (1982), the Vega 1/2 observations indicate dominance by SO_2 but at reduced levels and increased levels of elemental sulfur vapor (1986), the Earth-based microwave observations of Steffes et al. [1990] indicate SO_2 upper limits similar to the Vega 1/2 observations (1986), and the Earth-based infrared observations of Bézard et al. [1990] indicate only minor levels of COS (1989). Although this picture cannot be unambiguously ruled out, and although there may be some observational evidence for temporal and/or spatial variations in abundances of SO_2 and COS below the clouds, we feel that at present the Pioneer Venus, Venera 11/12, and the Earth-based observations [Bézard et al., 1990] of SO_2 and COS are the most reliable and we use these results as the basis for our discussion of sulfur chemistry.

Abundance of Sulfur on Venus and Earth. The observations reviewed above indicate that the dominant sulfur-bearing gas in the lower atmosphere of Venus is SO_2. The mean SO_2 mixing ratio of ~150 ppm calculated from the Pioneer Venus and Venera 11/12 gas chromatograph experiments [e.g., von Zahn et al., 1983] corresponds to a column density of $\sim 2.2 \times 10^{23}$ sulfur atoms cm^{-2}. In comparison, the major sulfur-bearing gases in the terrestrial nonurban troposphere and their mixing ratios [Prinn and Fegley, 1987] are COS (0.5 ppb), $(CH_3)_2S$ (~0.4 ppb), SO_2 (~0.3 ppb), and H_2S (~0.2 ppb). The corresponding column density for total sulfur is $\sim 2.0 \times 10^{16}$ atoms cm^{-2}, or about 10^7 times smaller than in the atmosphere of Venus. However, the total amount of sulfur in the Earth's crust [Ronov and Yaroshevsky 1976] and oceans [Turekian, 1969] corresponds to $\sim 1.3 \times 10^{26}$ sulfur atoms cm^{-2}, or ~600 times larger than total atmospheric sulfur on Venus. This comparison suggests that the high surface temperature on Venus has driven at least some of the sulfur, which would normally be in the crust, into the atmosphere. Furthermore, the high surface temperature may also allow interactions between sulfur-bearing gases in the atmosphere and reactive minerals on the surface of Venus.

Thermodynamic Stability of Liquid Sulfur. Mueller [1965] presented the first theoretical models of sulfur chemistry on Venus; however, he neglected COS in his calculations and no observations or upper limits for COS, H_2S, or SO_2 were available for comparison with his results. Despite these problems, his treatment is useful for understanding the complex features of gas-solid reactions involving sulfur. Following Mueller [1965], we begin by considering sulfur chemistry in the absence of other rock-forming elements.

The sulfur melting point is 388 K; thus any elemental sulfur on the surface would be liquid and would either evaporate or be oxidized by reaction with CO_2 in the overlying atmosphere. Evaporation would occur via reactions such as

$$S(\text{liq}) = \frac{1}{2}S_2(\text{vapor}) \qquad (100)$$

$$S(\text{liq}) = \frac{1}{3}S_3(\text{vapor}) \qquad (101)$$

$$S(liq) = \frac{1}{4}S_4(vapor) \quad (102)$$

$$\vdots \quad (103)$$

$$S(liq) = \frac{1}{8}S_8(vapor). \quad (104)$$

The saturated vapor pressure over liquid sulfur is given by the equations

$$P_{vap} = P_{S_2} + P_{S_3} + \cdots + P_{S_8} \quad (105)$$

$$\log_{10} P_{vap} = 4.56 - 3286/T \quad (106)$$

calculated from data in Rau et al. [1973] and Mills [1974]. At 740 K the sulfur vapor pressure is about 1.3 bars, which is substantially greater than the S_2 partial pressure deduced from the Venera 11/12 measurements. Thus, liquid sulfur should rapidly evaporate under Venusian surface conditions. Oxidation should also occur via reactions such as

$$S(liq) + 2CO_2 = SO_2 + 2CO \quad (107)$$

$$\log_{10} K_{107} = 8.80 - 13706(\pm 28)/T. \quad (108)$$

However, removal of liquid sulfur by oxidation is less effective and liquid sulfur could be in equilibrium with 150 ppm SO_2 at all altitudes above ~8.5 km ($T < 675$ K) on Venus. At these altitudes the saturated vapor pressure is also slightly lower (~0.5 bars at 675 K).

In this regard it is interesting to note that sulfur magmas have been suggested (as an alternative to carbonatite magmas) to explain some of the geologic features observed by the Magellan spacecraft [Kargel et al., 1991]. If these were erupted at high altitudes the sulfur magma would be stable against oxidation. The presence of other components in the magmas would also probably lower the thermodynamic activity and hence the saturated vapor pressure of the liquid sulfur. For now we conclude that although liquid sulfur may be present transiently on the Venusian surface, it is more likely that sulfur will be present instead in sulfide and/or sulfate minerals of rock-forming elements such as Fe, Ca, Mg, etc.

Equilibria Between Sulfide and Sulfate Minerals. The distribution of sulfur between sulfide (S^{2-}) and sulfate (SO_4^{2-}) minerals depends on the oxidation state of the Venusian surface as well as on the abundance of sulfur relative to other elements. As seen from Table 2, the Venera 13/14 and Vega 2 analyses indicate that sulfur is less abundant than other elements such as Fe, Mg, and Ca with which it can react to form sulfides and sulfates. Thus, under sufficiently reducing conditions sulfur will be present in sulfides while under sufficiently oxidizing conditions sulfur will be present in sulfates.

The most common sulfides on Earth are pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$ where x ~0–0.125), chalcopyrite ($CuFeS_2$), pentlandite [$(Fe, Ni)_9S_8$], and related sulfides of these elements [Deer et al., 1963]. Other sulfides such as galena (PbS) and sphalerite (ZnS) involve less abundant elements. No Ni was reported in the Venera 13/14 and Vega 2 analyses, but if, as is likely on cosmochemical grounds, the Venusian Fe/Ni ratio is similar to that on Earth, Ni will be a few % of Fe. Thus, by analogy with the Earth, pyrite, pyrrhotite, chalcopyrite, pentlandite, and related sulfides would also be expected to be the most important sulfides on Venus. Likewise, the most common sulfates on the Earth are gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), while other sulfates involve trace elements such as Ba and Sr, or are less common [Deer et al., 1963]. Thermodynamic data [DeKock, 1986] show that gypsum is thermodynamically unstable under Venusian surface conditions. If present it would rapidly dehydrate to form anhydrite. Thus, the most common sulfate on Venus is expected to be anhydrite. In particular, as we discuss later, sulfates of other abundant rock-forming elements such as $MgSO_4$ are unstable on the Venusian surface.

Neglecting the formation of COS, H_2S, SO_2 and other sulfur gases for the time being, the transition between pyrite and anhydrite can be calculated from equilibria such as

$$3FeS_2 + 6CaSiO_3 + 11O_2 = 6CaSO_4 + Fe_3O_4 + 6SiO_2 \quad (109)$$

originally proposed by Mueller [1965], or from the pyrite, calcite, anhydrite, wüstite (PCAW) buffer

$$2FeS_2 + 4CaCO_3 + 7O_2 = 4CaSO_4 + 2\text{“FeO”} + 4CO_2 \quad (110)$$

originally proposed by Lewis and Kreimendahl [1980], or from the analogous reactions

$$3FeS_2 + 6CaCO_3 + 11O_2 = 6CaSO_4 + Fe_3O_4 + 6CO_2 \quad (111)$$

$$3FeS_2 + 6CaMgSi_2O_6 + 11O_2 = 6CaSO_4 + Fe_3O_4 + 6MgSiO_3 + 6SiO_2 \quad (112)$$

$$3FeS_2 + 6CaAl_2Si_2O_8 + 11O_2 = 6CaSO_4 + Fe_3O_4 + 6Al_2SiO_5 + 6SiO_2. \quad (113)$$

Equation (111) is a modification of the PCAW buffer of Lewis and Kreimendahl [1980] and equations (112) and (113) exemplify sulfide/sulfate equilibria involving common igneous minerals such as pyroxenes and plagioclase. A related reaction forming $MgSO_4$ is

$$3FeS_2 + 6CaMgSi_2O_6 + 11O_2 = 6MgSO_4 + Fe_3O_4 + 6CaSiO_3 + 6SiO_2. \quad (114)$$

The equilibrium constants for these reactions are

$$\log_{10} K_{109} = -95.21 + 252320(\pm 1460)/T \quad (115)$$

$$\log_{10} K_{110} = -27.01 + 140256(\pm 966)/T \quad (116)$$

$$\log_{10}K_{111} = -47.04 + 225702(\pm 1412)/T \quad (117)$$

$$\log_{10}K_{112} = -93.42 + 243784(\pm 3212)/T \quad (118)$$

$$\log_{10}K_{113} = -102.56 + 250609(\pm 1574)/T \quad (119)$$

$$\log_{10}K_{114} = -93.16 + 225582(\pm 2954)/T. \quad (120)$$

Table 8 lists the equilibrium oxygen fugacities for reactions (109) - (114) at 740 K. In this table the f_{O_2} value for the PCAW buffer is calculated assuming a wüstite thermodynamic activity of 10^{-3} as proposed by Lewis and Kreimendahl [1980] from their chemical equilibrium models relating sulfur gas abundances and the oxidation state of Fe-bearing minerals.

These results show several important points, foremost of which is that the equilibrium oxygen fugacity for coexistence of pyrite + anhydrite depends on the mineral assemblage being considered. In the case of assemblages involving common igneous minerals such as diopside and anorthite, pyrite + anhydrite coexist at the f_{O_2} defined by the CO/CO_2 ratio in the Venusian atmosphere, while, as illustrated in Figure 7, other assemblages involving wollastonite (e.g., Mueller's sulfide/sulfate buffer) or calcite (e.g., Lewis and Kreimendahl's PCAW buffer) are in equilibrium under more reducing conditions. However, the PCAW buffer would be in equilibrium under Venus surface conditions if the wüstite activity were as high as ~0.07. Lewis and Kreimendahl [1980] interpreted the PCAW buffer as an oxygen fugacity buffer for the atmosphere of Venus; however, we feel that it is unlikely that any of the sulfide - sulfate reactions are f_{O_2} buffers. The results simply illustrate that under Venus surface conditions pyrite + anhydrite can coexist in some mineral assemblages but not in others.

Now that we know the conditions under which sulfur could be present as sulfide and sulfate on Venus, it is interesting to ask how these minerals will interact with the overlying atmosphere.

Thermodynamics of Pyrite Chemical Weathering on Venus. As first shown by Lewis [1968a, 1970a, 1971b, 1974] and later reinforced by the results of Barsukov et al. [1980, 1982], Khodakovsky [1982], Nozette and Lewis [1982], Volkov [1983], and Zolotov [1991c], at the mean Venusian surface temperature of ~740 K, iron sulfides should react spontaneously with the CO_2 and CO in the atmosphere of Venus to produce the reduced sulfur gas COS. Depending on the water vapor abundance, iron sulfides may also react spontaneously with H_2O to produce H_2S. The reactions studied by Lewis [1968a, 1970a] generally involved troilite (FeS); however, similar reactions exemplified by

$$3FeS_2 + 2CO + 4CO_2 = 6COS + Fe_3O_4 \quad (121)$$

$$\log_{10}K_{121} = 7.48 - 19334(\pm 441)/T \quad (122)$$

$$3FeS_2 + 6H_2O + 2CO = 6H_2S + 2CO_2 + Fe_3O_4 \quad (123)$$

$$\log_{10}K_{123} = 6.91 - 8726(\pm 360)/T \quad (124)$$

$$FeS_2 + FeSiO_3 + CO + CO_2 = Fe_2SiO_4 + 2COS \quad (125)$$

$$\log_{10}K_{125} = 2.66 - 5902(\pm 211)/T \quad (126)$$

$$FeS_2 + FeSiO_3 + 2H_2O + CO = Fe_2SiO_4 + 2H_2S + CO_2 \quad (127)$$

$$\log_{10}K_{127} = 2.43 - 2345(\pm 215)/T \quad (128)$$

are predicted to be responsible for the chemical weathering of pyrite on the surface of Venus.

Using the equilibrium constant expressions above, the COS and H_2S abundances resulting from pyrite weathering were calculated as a function of altitude on the surface of Venus. The results, which are displayed in Figures 14 and 15, show that pyrite weathering on the Venus surface should produce COS mixing ratios of ~5-30 ppm, substantially larger than the observed value of ~0.3 ppm [Bézard et al., 1990] and H_2S mixing ratios of ~40-100 ppb, substantially smaller than the preliminary value of 3±2 ppm obtained by the Pioneer Venus mass spectrometer [Hoffman et al., 1980a], and in agreement with the upper limit of 2 ppm from the Pioneer Venus gas chromatography experiment [Oyama et al., 1980]. The results given in the figures are for reactions (121) and (123); however, virtually identical COS and H_2S abundances are produced from reactions (125) and (127).

Lewis [1968a, 1970a] obtained very similar COS abundances of ~50 ppm but substantially larger H_2S abundances of ~5 ppm. As can be seen by inserting Lewis' assumed mixing ratios into the equilibrium constant expression for equation (123), the larger H_2S mixing ratio is simply due to the much larger H_2O mixing ratio of ~1000 ppm which he used. Lewis [1968a, 1970a] noted that his predicted COS and H_2S mixing ratios exceeded the upper limits of $\sim 10^{-6}$ and $\sim 3 \times 10^{-7}$, respectively, set by then available Earth-based spectroscopy [Cruikshank, 1967; Anderson et

TABLE 8. Sulfide/Sulfate Equilibria on the Surface of Venus

Mineral Assemblage	Equilibrium $\log_{10}f_{O_2}$ Value
py + wo + mag + anh + qtz	-22.3 ± 0.2
py + cal + anh + wü	-23.0 ± 0.2
py + cal + anh + mag	-22.4 ± 0.2
py + dp + anh + mag + en + qtz	-21.5 ± 0.4
py + an + anh + mag + ad + qtz	-21.5 ± 0.4
py + dp + $MgSO_4$ + mag + wo + qtz	-19.2 ± 0.4

Abbreviations: py = pyrite, wo = wollastonite, mag = magnetite, anh = anhydrite, qtz = quartz, cal = calcite, wü = wüstite, dp = diopside, en = enstatite, an = anorthite, ad = andalusite

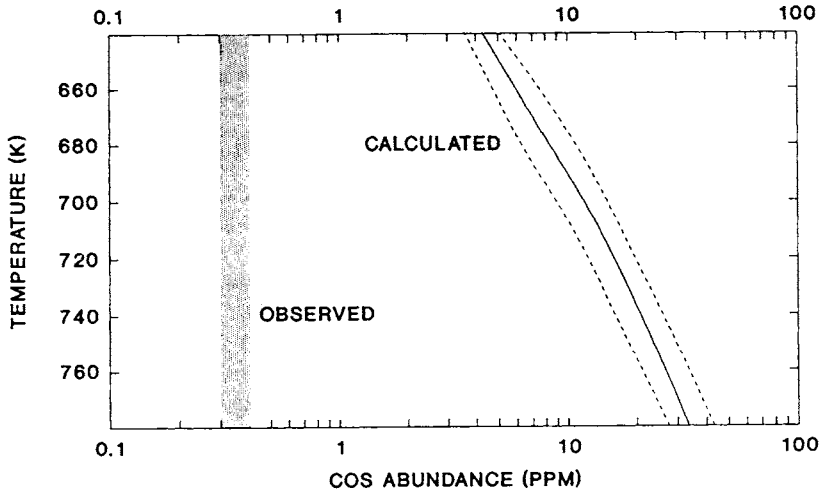

Fig. 14. A comparison of the COS abundance calculated from pyrite chemical weathering [reaction (121)] with the COS abundance of ~0.3–0.4 ppm observed by Bézard et al. [1990] in the 35 to 45 km altitude region on Venus. The dashed lines show the range of COS abundances allowed by the uncertainties in the thermodynamic data.

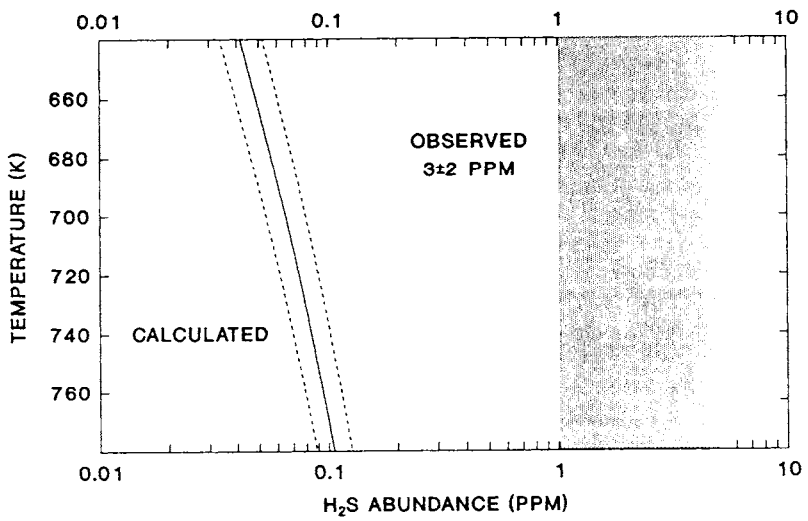

Fig. 15. A comparison of the H_2S abundance calculated from pyrite chemical weathering [reaction (123)] with the H_2S abundance of 3±2 ppm observed by the Pioneer Venus neutral mass spectrometer [Hoffman et al., 1980a] below 20 km. The dashed lines show the range of H_2S abundances allowed by the uncertainties in the thermodynamic data.

al., 1969; Kuiper, 1971] and explained the absence of COS and H_2S from the observable regions of Venus' atmosphere by the precipitation of HgS (cinnabar) at lower levels [Lewis, 1969, 1970b]. Mercury is highly volatile and if present at terrestrial abundance in Venus would be totally outgassed into the atmosphere [Lewis, 1969; Barsukov et al., 1981; Khodakovsky, 1982], and available for reaction with COS and H_2S. Neither Hg nor any other Hg-bearing compounds have been detected in the lower atmosphere of Venus but the upper limit on Hg compounds is <5 ppm [Hoffman et al., 1980a]. This upper limit is fairly high and does not rule out a role for Hg halide chemistry in the lower atmosphere of Venus. Because it has recently become possible to use Earth-based infrared spectroscopy to probe the lower atmosphere of Venus, we feel that Lewis' models for Hg halide chemistry merit re-examination. However, it is clear that HgS precipitation is not a viable mechanism for depleting COS. Other possible solutions must be sought to explain the apparent discrepancy between the large amounts of COS predicted to result from pyrite chemical weathering and the smaller amounts observed in the Venusian atmosphere. These are discussed next.

Kinetics of Pyrite Chemical Weathering on Venus. One possible explanation could be that pyrite weathering is a

relatively slow process so that chemical equilibrium is not attained and thus, the predicted COS mixing ratio is never reached. Indeed radar observations of Venus apparently provided support for this scenario. Pettengill et al. [1982, 1983, 1988], Ford and Pettengill [1983], and Jurgens et al. [1988a,b] discussed Pioneer Venus and Earth-based observations of radar "bright" regions with low emissivities in the Venus highlands and lowlands. More recently, Pettengill et al. [1991] and Tyler et al. [1991] discussed initial Magellan observations of these areas. The radar "bright" low emissivity regions were suggested to contain ~10–15 vol.% pyrite because of its dielectric constant and the published geochemical models suggesting the presence of iron sulfides on the Venusian surface [e.g., Lewis, 1968a, 1970a]. Furthermore, Jurgens et al. [1988b] concluded that the radar "bright" material is chemically stable on the surface of Venus. Assuming that 25% of the craters have "bright" ejecta and that the mean surface age is $\sim 10^9$ years, Jurgens et al. [1988b] speculated "that weathering to reduce brightness takes about 250 million years." If this material were pyrite, then the equilibrium concentration of COS would never be attained and the discrepancy between the thermodynamic predictions and spectroscopic upper limits would be resolved.

However, exactly the opposite situation is indicated by the recent experimental measurements of Fegley and Treiman [1990] and Treiman and Fegley [1991] on the rates of pyrite and pyrrhotite chemical weathering on the surface of Venus. Initially, thermodynamic calculations and magnetic properties led Fegley and Treiman [1990] to believe that pyrite decomposed directly to magnetite, and they derived a rate equation based on this assumption. However, further sample characterization by X-ray diffraction, optical microscopy, and scanning electron microscopy showed that pyrite oxidation is more complex and that the reaction product is composed of pyrrhotite Fe_7S_8 + magnetite Fe_3O_4 in varying proportions. The morphology of the reaction products indicates that pyrite oxidation to magnetite is a two stage process with the first stage being the conversion of pyrite to pyrrhotite and the second stage being the oxidation of pyrrhotite to magnetite. The revised rate equation for the pyrite $\rightarrow$ pyrrhotite conversion is

$$R = 10^{26.09(\pm 0.34)}\exp[-17,038(\pm 640)/T] \qquad (129)$$

which has units of sulfur atoms cm^{-2} sec^{-1} and an activation energy of 141.7 kJ $mole^{-1}$. At 740 K, the mean global surface temperature on Venus, the rate of the pyrite $\rightarrow$ pyrrhotite conversion is 1.2×10^{16} sulfur atoms cm^{-2} sec^{-1}, or about 260,000 times faster than the rate of anhydrite formation from SO_2 + calcite at the same temperature [Fegley and Prinn, 1989]. Thus, the conversion of pyrite to pyrrhotite is apparently an extremely rapid process under Venusian surface conditions.

Pyrrhotite is also thermodynamically unstable on the Venusian surface and is oxidized to magnetite. The preliminary study by Treiman and Fegley [1991] indicates that this is also a complex process with at least two steps: an initial step which may involve the growth of a critical number of magnetite nuclei and a second step during which oxidation proceeds. Their experiments showed that pyrrhotite oxidation to magnetite is also a rapid reaction although it is slower than the pyrite $\rightarrow$ pyrrhotite conversion. On a geologic timescale it therefore appears unlikely that either pyrite or pyrrhotite could survive on the Venusian surface. However, this conclusion must be tempered by the fact that only preliminary experiments done on short timescales are available. But, we note that the the ΔV for the pyrrhotite $\rightarrow$ magnetite conversion is negative (-7%) so the oxide coating will be porous. Thus, it is very unlikely that diffusion constraints would substantially decrease the pyrite and pyrrhotite weathering rates. One implication of these results is that the radar "bright" materials in the lowlands are probably neither pyrite nor pyrrhotite. On the other hand the radar "bright", low emissivity materials in the highlands may be pyrite (or pyrrhotite), but then some physical mechanisms are probably necessary to constantly re-expose fresh sulfides which will then be chemically weathered. Possible mechanisms which have been discussed are aeolian weathering, mass wasting, and volcanism [e.g., Arvidson et al., 1991; Fegley and Treiman 1990; Greeley and Arvidson, 1990; Prinn, 1985]. Once more laboratory data on the rates of pyrite and pyrrhotite oxidation are available, the plausibility of the different mechanisms proposed for the origin of the radar "bright", low emissivity materials can be evaluated quantitatively.

COS Gas Phase Chemistry. Another implication of the kinetic studies of pyrite and pyrrhotite oxidation is that the equilibrium abundance of COS can rapidly be produced by sulfide chemical weathering. However, in the absence of any destruction mechanism, the COS abundance in the lower atmosphere of Venus would then be expected to be approximately 20–100 times larger than that observed by Bézard et al. [1990]. How can this apparent discrepancy be explained?

One possible explanation is that no sulfides are ever exposed on the Venusian surface, and thus no sulfide chemical weathering takes place. However by analogy with the Earth, we argue that this possibility, although it cannot be unambiguously ruled out, is unlikely. Another possible explanation, which is illustrated in Figure 36 of von Zahn et al. [1983], is that COS is photochemically converted to SO_2 and/or elemental sulfur vapor by photochemical reactions in the lower atmosphere of Venus at ~30 km altitude. These proposed transformations are exemplified by the net reactions

$$COS + O_2 + h\nu \rightarrow SO_2 + CO \qquad (130)$$

$$COS + S + h\nu \rightarrow S_2 + CO \qquad (131)$$

which are disequilibrating reactions driven by sufficiently energetic solar ultraviolet photons below the clouds. However, as also postulated in von Zahn et al. [1983], these disequilibrating reactions are opposed by thermochemical reactions such as

$$SO_3 + 4CO \rightarrow COS + 3CO_2 \quad (132)$$

$$CO + S \rightarrow COS \quad (133)$$

which are suggested to take place in the lower atmosphere close to and at the Venusian surface. Depending on the availability of the required solar uv photons below the clouds and on the reaction rates involved in the photochemically driven disequilibrating reactions and in the thermochemically driven re-equilibrating reactions, these schemes may provide an explanation for the low abundance of COS in the Venusian atmosphere [von Zahn et al., 1983; Volkov, 1986]. However, at present this has not been demonstrated quantitatively, and the problem of why the observed COS abundance is significantly lower than the thermochemical equilibrium value remains unsolved.

Sulfur Dioxide and Sulfate Formation on Venus. Likewise, the observed SO_2 mixing ratio also presents a problem because chemical equilibrium models of gas-solid reactions predict that the SO_2 abundance in the lower atmosphere of Venus should be significantly lower than the observed value and should also be less than the abundances of COS and H_2S [Lewis, 1968a, 1970a; Lewis and Kreimendahl, 1980; Zolotov, 1985].

At chemical equilibrium, the SO_2 abundance in the lower Venusian atmosphere will be controlled by gas-solid reactions such as

$$SO_2 + CaCO_3 = CaSO_4 + CO \quad (134)$$

$$SO_2 + CaSiO_3 + CO_2 = CaSO_4 + SiO_2 + CO \quad (135)$$

$$SO_2 + CaMgSi_2O_6 + CO_2 = CaSO_4 + MgSiO_3 + SiO_2 + CO \quad (136)$$

$$SO_2 + CaAl_2Si_2O_8 + CO_2 = CaSO_4 + Al_2SiO_5 + SiO_2 + CO \quad (137)$$

which have the equilibrium constants

$$\log_{10}K_{134} = -1.82 + 2092(\pm 230)/T \quad (138)$$

$$\log_{10}K_{135} = -9.79 + 6548(\pm 229)/T \quad (139)$$

$$\log_{10}K_{136} = -9.55 + 5105(\pm 533)/T \quad (140)$$

$$\log_{10}K_{137} = -11.09 + 6411(\pm 259)/T. \quad (141)$$

As Figure 16 illustrates, the equilibrium SO_2 pressure for reaction (134) is significantly lower than the observed value from the Pioneer Venus [Oyama et al., 1980] and the Venera 11/12 spacecraft [Gel'man et al., 1979]. However, analogous reactions, such as

$$2SO_2 + Mg_2SiO_4 + 2CO_2 = 2MgSO_4 + SiO_2 + 2CO \quad (142)$$

$$SO_2 + CaMgSi_2O_6 + CO_2 = MgSO_4 + CaSiO_3 + SiO_2 + CO \quad (143)$$

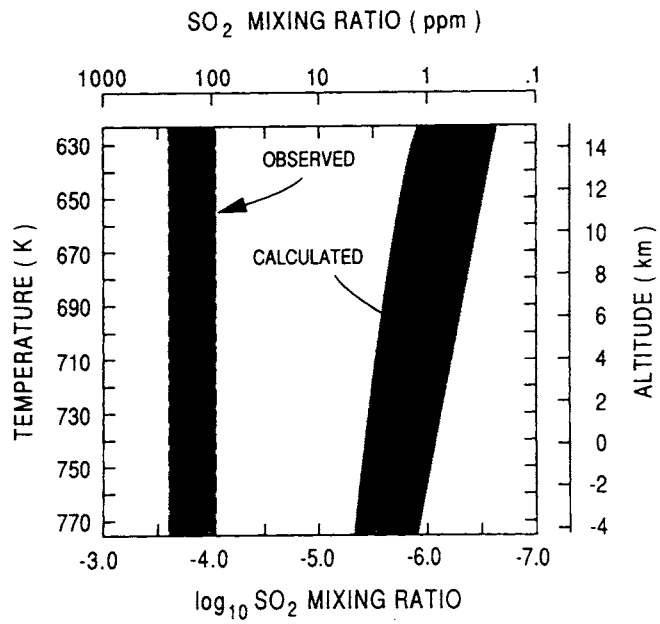

Fig. 16. A comparison of the SO_2 abundance calculated for reaction (134) with the observed SO_2 abundance in the atmosphere of Venus. The SO_2 mixing ratios observed at 22 km by the Pioneer Venus and the Venera 11/12 gas chromatograph experiments are 185±43 ppm and 130±35 ppm, respectively. In contrast, the SO_2 mixing ratios predicted from equilibrium with calcite $CaCO_3$ and anhydrite $CaSO_4$ on the Venus surface are less than 10 ppm. This dichotomy suggests that sulfur gases in the atmosphere of Venus are not in equilibrium with the surface of Venus.

$$SO_2 + MgSiO_3 + CO_2 = MgSO_4 + SiO_2 + CO \quad (144)$$

$$SO_2 + MgCO_3 = MgSO_4 + CO \quad (145)$$

which form $MgSO_4$, are predicted to be unimportant on Venus. This is easily seen by using the equilibrium constants

$$\log_{10}K_{142} = -19.81 + 6409(\pm 132)/T \quad (146)$$

$$\log_{10}K_{143} = -9.56 + 2053(\pm 485)/T \quad (147)$$

$$\log_{10}K_{144} = -9.80 + 3495(\pm 100)/T \quad (148)$$

$$\log_{10}K_{145} = -1.18 - 558(\pm 74)/T \quad (149)$$

to calculate the equilibrium SO_2 partial pressures. In all cases the calculated values are significantly higher than the observed SO_2 abundance. In contrast to our work, Zolotov [1991a] has concluded that $MgSO_4$ is stable at high altitudes on Venus. However, we are unable to reproduce his results and predict that $MgSO_4$ is unstable on the surface of Venus. Likewise, thermochemical data [DeKock, 1986] for sulfates of other abundant rock-forming elements (Fe, Al, Na, K, etc.) show that these sulfates are also unstable on the surface of Venus. Thus at chemical equilibrium the SO_2 pressure will be regulated by anhydrite formation. But then how can the observed SO_2 pressure, which is approximately 100 times larger than the equilibrium value produced by reaction (134) be explained?

Kinetics of Anhydrite Formation on Venus. The most plausible explanation is that the reaction of SO_2 with Ca-bearing minerals on the surface of Venus is a slow reaction that does not reach chemical equilibrium. This was suggested by von Zahn et al. [1983] after the Pioneer Venus and Venera 11/12 missions and was confirmed by the experimental results of Fegley and colleagues [Fegley, 1987, 1988, 1990; Fegley and Prinn, 1989].

These experiments measured the rate of reaction (134) as a function of temperature in the range 873–1123 K by heating high purity natural calcite crystals of known weight and surface area in CO_2–SO_2 gas mixtures at ~1 atmosphere pressure. The gas mixtures nominally contained 1% SO_2 by volume and thus had a SO_2 molecular number density about the same as that at the surface of Venus. The gas mixtures also typically contained <1 ppm O_2 and ≤10 ppm H_2O as impurities, but experiments done with gas mixtures containing up to 100 ppm O_2 showed that the rates were independent of the f_{O_2} within this range [Fegley and Prinn, 1989]. We also note that the water vapor content of the experimental gas mixtures is similar to the water vapor mixing ratio at the surface of Venus (~20 ppm derived by Moroz et al. [1979, 1980, 1983] and 10±4 ppm calculated by Lewis and Grinspoon [1990]). The experimental rate equation [Fegley and Prinn, 1989] is

$$R = 10^{19.64(\pm 0.28)}\exp[-15,248(\pm 2970)/T] \qquad (150)$$

which has units of SO_2 molecules $cm^{-2}sec^{-1}$. By taking into account the surface area distribution as a function of altitude on Venus, it is possible to derive the global mean rate of $CaSO_4$ formation from reaction (134) on Venus. This rate is $\sim 4.6 \times 10^{10}$ molecules $cm^{-2}sec^{-1}$, which is equivalent to $\sim 1\mu m$ of $CaSO_4$ being deposited per year. As Figure 17 illustrates, the thickness of the $CaSO_4$ layers produced in the laboratory experiments is $\sim 15\mu m$, equivalent to ~15 years of chemical weathering on the surface of Venus. Presumably aeolian weathering [Marshall et al., 1988] will remove the thin $CaSO_4$ layers on shorter timescales, so the laboratory rate data are applicable to Venus. Furthermore, we also note that the S/Ca ratios measured by the Venera 13, 14, and Vega 2 spacecraft are less than that expected if all Ca were combined in $CaSO_4$ [e.g., see Fig. III.106 in Zolotov and Khodakovsky, 1989]. Thus, at present the surface of Venus is still a net sink for SO_2 loss via anhydrite formation.

Unpublished laboratory experiments, illustrated in Fegley and Prinn [1989], also show that the reaction of SO_2 with diopside, which is predicted thermodynamically to occur via reaction (136), is slower than the analogous reaction of SO_2 with calcite. As shown in Figure 18, a natural diopside crystal reacted under conditions similar to those experienced by the calcite crystal shown in Figure 17 has undergone much less conversion to anhydrite.

What do these kinetic data imply for the attainment of chemical equilibrium between SO_2 and Ca-bearing minerals on the surface of Venus? The rate of the reaction between SO_2 + $CaCO_3$, which is faster than the reaction between SO_2 + diopside, is still so slow that ~1.9 Ma are required to reduce the observed SO_2 pressure in the Venusian atmo-

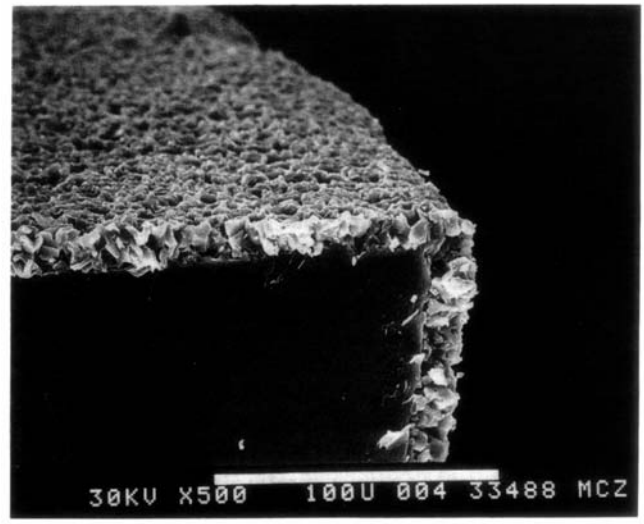

Fig. 17. A scanning electron micrograph of the fracture surface of a calcite crystal which has partially reacted with a gas mixture having the nominal composition 1% SO_2 + 99% CO_2. The outer surfaces of the crystal are coated with anhydrite $CaSO_4$. The reaction conditions were 850°C for 192 hours. The scale bar is 100μm long. Photo from Fegley and Prinn [1989].

Fig. 18. A scanning electron micrograph of an external surface of a natural diopside crystal which has partially reacted with a gas mixture having the nominal composition 1% SO_2 + 99% CO_2. The surface is partially covered with platelets of $CaSO_4$, presumed to be anhydrite, surrounded by silicate material, presumed to be unreacted diopside plus the thermodynamically stable reaction products silica + enstatite. The reaction conditions were 833°C for 48 hours. The scale bar is 50μm long. Photo from Fegley and Prinn [1989].

sphere to the equilibrium partial pressure which is ~1% of the observed value. Thus, neither reaction (134) nor reaction (136), which was recently proposed as a SO_2 buffer by Wood and Hashimoto [1991], appear capable of buffering variations in the SO_2 pressure in the Venusian atmosphere.

Implications for Venus Volcanism. Instead, as discussed by Fegley and Prinn [1989], SO_2 on Venus is apparently in steady state because the constant removal of SO_2 from the atmosphere by reaction with $CaCO_3$ and other Ca-bearing minerals on the surface of Venus would otherwise drain all SO_2 from the atmosphere on a geologically short timescale. This would lead to the disappearance of the H_2SO_4 droplet clouds, that are produced by the photochemical oxidation of atmospheric SO_2. Thus, a source is needed to replace the SO_2 lost by anhydrite formation.

The most plausible source is volcanism, which has occurred on Venus in the past [e.g., Basilevsky and Head, 1988] and which may have caused the increased SO_2 levels that were observed by the Pioneer Venus orbiter [Esposito, 1984; Esposito et al., 1988]. The volcanism rate that is needed to balance the rate of SO_2 depletion from the Venusian atmosphere is a function of the sulfur content of the erupted material (gas + magma) and the degassing efficiency of the erupted material. This efficiency is close to 100% as indicated by experiments on the rate of pyrite oxidation [Fegley and Treiman, 1990] and experiments on the rate of pyrrhotite oxidation [Treiman and Fegley, 1991]. Assuming that the rate of SO_2 depletion from the Venusian atmosphere is given by the rate of reaction (134) and using different geochemical models for the composition of the erupted material, Fegley and Prinn [1989] estimated that the rate of volcanism on Venus is currently in the range of 0.4–11 $km^3\ yr^{-1}$. In particular, assuming that the erupted material has the mean composition from the Venera 13, 14, and Vega 2 analyses of the Venus surface, the rate of volcanism is ~1 $km^3\ yr^{-1}$.

This geochemically estimated rate is in good agreement with several geophysical estimates [Grimm and Solomon, 1987; Spohn, 1991]. It is also similar to the generally quoted rate of ~1 $km^3\ yr^{-1}$ for subaerial volcanism on the Earth [Sapper, 1929 quoted in Ivanov and Freney, 1983] and to the rate of ~20 $km^3\ yr^{-1}$ for mid-ocean ridge formation on the Earth [Parsons, 1981]. Assuming that the present rate of volcanism on Venus is indeed similar to or slightly less than that on the Earth qualitatively suggests that the reaction of SO_2 with calcite controls the rate of SO_2 depletion from the Venusian atmosphere and also implies that calcite is an abundant mineral on the Venus surface. If calcite were totally absent, and the SO_2 depletion rate were controlled by the slower reaction with diopside (which is presumably more representative of SO_2 reactions with Ca-bearing silicates), the volcanism rate on Venus would be much lower than suggested by the independent geophysical estimates and would also be much lower than the terrestrial volcanism rates.

Likewise, the significantly higher geophysical estimates of ~200–300 $km^3\ yr^{-1}$ for Venus volcanism [Solomon and Head, 1982; Turcotte, 1989] can confidently be ruled out on the basis of the laboratory measurements of SO_2 reaction rates because no reaction is rapid enough to keep pace with the large SO_2 injection rates implied by these much larger volcanism rates. As a consequence, the SO_2 concentration in the Venusian atmosphere would be rapidly increasing with time, contrary to the limited observational evidence which is consistent with a time independent SO_2 mixing ratio below the clouds and a time dependent decrease in the SO_2 mixing ratio above the clouds.

Hydrogen Halides and Halogen-Bearing Minerals

Atmospheric Abundances of HCl and HF. HCl and HF were discovered in the atmosphere of Venus by Connes et al. [1967] using high resolution Fourier transform infrared spectroscopy. They found 0.6±0.12 ppm HCl and $5^{+5}_{-2.5}$ ppb HF at the ~100 mb level of the atmosphere (i.e., at the cloud tops). A re-analysis of the Connes et al. data by Young [1972] gave a slightly lower HCl mixing ratio of 0.4 ppm and a slightly higher HF mixing ratio of 10 ppb. However, the only other spectroscopic measurements of HCl and HF on Venus are the observations of DeBergh et al. [1989] at 3.6–3.9 μm which found ~0.4 ppm HCl at the ~35 mb level and the observations of Bézard et al. [1990] at 2.3μm of the night side of Venus which found ~0.5 ppm HCl and ~4.5 ppb HF in the 35 to 45 km region below the clouds.

Although HCl and HF are trace constituents in the atmosphere of Venus, their abundances are orders of magnitude greater than in the terrestrial atmosphere. Taking an HCl mixing ratio of 0.5 ppm the corresponding column density on Venus is $\sim 7 \times 10^{20}$ HCl molecules cm^{-2}. In contrast, the total Cl column density ($HCl + CH_3Cl + 2CF_2Cl_2 + 3CFCl_3 + 3CH_3CCl_3 + 4CCl_4$) in the nonurban terrestrial troposphere is $\sim 6 \times 10^{16}$ Cl atoms cm^{-2} (a mixing ratio of ~3.6 ppb total Cl [Prinn and Fegley, 1987]). Likewise, the HF mixing ratio of 5 ppb on Venus corresponds to $\sim 7 \times 10^{18}$ HF molecules cm^{-2} versus a total F column density ($2CF_2Cl_2 + CFCl_3 + 4CF_4 + HF$) in the nonurban terrestrial troposphere of $\sim 4 \times 10^{16}$ F atoms cm^{-2} (a mixing ratio of ~2.1 ppb total F [Prinn and Fegley 1987]).

Thus, HCl on Venus is ~10,000 times more abundant than total atmospheric Cl on Earth. Furthermore, about 70% of the total Cl in the terrestrial atmosphere is in man-made compounds such as the chlorofluorocarbons and CCl_4, while the remaining 30% (HCl) is produced from sea salt sprayed into the atmosphere. Likewise, HF on Venus is ~200 times more abundant than total atmospheric F on Earth, which is almost totally due to man-made compounds such as the chlorofluorocarbons and CF_4. However, the atmospheric abundances of HCl and HF on Venus are a direct reflection of the high surface temperature of Venus.

Origin of Atmospheric HCl and HF on Venus. Shortly after the discovery of HCl and HF on Venus, Lewis [1968a, 1970a] and Mueller [1968, 1969] proposed that the atmospheric abundances of HCl and HF are buffered by chemical equilibria between halogen-bearing minerals and other

silicates on the surface of Venus. The corrosive nature of both HCl and HF intuitively suggests that this explanation is reasonable. Furthermore, the essentially identical values observed for both HCl and HF by Connes et al. [1967] above the clouds and by Bézard et al. [1990] below the clouds suggests that the abundances of these two gases reflect equilibrium values. Alternatively, the HCl and HF abundances could be controlled by episodic phenomena, such as volcanic eruptions. However if this were the case then the average $d[HCl]/dt \sim d[HF]/dt \sim 0$ over the past 20 years, which implies fairly long reaction times for these highly corrosive gases. Finally, a calculation of the Cl/C and F/C atomic ratios on the Earth's surface [oceans + sediments + crust values from Smith [1981] and Ronov and Yaroshevsky [1976]] shows that both the Cl/C ratio of ~0.12 and the F/C ratio of ~0.09 are significantly greater than the Venusian atmospheric Cl/C and F/C atomic ratios. Cosmochemical models predict similar Cl and F inventories for both Venus and Earth [Fegley and Lewis, 1980]. Thus, this comparison suggests that the HCl and HF abundances in the atmosphere of Venus do not represent the total inventories of Cl and F for the planet and that significant amounts of Cl and F are still present on the surface of Venus.

HCl Reactions with Cl-Bearing Minerals. Gas-solid reactions that might buffer the HCl pressure in the Venusian atmosphere were first considered in detail by Lewis [1970a]. His reactions along with our linear fits to the updated equilibrium constants in the 600 to 800 K range are listed in Table 9. These equilibrium constants were calculated using thermodynamic data from Robie et al. [1979], Hemingway et al. [1982], and Sharp et al. [1989], who give thermodynamic data for sodalite. Lewis [1970a] used the sodalite data of Wellman [1969] in his calculations; however, the Sharp et al. [1989] data are more accurate and are preferred. The equilibrium HCl mixing ratios at 740 K and 20 ppm H_2O are also listed in Table 9. Inspection of the equilibrium constant expressions for the reactions in Table 9 shows that

$$X_{HCl} \propto X_{H_2O}^{\frac{1}{2}} \tag{151}$$

for reactions (9.1)–(9.5) and that

$$X_{HCl} \propto X_{H_2O}^{\frac{3}{2}} \tag{152}$$

for reaction (9.6). Thus, if 100 ppm H_2O were used instead, the calculated HCl mixing ratios would be only $\sqrt{5}$ times larger for reactions (9.1)–(9.5) and ~11 times larger for reaction (9.6). However, it is unlikely that the water vapor mixing ratio at the surface of Venus is this large.

Of the buffers originally proposed by Lewis [1970a], only reaction (9.2) represents chemical equilibrium. However, this reaction is not an appropriate HCl buffer for the Venusian atmosphere because the equilibrium HCl mixing ratio is ~40 times larger than the observed value. The discrepancy between the equilibrium predictions and the observations is too large to be attributed to the uncertainties in the thermodynamic data and in the HCl observations.

Orville [1974] noted that reactions (9.1) and (9.3), which were the buffers favored by Lewis [1970a], cannot be stable equilibria anywhere on the surface of Venus. Reaction (9.1) involves nepheline + quartz which are unstable relative to albite. Reaction (9.3) involves jadeite, which is unstable below ~10 kilobars pressure. We also note that reactions (9.4)–(9.6) are not stable equilibria. They all involve the assemblage sodalite + quartz which is metastable with respect

TABLE 9. Possible HCl Buffers on Venus (Lewis, 1970a)

9.1	$2HCl + CaSiO_3 + 2NaAlSiO_4 = 2NaCl + CaAl_2Si_2O_8 + SiO_2 + H_2O$
	wollastonite + nepheline + halite + anorthite + quartz
	$\log_{10}K_{9.1} = -6.45 + 10231(\pm 271)/T$
	$X_{HCl} \sim 9 \times 10^{-8}$
9.2	$2HCl + 2NaAlSi_3O_8 = 2NaCl + Al_2SiO_5 + 5SiO_2 + H_2O$
	analbite + halite + andalusite + quartz
	$\log_{10}K_{9.2} = -9.20 + 8723(\pm 490)/T$
	$X_{HCl} \sim 2 \times 10^{-5}$
9.3	$2HCl + 2NaAlSi_2O_6 = 2NaCl + Al_2SiO_5 + 3SiO_2 + H_2O$
	jadeite + halite + andalusite + quartz
	$\log_{10}K_{9.3} = -3.97 + 7138(\pm 488)/T$
	$X_{HCl} \sim 7 \times 10^{-7}$
9.4	$2HCl + 2NaAlSi_3O_8 + 6NaAlSiO_4 = Al_2SiO_5 + 2Na_4[AlSiO_4]_3Cl + 5SiO_2 + H_2O$
	analbite + nepheline + andalusite + sodalite + quartz
	$\log_{10}K_{9.4} = -15.75 + 14347(\pm 2137)/T$
	$X_{HCl} \sim 9 \times 10^{-14}$
9.5	$2HCl + 8NaAlSiO_4 = 2Na_4[AlSiO_4]_3Cl + Al_2SiO_5 + SiO_2 + H_2O$
	nepheline + sodalite + andalusite + quartz
	$\log_{10}K_{9.5} = -14.31 + 15718(\pm 2191)/T$
	$X_{HCl} \sim 2 \times 10^{-7}$
9.6	$6HCl + 2Na_4[AlSiO_4]_3Cl + 3CaSiO_3 = 8NaCl + 3CaAl_2Si_2O_8 + 3SiO_2 + 3H_2O$
	sodalite + wollastonite + halite + anorthite + quartz
	$\log_{10}K_{9.6} = -12.80 + 25070(\pm 1951)/T$
	$X_{HCl} \sim 2 \times 10^{-17}$

to albite + halite or with respect to marialite-bearing assemblages. Furthermore, reactions (9.4) and (9.5) also include nepheline + andalusite, which are metastable with respect to albite + corundum.

We emphasize that these objections, which are based on well known phase equilibria determined by experimental petrology, rule out the HCl buffers proposed by Lewis [1970a]. The agreement between the calculated and observed HCl mixing ratios for reactions (9.1) and (9.3), which has been cited by several authors [e.g., Prinn, 1985; von Zahn et al., 1983] as evidence that these reactions are buffering HCl in the Venusian atmosphere, is merely a coincidence.

Lewis [1970a] also proposed that nepheline is absent from the surface of Venus because otherwise HCl would react to form sodalite and thus be removed from the atmosphere. In this regard we note that nepheline is the most characteristic mineral of terrestrial alkaline rocks and occurs as a primary phase in many volcanic rocks with different mineralogical and chemical compositions [Deer et al., 1963]. We also point out that the Venera 8 and 13 sites have been interpreted as high-potassium alkaline basalts and that the calculated normative composition at the Venera 13 site includes 8% nepheline [Volkov et al., 1986]. By analogy with the Earth, we feel that it is unlikely that nepheline is absent from the surface of Venus.

Lewis' conclusion was based on very low HCl pressures calculated for reactions involving sodalite. However, in some cases the low HCl pressures are simply a reflection of the incorrect sodalite data from Wellman [1969]. Sharp et al. [1989] show that Wellman's [1969] data are based on a metastable equilibrium and find that sodalite is in fact less stable than Wellman's data indicate. The difference is substantial; for reaction (9.5) Wellman's sodalite data yield $X_{HCl} \sim 3 \times 10^{-13}$ versus $\sim 2 \times 10^{-7}$ as shown in Table 9. As noted above, reactions (9.4)–(9.6) cannot be stable equilibria. Thus, we interpret the very low HCl pressures calculated for some sodalite reactions as showing that the non-equilibrium mineral assemblages involved are not found on the surface of Venus.

Taking into account stable phase equilibria and using terrestrial petrology as a guide, we propose five other potential buffering reactions for HCl on Venus. These reactions are

$$12HCl + 6CaSiO_3 + 5Na_4[AlSiO_4]_3Cl = 17NaCl + 6CaAl_2Si_2O_8 + 3NaAlSi_3O_8 + 6H_2O \quad (153)$$

$$2HCl + 9NaAlSiO_4 = Al_2O_3 + NaAlSi_3O_8 + 2Na_4[AlSiO_4]_3Cl + H_2O \quad (154)$$

$$2HCl + 8NaAlSi_3O_8 = 2Na_4[AlSi_3O_8]_3Cl + Al_2SiO_5 + 5SiO_2 + H_2O \quad (155)$$

$$HF + Ca_5(PO_4)_3Cl = Ca_5(PO_4)_3F + HCl \quad (156)$$

$$2H_2O + KMg_3AlSi_3O_{10}Cl_2 = KMg_3AlSi_3O_{10}(OH)_2 + 2HCl. \quad (157)$$

The equilibrium constants for reactions (153)–(156) are given by the equations

$$\log_{10}K_{153} = -20.17 + 49384(\pm4884)/T \quad (158)$$

$$\log_{10}K_{154} = -13.56 + 16150(\pm2259)/T \quad (159)$$

$$\log_{10}K_{155} = -14.92 + 15143(\pm1566)/T \quad (160)$$

$$\log_{10}K_{156} = 0.06 + 2837(\pm845)/T \quad (161)$$

from 600 to 800 K. Another potential HCl buffer is analogous to reaction (156):

$$H_2O + Ca_5(PO_4)_3Cl = Ca_5(PO_4)_3OH + HCl \quad (162)$$

but the equilibrium constant

$$\log_{10}K_{162} = -0.16 - 2283(\pm496)/T \quad (163)$$

indicates that coexisting hydroxy-apatite and chlor-apatite present anywhere on the surface of Venus will yield HCl mixing ratios below the observed value (e.g., 0.002 to 0.05 ppm HCl for buffering at 740 K). This result along with the ability of reaction (156) to provide the required amounts of HCl from buffering by a solid solution of fluor- and chlor-apatite, suggests that hydroxy-apatite is absent from the surface of Venus.

The equilibrium constant for reaction (157) cannot be calculated because no thermodynamic data are available for chlor-phlogopite. This reaction is proposed as a potential HCl buffer on Venus because chlorine is a common, if minor, constituent of micas such as phlogopite on the Earth.

However, our preferred HCl buffers are reactions (153) and (154). As shown in Figures 19a and b, within the uncertainties of the thermodynamic data, both buffers provide the required amounts of HCl with reaction (153) giving a closer match to the observed HCl mixing ratio. If reaction (153) is responsible for buffering HCl in the Venusian atmosphere then halite is stable on the Venusian surface. The lower HCl equilibrium mixing ratios resulting from reaction (154) cannot be used to argue that the assemblage sodalite + albite + nepheline is absent from the surface of Venus because within the uncertainties of the thermodynamic data, the equilibrium HCl mixing ratio matches the observed value. In fact, the mineral assemblage sodalite + nepheline ± albite is common in terrestrial nepheline-syenites [Deer et al., 1963] and by analogy with the Earth would also be expected on Venus as well.

Reaction (155) involving the scapolite marialite is also a possible buffer for HCl on Venus. Using equation (160) calculated with the marialite data of Semenov et al. [1981], we find that at 740 K the equilibrium HCl mixing ratio is ~0.8 ppm. The uncertainty in the thermodynamic data allow a range of HCl mixing ratios from ~0.07 ppm to ~9 ppm at this temperature. Thus, reaction (155) may also be a viable HCl buffer. However, as noted previously, marialite may

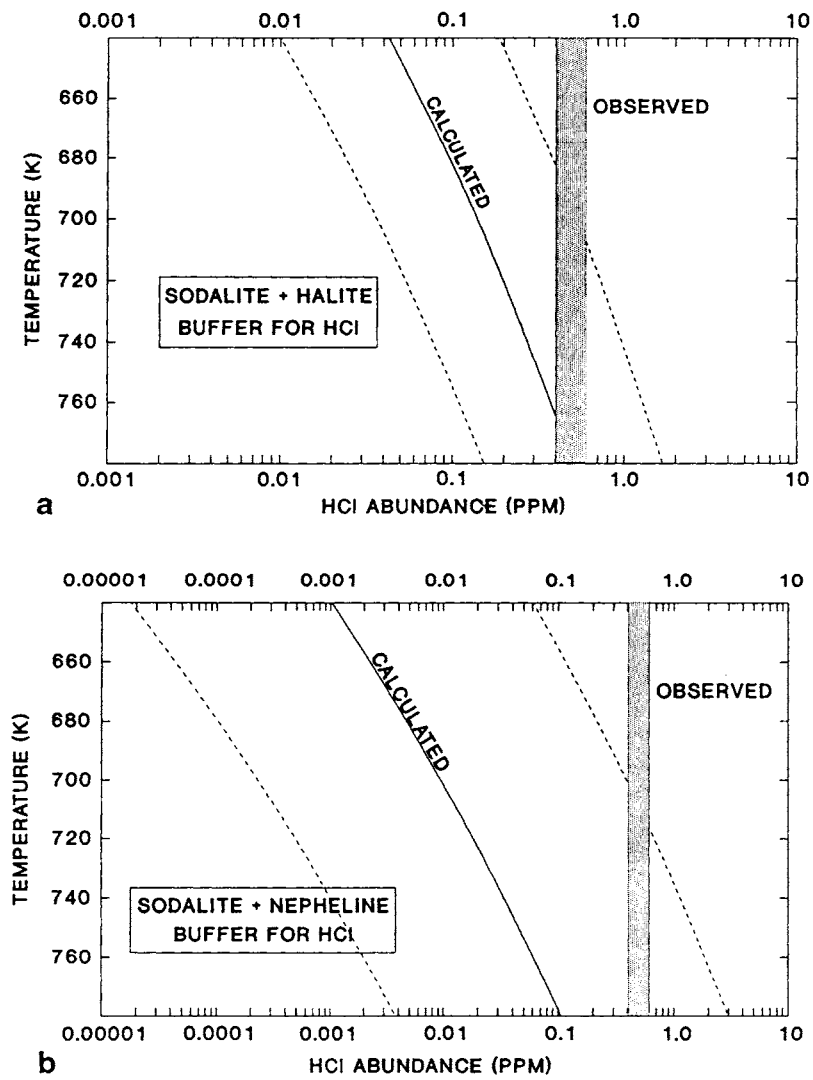

Fig. 19. (a) A comparison of the HCl abundance calculated for reaction (153) with the observed HCl abundance [Bézard et al., 1990; Connes et al., 1976; DeBergh et al., 1989] in the atmosphere of Venus. The dashed lines indicate the range of HCl values allowed by the uncertainties in the thermodynamic data. Refer to Fig. 2 to relate temperatures to altitudes on the surface of Venus. (b) As in (a) but for reaction (154).

not be as stable as the Semenov et al. data predict and thus reaction (155) may not be important for Venus. Further studies of the thermodynamic properties of well characterized marialite samples are required to resolve this issue.

HF Reactions with F-Bearing Minerals. Lewis [1970a] also considered a number of gas-solid reactions as possible HF buffers on Venus. These are listed in Table 10 along with our linear fits to the updated equilibrium constants in the 600 to 800 K range. The fits were calculated using thermodynamic data from Robie et al. [1979], Hemingway et al. [1982], and the JANAF Tables [Chase et al., 1985]. The equilibrium HF mixing ratios in Table 10 are calculated at 740 K for 20 ppm H_2O. However, like several of the HCl buffers in Table 9, the HF mixing ratio is proportional to $X_{H_2O}^{\frac{1}{2}}$.

Of the reactions listed in Table 10, only a few yield equilibrium HF mixing ratios low enough to match or come close to the observed value. Lewis [1970a] originally suggested reaction (10.2) in Table 10 as the HF buffering reaction on Venus. However, Orville [1974] noted that åkermanite, which is involved in reaction (10.2), is thermodynamically unstable at CO_2 pressures above ~0.1 bars and will react to form diopside + calcite. Thus, the åkermanite + fluorite + quartz + enstatite assemblage in reaction (10.2) cannot exist on the Venusian surface. The agreement between the calculated HF mixing ratio for this reaction and the observed

TABLE 10. Possible HF Buffers on Venus (Lewis, 1970a)

10.1	$2HF + CaSiO_3 = CaF_2 + SiO_2 + H_2O$
	wollastonite + fluorite + quartz
	$\log_{10}K_{10.1} = -6.53 + 10432(\pm109)/T$
	$X_{HF} \sim 8 \times 10^{-8}$
10.2	$4HF + Ca_2MgSi_2O_7 = 2CaF_2 + SiO_2 + MgSiO_3 + 2H_2O$
	åkermanite + fluorite + quartz + enstatite
	$\log_{10}K_{10.2} = -14.12 + 22415(\pm244)/T$
	$X_{HF} \sim 4 \times 10^{-8}$
10.3	$2HF + CaMgSiO_4 = CaF_2 + MgSiO_3 + H_2O$
	monticellite + fluorite + enstatite
	$\log_{10}K_{10.3} = -6.82 + 10988(\pm215)/T$
	$X_{HF} \sim 4 \times 10^{-8}$
10.4	$2HF + MgSiO_3 = MgF_2 + SiO_2 + H_2O$
	enstatite + sellaite + quartz
	$\log_{10}K_{10.4} = -6.40 + 9464(\pm135)/T$
	$X_{HF} \sim 3 \times 10^{-7}$
10.5	$2HF + Mg_2SiO_4 = MgF_2 + MgSiO_3 + H_2O$
	forsterite + sellaite + enstatite
	$\log_{10}K_{10.5} = -6.64 + 10314(\pm141)/T$
	$X_{HF} \sim 1 \times 10^{-7}$
10.6	$6HF + 2CaSiO_3 + 3NaAlSi_3O_8 = Na_3AlF_6 + 10SiO_2 + Ca_2Al_2SiO_7 + 3H_2O$
	wollastonite + analbite + cryolite + quartz + gehlenite
	$\log_{10}K_{10.6} = -22.84 + 22877(\pm894)/T$
	$X_{HF} \sim 2 \times 10^{-5}$
10.7	$2HF + KAlSi_2O_6 + 3MgSiO_3 = KMg_3AlSi_3O_{10}F_2 + 2SiO_2 + H_2O$
	leucite + enstatite + fluorphlogopite + quartz
	$\log_{10}K_{10.7} = -8.24 + 12250(\pm1841)/T$
	$X_{HF} \sim 3 \times 10^{-8}$
10.8	$2HF + KAlSi_3O_8 + 3MgSiO_3 = KMg_3AlSi_3O_{10}F_2 + 3SiO_2 + H_2O$
	sanidine + enstatite + fluorphlogopite + quartz
	$\log_{10}K_{10.8} = -6.61 + 11236(\pm1848)/T$
	$X_{HF} \sim 2 \times 10^{-8}$
10.9	$2HF + KAlSi_2O_6 + 2Mg_2SiO_4 = KMg_3AlSi_3O_{10}F_2 + MgSiO_3 + H_2O$
	leucite + forsterite + fluorphlogopite + enstatite
	$\log_{10}K_{10.9} = -8.71 + 13948(\pm1834)/T$
	$X_{HF} \sim 4 \times 10^{-9}$

value, which has been cited by several authors [e.g., Prinn, 1985; von Zahn et al., 1983] as evidence that reaction (10.2) is buffering HF on Venus, is again only a coincidence.

Likewise, several of the other HF buffers suggested by Lewis [1970a] involve mineral assemblages known to be unstable or metastable. Reaction (10.7) involves leucite + quartz which react to form K-feldspar and reaction (10.9) involves leucite + enstatite which react to form K-feldspar + olivine. Neither reaction can be considered as a HF buffer because the mineral assemblages involved will not exist at equilibrium on the surface of Venus.

Only reaction (10.8), which is the stability limit for fluorphlogopite in felsic (i.e., granitic) rocks, may be a viable HF buffer. However, at Venusian surface temperatures, K-feldspar is probably totally ordered [Ribbe, 1983; Yund and Tullis, 1983] and thus microcline should be used instead of sanidine (as done by Lewis) in this reaction. This changes the equilibrium constant to

$$\log_{10}K_{10.8} = -5.53 + 10765(\pm1848)/T \qquad (164)$$

and the equilibrium HF mixing ratio at 740 K to $\sim 1 \times 10^{-8}$. As shown in Figure 20a, within the uncertainties of the thermodynamic data, this reaction is a viable HF buffer on Venus.

Again taking into account stable phase equilibria and using terrestrial petrology as a guide, we propose four additional gas-solid reactions as HF buffers on Venus. These reactions and the corresponding equilibrium constants are

$$2HF + 3Mg_2SiO_4 + KAlSi_3O_8 = KMg_3AlSi_3O_{10}F_2 + 3MgSiO_3 + H_2O \qquad (165)$$

$$\log_{10}K_{165} = -6.23 + 13313(\pm1852)/T \qquad (166)$$

involving the mineral assemblage forsterite + microcline + fluor-phlogopite + enstatite which governs the stability of fluor-phlogopite in mafic (i.e., basaltic) rocks,

$$2HF + NaAlSiO_4 + 2CaMgSi_2O_6 + 3MgSiO_3 = NaCa_2Mg_5Si_7AlO_{22}F_2 + SiO_2 + H_2O \qquad (167)$$

$$\log_{10}K_{167} = -6.88 + 12098(\pm1120)/T \qquad (168)$$

involving the mineral assemblage nepheline + diopside + en-

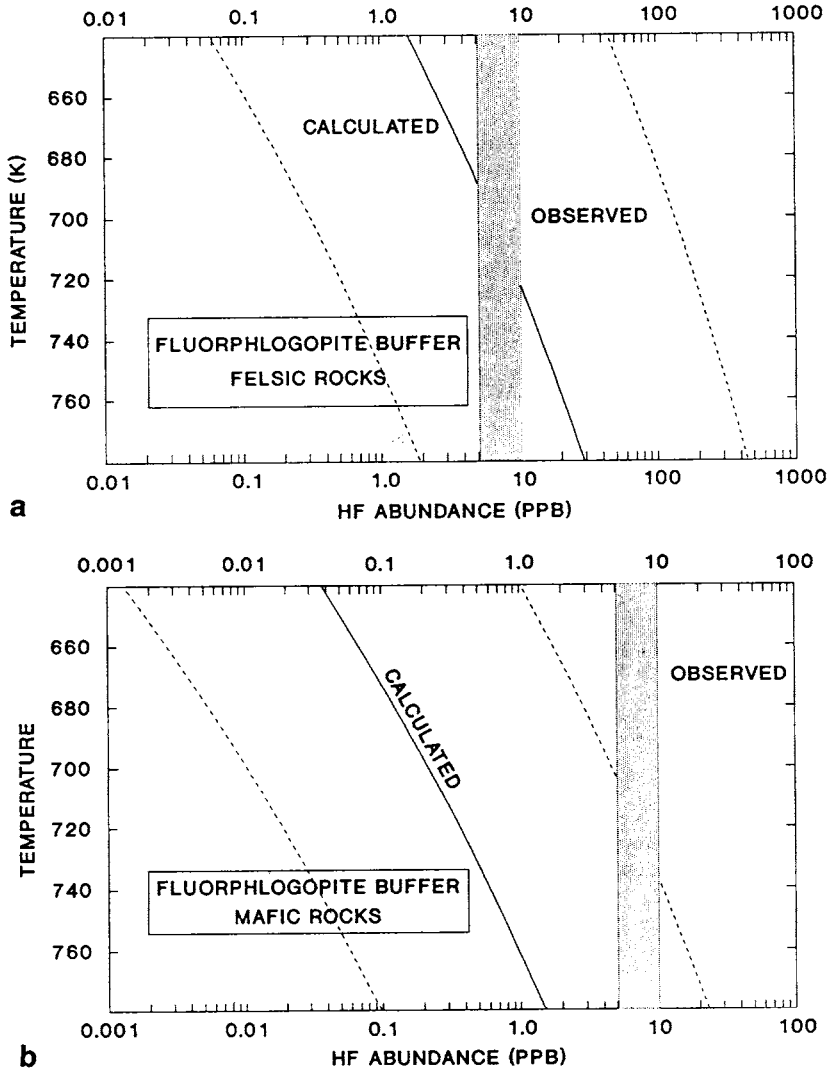

Fig. 20. (a) A comparison of the HF abundance calculated for reaction (10.8) in Table 10 with the observed HF abundance [Bézard et al., 1990; Connes et al., 1967] in the atmosphere of Venus. The dashed lines indicate the range of HF values allowed by the uncertainties in the thermodynamic data. This buffering reaction was originally proposed by Lewis [1970a]. Refer to Fig. 2 to relate temperatures to altitudes on the surface of Venus. (b) As in (a) but for reaction (165).

statite + fluor-edenite + quartz which governs the stability of fluor-edenite in felsic (i.e., granitic rocks,

$$2HF + NaAlSiO_4 + 2CaMgSi_2O_6 + Mg_2SiO_4 + MgSiO_3 = NaCa_2Mg_5Si_7AlO_{22}F_2 + H_2O \quad (169)$$

$$\log_{10} K_{169} = -6.93 + 12852(\pm 1104)/T \quad (170)$$

involving the mineral assemblage nepheline + diopside + enstatite + forsterite + fluor-edenite which governs the stability of fluor-edenite in mafic (i.e., basaltic) rocks, and

$$2HF + SiO_2 + 2CaMgSi_2O_6 + 3MgSiO_3 = Ca_2Mg_5Si_8O_{22}F_2 + H_2O \quad (171)$$

$$\log_{10} K_{171} = -7.39 + 11113(\pm 1223)/T \quad (172)$$

involving the mineral assemblage quartz + diopside + enstatite + fluor-tremolite which governs the stability of fluor-tremolite in felsic rocks. The analogous reaction for fluor-tremolite in mafic rocks was also considered. This reaction is

$$2HF + 2CaMgSi_2O_6 + 5MgSiO_3 = Ca_2Mg_5Si_8O_{22}F_2 + Mg_2SiO_4 + H_2O \quad (173)$$

$$\log_{10} K_{173} = -7.34 + 10359(\pm 1250)/T. \quad (174)$$

However, in this case the equilibrium HF pressures are significantly higher than the observed value except at altitudes

above ~10 km where the calculated and observed HF abundances overlap because of the uncertainties in the thermodynamic data. Thus, this reaction is probably not a viable buffer for HF.

The calculated equilibrium HF mixing ratios as a function of altitude for these reactions are displayed in Figures 20b–22. The equilibrium HF mixing ratios for reactions (167) and (169) are similar and are very close to the observed value; however, within the uncertainties in the thermodynamic data, all four reactions are viable HF buffers over a range of altitudes on the Venusian surface.

We also examined the stability of fluor-pargasite (a fluor-hornblende) using thermodynamic data from Westrich [1981], Westrich and Navrotsky [1981], and Robie et al. [1979]. The reaction studied and the equilibrium constant in the 600 to 800 K range are

$$4HF + CaAl_2Si_2O_8 + 2NaAlSiO_4 + 3CaMgSi_2O_6 + 2Mg_2SiO_4 + MgAl_2O_4 = 2NaCa_2Mg_4Al_3Si_6O_{22}F_2 + 2H_2O \quad (175)$$

$$\log_{10}K_{175} = -10.22 + 16102(\pm 1918)/T. \quad (176)$$

At 740 K, the HF mixing ratio needed to stabilize fluor-pargasite on the Venusian surface is ~600 ppb, or about 100 times greater than the observed value. At altitudes of

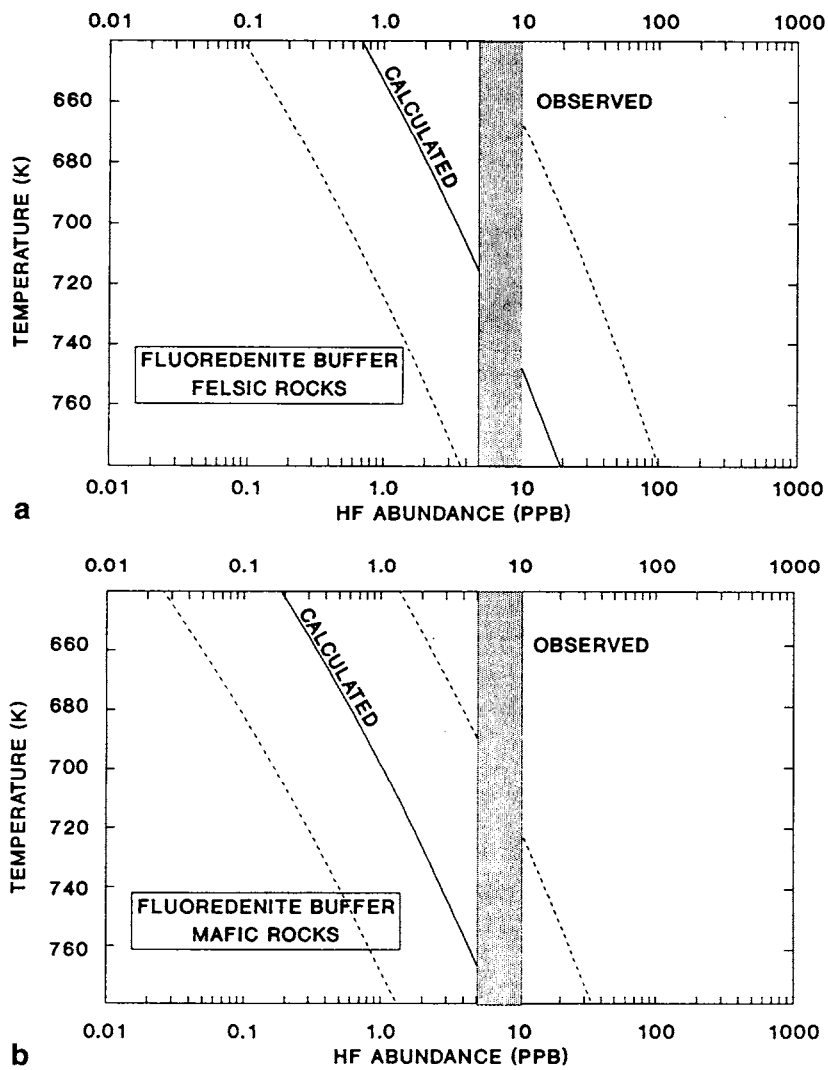

Fig. 21. (a) A comparison of the HF abundance calculated for reaction (167) with the observed HF abundance [Bézard et al., 1990; Connes et al., 1967] in the atmosphere of Venus. The dashed lines indicate the range of HF values allowed by the uncertainties in the thermodynamic data. Refer to Fig. 2 to relate temperatures to altitudes on the surface of Venus. (b) As in (a) but for reaction (169).

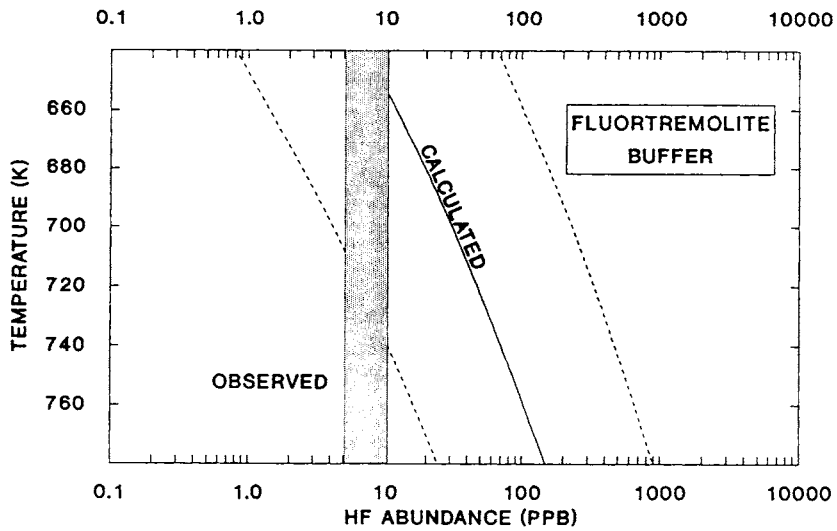

Fig. 22. A comparison of the HF abundance calculated for reaction (171) with the observed HF abundance [Bézard et al., 1990; Connes et al., 1967] in the atmosphere of Venus. The dashed lines indicate the range of HF values allowed by the uncertainties in the thermodynamic data. Refer to Fig. 2 to relate temperatures to altitudes on the surface of Venus.

~9 km and above, the uncertainties in the thermodynamic data permit fluor-pargasite to be stable; however, then the kinetics of reaction (175) become an important issue. Experimental studies of reaction (175) could resolve this question and would also be important for assessing fluor-pargasite stability on the Earth.

Another buffer that we examined involved fluor-topaz $Al_2SiO_4F_2$. This reaction is

$$Al_2SiO_4F_2 + H_2O = Al_2SiO_5 + 2HF \qquad (177)$$

$$\log_{10}K_{177} = 7.65 - 10115(\pm 283)/T. \qquad (178)$$

However, reaction (177) is not a viable HF buffer anywhere on the surface of Venus. For example, at 740 K the equilibrium HF mixing ratio is ~450 ppb, approximately 90 times higher than the observed value.

For the sake of completeness, we also studied the HF analog to reaction (156) above:

$$H_2O + Ca_5(PO_4)_3F = Ca_5(PO_4)_3OH + HF. \qquad (179)$$

$$\log_{10}K_{179} = -0.22 - 5120(\pm 498)/T. \qquad (180)$$

If discrete grains of hydroxy-apatite and fluor-apatite are present on the surface of Venus, then HF should be buffered at a mixing ratio of $\sim 1.4 \times 10^{-12}$. This value is appropriate for 740 K, but buffering at both higher and lower altitudes also yields equilibrium HF mixing ratios orders of magnitude lower than the observed value of ~5 ppb. This result reinforces our earlier conclusions that hydroxy-apatite is absent from the surface of Venus.

Apatites are common accessory minerals in almost all igneous rocks on the Earth and are the most abundant P-bearing minerals [Deer et al., 1963]. Furthermore, fluor-apatite is by far the most commonly found member of the apatite group. In addition, using the equilibrium constant for reaction (156) and assuming ideal solid solution, we calculate that a solid solution of fluor- and chlor-apatite is stable on the surface of Venus. Thus, we suggest that fluor-apatite solid solutions with chlor-apatite are probably present as an accessory mineral on the Venusian surface, but that hydroxy-apatite is probably absent. In fact, if we assume that fluor-apatite is present on Venus, and calculate the hydroxy-apatite thermodynamic activity for reaction (179) at 740 K, we find that it is $\sim 3 \times 10^{-4}$. This activity is far too low for hydroxy-apatite to be a significant component in solid solution with fluor-apatite, and again demonstrates the difficulty in finding any water-bearing minerals stable under Venusian surface conditions.

In summary, we emphasize that HCl and HF are reactive gases which are likely to be in chemical equilibrium with the surface mineralogy in at least some regions of the surface of Venus. The virtually identical HCl and HF mixing ratios observed 20 years apart in two different regions of the Venusian atmosphere also suggest that the observed abundances are equilibrium values. The alternative that HCl and HF are controlled by episodic phenomena such as volcanism appears less likely to us because the observed constancy in the HCl and HF mixing ratios then implies fairly sluggish reaction rates for these corrosive gases. Although quantitative data are lacking, common experience, such as the use of HF for glass etching, implies that HF reactions with silicates should be rapid under Venusian surface conditions.

We suggest that the best way to resolve the questions about which mechanisms (chemical equilibrium reactions or episodic phenomena) are controlling the abundances of HCl and HF on Venus is to study experimentally the thermody-

namics and kinetics of several potential buffering reactions. The most attractive candidates for experimental study of HCl buffers are reactions (153) and (154) which provide the required amounts of HCl and which involve common mineral assemblages in nepheline-syenite rocks on the Earth. The most attractive candidates for experimental study of HF buffers are reactions (165), (167), (169), (171), and reaction (10.8) in Table 10. The latter reaction was originally suggested by Lewis [1970a]. All the HF reactions also involve stable mineral assemblages observed in different rock types on the Earth and their study will thus yield information relevant to terrestrial petrology as well.

Cl-Bearing Cloud Condensates. Chlorine-bearing cloud particles were apparently detected by several experiments on the Venera 11/12, Venera 13/14, and Vega 1/2 spacecraft. However, these reports have met with considerable skepticism because of the geochemical problems involved in identifying any plausible Cl-bearing condensates that could be present at the required abundance in the cloud-forming region of the Venusian atmosphere. We review this situation by first presenting the observational evidence and then discussing the theoretical arguments involved.

Surkov et al. [1981] reported that the Venera 11/12 X-ray fluorescence (XRF) experiment detected Cl in the Venusian clouds and reported S/Cl mass ratios of ~0.1. An upper limit of 2% (by mass) was also established for the Cl/Hg mass ratio. Furthermore, Petryanov et al. [1981] reported that the XRF experiment also detected Fe in the cloud layers. Surkov et al. [1982] subsequently reported that the XRF experiment on the Venera 13/14 spacecraft measured S/Cl mass ratios of ~7 in the Venus clouds. Finally, an X-ray radiometric experiment [Andreichikov et al., 1987] and a mass spectrometer experiment [Surkov et al., 1987] on the Vega 1/2 spacecraft also reported the presence of Cl in the clouds. However, none of these experiments provided any information on the putative Cl-bearing compounds present in the cloud layers. What Cl-bearing compounds have been suggested to be present and how plausible are they on theoretical grounds?

One possible Cl-bearing cloud condensate which has been discussed in the literature is HCl [e.g., Lewis, 1968a,b, 1969, 1970c, 1971c]. However, the presence of HCl solution clouds is inconsistent with observational data on HCl and H_2O abundances, cloud particle refractive indices, and with the Venera 11–14 data [Esposito et al., 1983; Krasnopolsky, 1986]. Mercury chlorides were also suggested by Lewis [1969], but neither the Pioneer Venus mass spectrometer [Hoffman et al., 1980a] nor the Venera 11/12 XRF experiment [Surkov et al., 1981] has detected any Hg-bearing gases or condensates in the Venusian atmosphere. However, as noted before, the upper limits on Hg compounds are fairly high. Although Hg halides are probably unimportant as major cloud-forming condensates, they still may be present at sub-ppm levels in the lower atmosphere of Venus.

Iron chlorides and their hydrates (produced either from gas–solid reactions at the surface of Venus or from volcanic gases) have been discused by several groups as possible cloud-forming condensates [Kuiper, 1969, 1971; Knollenberg and Hunten, 1980; Krasnopolsky, 1985, 1989; Krasnopolsky and Parshev, 1979]. However, one problem with this suggestion is that the required abundance of Fe chlorides (a mixing ratio of ~10 ppm by volume) is much larger than the equilibrium abundance of $FeCl_2$ or of $FeCl_3$ supplied by gas–solid reactions with the surface of Venus. This point was probably first emphasized by Lewis [1970a] who considered the reactions

$$Fe_3O_4 + 6HCl + CO = 3FeCl_2 + 3H_2O + CO_2 \quad (181)$$

$$2Fe_3O_4 + 18HCl = 6FeCl_3 + 8H_2O + H_2 \quad (182)$$

which have the equilibrium constants

$$\log_{10}K_{181} = 8.23 - 11038(\pm 354)/T \quad (183)$$

$$\log_{10}K_{182} = -2.31 - 20544(\pm 1595)/T. \quad (184)$$

At 740 K reaction (181) yields an $FeCl_2$ mixing ratio of $\sim 10^{-11.7}$ at equilibrium, while reaction (182) yields an even lower $FeCl_3$ mixing ratio of $\sim 10^{-15.2}$ at equilibrium. The latter calculation assumes that the H_2 partial pressure is fixed by equilibrium with Fe-bearing silicates on the surface of Venus. However, if the significantly higher H_2 mixing ratio of 10 ppm estimated by Kumar et al. [1981] is used instead, the calculated $FeCl_3$ mixing ratio decreases to $\sim 10^{-15.8}$. Thus, gas–solid reactions at the surface of Venus are unable to produce the required mixing ratios of Fe chlorides needed to explain the reported Cl mass densities.

Likewise, Fe chloride production from volcanism also seems unlikely. This can be illustrated by again considering reaction (181). Chemical equilibrium at typical magmatic temperatures of 1200 to 1600 K will give only ~0.09–0.2 ppb of $FeCl_2$ instead of the required 10 ppm (10,000 ppb). However, the $FeCl_2$ mixing ratio can be increased to 10 ppm but only by also increasing the HCl mixing ratio to ~78–167 ppm. We conclude that volcanic production of $FeCl_2$ cannot be unambiguously ruled out but that this alternative requires specific volcanic gas compositions unlike the observed composition of the Venusian atmosphere.

Aluminum chlorides ($AlCl_3$ and Al_2Cl_6) have also been suggested by Krasnopolsky and colleagues [Krasnopolsky, 1985, 1989; Krasnopolsky and Parshev, 1979] to explain the Venera and Vega observations. However, this proposal must also be rejected because the volatility of Al chlorides is too low to provide the necessary Cl mass densities [Lewis and Fegley, 1982]. They noted that the reaction

$$CaAl_2Si_2O_8 + CO_2 + 6HCl = CaCO_3 + 2SiO_2 + 3H_2O + 2AlCl_3 \quad (185)$$

which has the equilibrium constant

$$\log_{10}K_{185} = -8.80 - 13056(\pm 165)/T \quad (186)$$

will control the abundance of $AlCl_3$ gas evolved from felsic

rocks on the surface of Venus. At 740 K, the equilibrium mixing ratio of $AlCl_3$ is only $10^{-23.1}$, which is about 18 orders of magnitude too low to provide the observed cloud condensate mass densities. Similar calculations by J.S. Lewis (personal communication, 1991) also show that a volcanic origin for $AlCl_3$ is implausible.

Lewis and Fegley [1982] also critically assessed the plausibility of As and Sb chlorides as cloud-forming condensates. These compounds had previously been suggested by Soviet scientists [e.g., Barsukov et al., 1981] who calculated that chlorides were the dominant As- and Sb-bearing gases in the atmosphere of Venus and that the mixing ratios of these species were large enough to explain the observed cloud condensate densities. However, using more recent thermodynamic data for a large number of As and Sb gases and condensed phases, Lewis and Fegley [1982] showed that in fact the dominant As- and Sb-bearing gases are sulfides and not chlorides and that in any case the volatility of As and Sb compounds is sufficiently low that they are unable to provide the necessary mass densities.

Thus, exhaustive thermodynamic modelling has so far failed to provide any geochemically plausible mechanism to explain the reported Cl-bearing cloud condensates. In the absence of any other quantitative proposal for explaining these observations, we conclude that the spacecraft results must be regarded as provisional and need to be confirmed independently by other investigators.

Sulfur Hexafluoride. Finally, we will consider the detection of 0.2 ppm SF_6 which was claimed by the Venera 13/14 gas chromatography experiment [Mukhin et al., 1983]. This result is suspect because the reported SF_6 concentration is orders of magnitude greater than is predicted from thermochemical equilibrium between HF and SO_2. This is easily illustrated by considering the reaction

$$6HF + CO_2 + SO_2 = SF_6 + 3H_2O + CO \qquad (187)$$

which has the equilibrium constant

$$\log_{10} K_{187} = -23.76 - 13959(\pm 337)/T. \qquad (188)$$

Thermochemical equilibrium at the Venusian surface temperature of 740 K yields a SF_6 mixing ratio of $\sim 3 \times 10^{-72}$, while equilibrium at an altitude of ~47 km (T ~380 K), in the middle of the altitude range where SF_6 was reported, yields an even lower mixing ratio of $\sim 2 \times 10^{-95}$. These equilibrium values are approximately 65 to 88 orders of magnitude smaller than the reported mixing ratio of 0.2 ppm.

Zolotov and Khodakovsky [1985] attempted to explain the reported SF_6 abundance by recourse to equilibrium chemistry in putative volcanic gases. Their calculations assumed that the total F atomic abundance in the volcanic gases exceeded the total H atomic abundance thus forcing the excess fluorine to react with sulfur. However, their theoretical results are suspect for the following reasons. First, their assumed fluorine abundance (F/C ~0.001) is $\sim 2 \times 10^5$ times higher than the observed HF/CO_2 mixing ratio in the Venusian atmosphere. Second, their results predict much larger amounts of CF_4 which has not been observed on Venus. This point is illustrated using their published results and considering the reaction

$$SF_6 + F_2 + CO_2 = CF_4 + SF_4 + O_2. \qquad (189)$$

At 1400 K reaction (189) has an equilibrium constant of $10^{6.05}$. Combining this with their calculated mixing ratios for F_2, CO_2, SF_4, and O_2 displayed in Figure 1 of Zolotov and Khodakovsky [1985], we find that the ratio of the abundances of CF_4 and SF_6 is $CF_4/SF_6 \sim 10^{8.4}$, corresponding to ~50 ppm CF_4 if the SF_6 abundance is 0.2 ppm as reported by Mukhin et al. [1983]. The arguments outlined in this section therefore cause us to reject the reported detection of SF_6.

Nitrogen and Nitrogen Compounds

Molecular Nitrogen. Molecular nitrogen is the second most abundant constituent of the Venusian atmosphere. Its presence was first deduced from gas absorption experiments on the Venera 4,5,6 spacecraft. The resulting upper limits on N_2 ranged from <2% to <9.5% [Vinogradov et al., 1971]. As noted by von Zahn et al. [1983], the subsequent more sophisticated N_2 analyses by the Pioneer Venus and Venera 11/12 mass spectroscopy and gas chromatography experiments also gave N_2 mixing ratios (see Table 1). However, the values determined by the Pioneer Venus gas chromatograph, the Venera 11/12 mass spectrometer, and the Venera 11/12 gas chromatograph do not agree within the stated uncertainties. Furthermore, the Pioneer Venus gas chromatography results show an apparent decrease in N_2 with decreasing altitude [Oyama et al., 1980]. These data were critically assessed by von Zahn et al. [1983] who gave a recommended value of 3.5±0.8% below 45 km altitude, which is adopted here.

Ammonia. Surkov et al. [1974] reported that the Venera 8 spacecraft detected ammonia in the atmosphere of Venus at mixing ratios from 100 to 1,000 ppm. This detection was based on the color change observed when Venusian atmospheric gas reacted with bromophenol blue (tetrabromophenol-sulphaphthalein), a pH indicator which turns blue on exposure at basic pH values. The spacecraft measurements were done at 44 km (2 bars) and 32 km (8 bars).

This reported detection of NH_3 is in conflict with significantly lower upper limits determined by Earth-based and Earth-orbital spectroscopic observations in the ultraviolet, infrared, and microwave regions. Kuiper [1971] gave an upper limit of 30 ppb from infrared spectroscopy, Owen and Sagan [1972] gave an upper limit of 0.1 ppm from ultraviolet spectroscopy, and Smirnova and Kuz'min [1974] gave an upper limit of 16 ppm from microwave spectroscopy. The first two values refer to the cloud top region while the microwave value is for the lower atmosphere below the clouds.

The reported NH_3 abundance is also in conflict with thermodynamic predictions. From a consideration of the equilibrium

$$N_2 + 3H_2 = 2NH_3 \qquad (190)$$

and observational upper limits on CO and H_2O, which allowed him to thermodynamically calculate an upper limit on the H_2 partial pressure, Mueller [1964b] concluded "that no significant quantity of ammonia can occur if P_{N_2} has any reasonable value for a terrestrial planet of this size." However Mueller did not actually present any calculated upper limits for NH_3 on Venus.

After the Venera 8 results were reported, a more quantitative argument against NH_3 was made by Goettel and Lewis [1974] who noted that the reported detection of NH_3 disagreed with the abundance predicted from the thermochemical reaction

$$N_2 + 3CO + 3H_2O = 2NH_3 + 3CO_2 \qquad (191)$$

which has the equilibrium constant

$$\log_{10} K_{191} = -17.39 + 11396(\pm 54)/T \qquad (192)$$

from 298 to 800 K. For example, at 740 K, where gas phase equilibrium is most likely to be attained, reaction (191) yields a NH_3 mixing ratio of $\sim 10^{-28}$, orders of magnitude below the reported values. As Figure 1 of Goettel and Lewis [1974] illustrates, the equilibrium NH_3 mixing ratio increases rapidly with decreasing temperature. However, reaction (191) is probably kinetically inhibited at low temperatures and equilibrium cannot be attained. But in any case, Goettel and Lewis [1974] also emphasized that the maximum NH_3 mixing ratio is limited by the amounts of CO and H_2O in the Venusian atmosphere. The CO mixing ratios of 20–30 ppm observed below the clouds [Oyama et al., 1980; Gel'man et al., 1979] and the stoichiometry of reaction (191) limit the maximum NH_3 mixing ratio to 13–20 ppm. The reported mixing ratios of 100 to 1000 ppm are thus physically impossible. Florensky et al. [1978] also present calculations (their Figure 1) which also illustrate that the reported NH_3 mixing ratios violate mass balance constraints.

Finally, it should be noted that Young [1977] has proposed a more plausible explanation for the Venera 8 results. He pointed out that bromophenol blue turns violet red in concentrated H_2SO_4 and speculated that the Venera 8 experiment had actually reacted with the concentrated sulfuric acid which makes up the cloud droplets. Young's observation in concert with the spectroscopic upper limits and the chemical arguments lead us to reject the Venera 8 result as an experimental artifact.

N-Bearing Minerals. There is no observational evidence for any nitrogen-bearing minerals on the surface of Venus. Furthermore, theoretical arguments suggest that pure nitrogen-bearing phases are unlikely to be present on the Venusian surface. For example, nitride minerals, if present, would spontaneously be oxidized via reactions such as

$$2AlN + 3CO_2 = Al_2O_3 + N_2 + 3CO \qquad (193)$$

$$2TiN + 4CO_2 = 2TiO_2 + N_2 + 4CO \qquad (194)$$

with the overlying atmosphere. Likewise, pure nitride minerals are also thermodynamically unstable on the Earth. However, the small amounts (~10 – 100 ppm) of nitrogen which are commonly found in igneous and metamorphic minerals on the Earth [reviewed by Wlotzka, 1972] may be present as dissolved nitrides and/or oxynitrides. By analogy with the Earth, a similar situation is also expected on Venus. The dissolved nitrogen is probably unimportant from the perspective of atmosphere–surface chemistry but may nevertheless constitute a significant fraction of the nitrogen inventory on Venus.

Other possible N-bearing minerals are ammonium silicates. One well known example is the ammonium silicate buddingtonite $NH_4AlSi_3O_8 \cdot \frac{1}{2}H_2O$, which has been synthesized under hydrothermal conditions (550–650°C, 2 kbars) by Barker [1964] and which occurs naturally as pseudomorphs after plagioclase in andesitic rocks which have been hydrothermally altered by NH_3-rich hot-spring waters [Erd et al., 1964]. No calorimetric data are available to quantitatiavely assess the stability of buddingtonite under Venusian surface conditions. However, the conditions required for buddingtonite synthesis in the laboratory, the preliminary phase equilibrium studies (under hydrothermal conditions) of Hallam and Eugster [1976], and its natural occurrences suggest that buddingtonite would be unstable on the Venusian surface because of the low water vapor partial pressures. One possible decomposition reaction is

$$3CO_2 + 2NH_4AlSi_3O_8 \cdot \frac{1}{2}H_2O = 5H_2O + N_2 + 3CO + Al_2SiO_5 + 5SiO_2. \qquad (195)$$

Other NH_4^+-bearing minerals are micas and clay minerals [Hallam and Eugster, 1976; Wlotzka, 1972]. However, we also expect that these minerals will decompose under the high temperatures and low water vapor partial pressures present at the surface of Venus.

Finally, by analogy with the Earth where nitrate ions are sometimes found in solid solution in calcite [Wlotzka, 1972] one may ask whether nitrate might also be found dissolved in carbonates on Venus. We have examined this possibility by studying the reaction

$$CaCO_3 + N_2 + \frac{5}{2}O_2 = Ca(NO_3)_2 + CO_2 \qquad (196)$$

which has the equilibrium constant

$$\log_{10} K_{196} = -20.37 + 6528(\pm 145)/T. \qquad (197)$$

This was calculated using data from Parker et al. [1971] for $Ca(NO_3)_2$. Rearranging the equilibrium constant expression for reaction (197) yields

$$(a_{nitrate}/a_{calcite}) \sim 10^{-67} \qquad (198)$$

at 740 K. Thus nitrate solid solution in carbonate can safely be neglected under Venusian surface conditions.

The arguments above therefore lead us to conclude that no nitrogen-bearing minerals are stable anywhere on the

Venusian surface. As mentioned before small amounts of nitrogen may be dissolved in silicate minerals, but if present these substitutions are unlikely to be important for atmosphere–surface chemical interactions.

ATMOSPHERE–SURFACE INTERACTIONS ON MARS

As mentioned in the Introduction, atmosphere–surface interactions on Mars are qualitatively different from those on Venus. The significantly lower global mean surface temperature and global mean surface pressure are two important factors contributing to this difference. Thus, for example, the lower temperatures on Mars, which can drop to ~ 148 K in the polar winter [Neugebauer et al., 1971], lead to condensation/evaporation cycles involving condensible gases in the Martian atmosphere [e.g., see Leighton and Murray, 1966]. These cycles are exemplified by the annual condensation and sublimation of CO_2, the dominant atmospheric gas, and the condensation and evaporation of water vapor, an important minor component. As shown by *Viking* lander pressure measurements, the former process changes the Martian atmospheric pressure by ~37% relative to the global mean pressure of ~6 millibars [Hess et al., 1980]. The latter process results in temporal and spatial variations in the atmospheric abundance of water vapor [e.g., Jakosky and Haberle, 1991, and references therein]. Furthermore, the Martian surface (and/or dust suspended in the atmosphere) may also be involved in stabilizing the CO_2 atmosphere against irreversible photochemical destruction to CO and O_2 [Kong and McElroy, 1977; Huguenin et al., 1977; Atreya and Blamont, 1990; but see Lindner and Jakosky, 1985 for an alternative viewpoint]. Basic information about the composition of the atmosphere and surface of Mars is given in Tables 11 and 12. A representative atmospheric (P,T) profile is illustrated in Figure 23 and the Martian hypsometric curve is shown in Figure 24. Recent, detailed reviews of many aspects of Martian atmospheric chemistry and structure, surface composition, and volatile exchange processes are given in a volume on Mars edited by Kieffer et al. [1991]. Thus, we will not discuss these topics in detail but will instead selectively contrast atmosphere–surface chemical interactions on Mars to those on Venus.

TABLE 11. Composition of the Atmosphere of Mars*

Gas	Mixing Ratio†	Original References
CO_2	0.953	Kuiper 1952
		Owen 1991
H_2O‡	15 ppt. μm (~ 0.02%)	Spinrad et al. 1963
		Kaplan et al. 1964
CO	$(8 \pm 3) \times 10^{-4}$	Kaplan et al. 1969
	$(5 - 75) \times 10^{-4}$	Kakar et al. 1977
	$(6 \pm 1.5) \times 10^{-4}$	Clancy et al. 1990
O_2	$(1.3 \pm 0.08) \times 10^{-3}$	Barker 1972
	$(1.3 \pm 0.13) \times 10^{-3}$	Carleton & Traub 1972
	$\sim 1.1 \times 10^{-3}$	Trauger & Lunine 1983
N_2	2.7%	Owen et al. 1977
^{40}Ar	1.6%	Owen et al. 1977
O_3‡	~ (0.04 – 0.2) ppm	Barth & Hord 1971
HDO	.036±.008 ppt. μm	Owen et al. 1988
	.061±.0013 ppt. μm	Bjoraker et al. 1989

*Excluding the noble gases Ne, Kr, and Xe.
‡Exhibits temporal & spatial variability
†The mixing ratios but not the column densities of non-condensible gases are seasonally variable due to the varying CO_2 abundance.

TABLE 12. Average Composition of the Surface of Mars*

Oxide/Halide	Concentration(%)	Method
MgO	6.0	Viking XRF analysis
Al_2O_3	7.2	Viking XRF analysis
SiO_2	43.0	Viking XRF analysis
K_2O	0.2	Analysis of Shergotty
CaO	5.8	Viking XRF analysis
TiO_2	0.6	Viking XRF analysis
MnO	0.5	Analysis of Shergotty
Fe_2O_3	18.0	Viking XRF analysis
SO_3	7.2	Viking XRF analysis
Na_2O	1.3	Analysis of Shergotty
P_2O_5	0.8	Analysis of Shergotty
Cr_2O_3	0.2	Analysis of Shergotty
Cl	0.6	Viking XRF analysis
H_2O	≤ 1	Viking GC-MS analysis
CO_3	<2	Viking LR simulation
Total	94.4	

*After Banin et al. [1991]

Thermochemical Weathering Reactions

We will begin by discussing thermochemical weathering reactions, which were the first types of atmosphere–surface reactions considered on Mars. Beginning in the early 1960's, polarimetric measurements and reflection spectroscopy indicating the presence of goethite [$\alpha - FeO(OH)$] [Dollfus, 1961; Huguenin 1974, and references therein] led several authors to investigate the thermodynamic stabilities of goethite and other Fe–bearing minerals such as hematite and siderite $FeCO_3$ on the Martian surface [Adamcik, 1963; Fish, 1966; O'Connor, 1968a]. At about the same time, several of these studies indicated that goethite was thermodynamically unstable under present conditions on the Martian surface. This realization then led to theoretical models of the production and survival of "fossil" weathering products from Martian paleo-environments [e.g., O'Connor, 1968b]. Subsequently, the *Viking* data on different chemical and physical properties of the Martian surface spurred further thermodynamic modelling of possible gas–solid weathering reactions involving common minerals found in igneous rocks, the stability of different hydrated salts, and related topics [Gooding, 1978; Sidorov and Zolotov, 1986; Suleimenov et al., 1986; Zolotov, 1989; Zolotov and Sidorov 1986). These theoretical studies have led to detailed predictions about the thermodynamically preferred weathering reactions and the thermodynamically stable weathering products on the Martian surface.

Atmospheric Composition and Evidence for Disequilibrium. However, despite the emphasis which has been placed on thermodynamic modelling, it is not at all clear which (if any) thermochemically driven gas–solid reactions can pro-

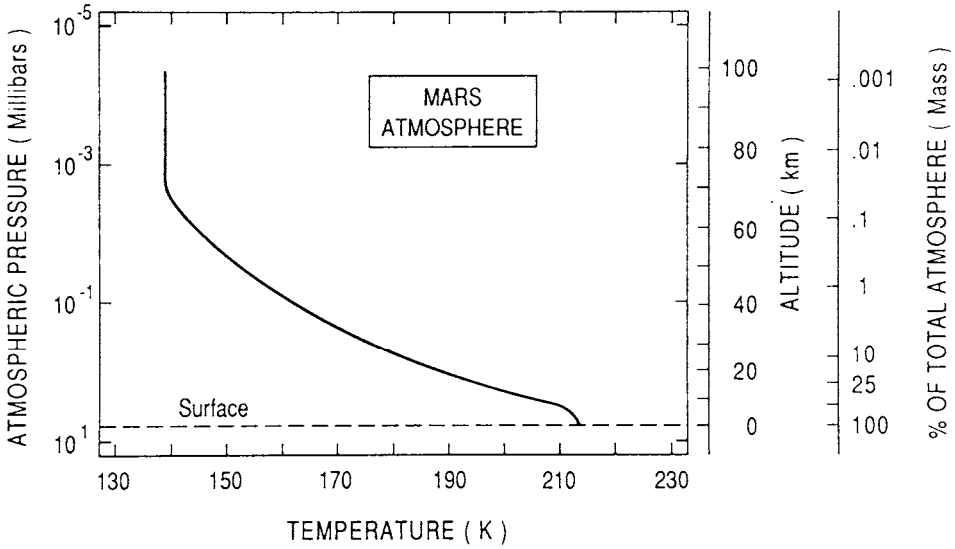

Fig. 23. A representative pressure–temperature profile for the atmosphere of Mars in the 0 to 100 km altitude region. The mean atmospheric model given by Barth [1985] was used to construct this plot. Refer to papers in Kieffer et al. [1991] for a discussion of the temporal and spatial variations in the Martian atmospheric structure.

ceed in the present environment at the surface of Mars. For example, it is obvious that the major carbon and oxygen bearing gases in the Martian atmosphere are not in thermodynamic equilibrium with each other. Prior to the discovery of O_2 in the Martian atmosphere, O'Connor [1968a] erroneously assumed that reaction (26) was responsible for buffering the oxygen fugacity of the Martian atmosphere. If this were the case, which it is not, chemical equilibrium at the Martian mean surface temperature of 215 K would lead to an oxygen fugacity of $\sim 10^{-123}$ bars. However, the observed oxygen fugacity at the Martian surface is $\sim 10^{-5.1}$ bars, or almost 120 orders of magnitude larger. Conversely, the observed O_2/CO_2 ratio of $\sim 10^{-2.9}$ in the Martian atmosphere would lead to a CO mixing ratio of $\sim 10^{-62}$ if chemical equilibrium were attained at 215 K. This is also dramatically lower than the observed value. A powerful disequilibrating mechanism is clearly responsible for maintaining the observed CO and O_2 abundances in the Martian atmosphere. As is well known, this mechanism is the photochemical destruction of CO_2 [e.g., see McElroy and Donahue, 1972; Parkinson and Hunten, 1972; Barth et al., 1991].

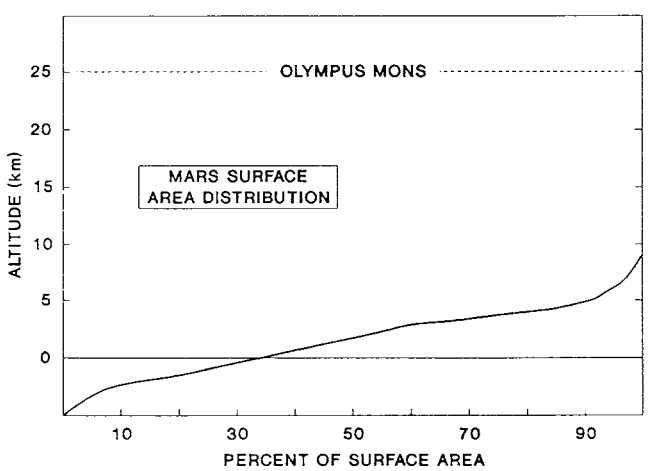

Fig. 24. Surface area distribution on Mars as a function of altitude. The highest observed point is Olympus Mons at 25 km. The lowest observed point is Hellas Planitia at −5 km. The reference (0 km) level is defined by a mathematical fit to the Martian gravitational field combined with radio occultation data giving the location of the 6.1 millibar isobaric surface. For reference the equatorial radius of Mars is 3393.4 km. Data from Wu et al. [1991], and references therein) were used to construct this plot.

Likewise, the CO_2 in the Martian atmosphere is not in chemical equilibrium with putative crustal minerals. Earth-based reflection spectroscopy indicates that pyroxene is present on the Martian surface [e.g., Adams and McCord, 1969]. As we discuss later, if silicates such as enstatite and wollastonite were in chemical equilibrium with the Martian atmosphere, all the atmospheric CO_2 would be locked up in carbonate minerals and the dominant atmospheric constituents would be N_2 and Ar. Again, this is clearly not the case. These two examples illustrate that atmosphere–surface interactions on Mars are probably not controlled by thermochemistry, because otherwise the atmospheric composition would be vastly different than is observed. However, it is also important to recognize that some thermochemical reactions, such as the annual condensation and sublimation of CO_2 do occur. What can be said about the likelihood of different types of gas–solid reactions taking place on Mars?

Gas–Solid Reaction Rates on the Martian Surface. Unfortunately, virtually nothing is known about the kinetics

of the relevant reactions, and aside from some general considerations about gas–solid reaction rates given by Gooding [1978; Gooding et al., 1991], the topic has virtually been ignored in the literature. This is mainly due to the lack of relevant experimental data. Qualitatively, we would expect that the low surface temperature of Mars coupled with the low atmospheric density will act in concert to slow down the rates of gas–solid reactions. As a result, many thermodynamically favorable weathering reactions will probably be kinetically inhibited. This qualitative impression can be schematically illustrated by considering a typical gas–solid reaction such as anhydrite formation, which was discussed earlier. Assuming that the experimentally determined reaction rate law [equation (150)] is valid down to 215 K, the lower surface temperature on Mars means that anhydrite formation would proceed $\sim 10^{22}$ times slower than on Venus. Although this effect will be less severe for reactions with lower activation energies, we conclude that (at least some) gas–solid reactions will not take place even though they are thermodynamically favorable.

A similar conclusion was reached by Stephens and Stevenson [1990]. They used high temperature data on the kinetics of the reaction

$$\mathrm{CaO(lime)} + \mathrm{CO_2(g)} \rightarrow \mathrm{CaCO_3(calcite)} \qquad (199)$$

to estimate the diffusivity of CO_2 through carbonate layers, which are predicted to form on silicates under Martian surface conditions. Their results gave $D_{CO_2} \sim 10^{-27}$ cm^{-2} sec^{-1}, although the exact temperature to which this diffusion constant applies was not given by them. For comparison, using their equation for the layer thickness

$$l \sim 0.06(\mathrm{Dt})^{0.5} \qquad (200)$$

we estimate that $D_{CO_2} \sim 10^{-13}$ in order to grow a 1 μm thick layer in one terrestrial year. (From our previous discussion we recall that the anhydrite formation rate on Venus is predicted to be $\sim$1 μm per terrestrial year.) This D value is about 14 orders of magnitude larger than the diffusion coefficient estimated by Stephens and Stevenson [1990]. In other words, two independent estimates suggest that gas–solid reactions are probably kinetically inhibited under Martian surface conditions.

Evidence from Antarctic Analogs. On the other hand, qualitative evidence from studies of chemical weathering reactions in Antarctic soils [e.g., Ugolini and Jackson, 1982] suggests that some gas–solid reactions may take place on the Martian surface. For example, Gibson et al. [1983] argue that climatic conditions in Antarctic dry valleys are (roughly) analogous to those on the Martian surface and that chemical weathering processes in the dry valleys therefore provide a guide to those taking place on Mars. They document the formation of various carbonate, halide, and sulfate minerals and the mobility of water soluble cations and anions such as Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-}, and NO_3^{2-}. However, as Gibson et al. [1983] also note, isotopic data indicate that some of the observed alteration minerals such as sulfates are probably derived from a marine source.

Independent studies of weathering products found on the exteriors and in fractures of meteorites found in Antarctica also provide support for the idea that thermochemical weathering reactions may take place under present day conditions on the Martian surface. Velbel et al. [1991] studied the Mg carbonate weathering products ($MgCO_3 \cdot 3H_2O$ nesquehonite $\pm$ hydromagnesite $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) found on ordinary chondrites and provided evidence that the weathering products are formed from the meteorite itself and do not represent contamination or products derived from terrestrial sea-salts. Furthermore, they calculated that nesquehonite formation via the reaction

$$\mathrm{Mg_2SiO_4} + 6\mathrm{H_2O(liq)} + 2\mathrm{CO_2(g)} = 2[\mathrm{MgCO_3 \cdot 3H_2O}] + \mathrm{SiO_2} \qquad (201)$$

is thermodynamically favorable under some Antarctic conditions (T$\sim$273 K and $P_{CO_2} \sim 10^{-3.5}$ bars) even if water activities are as low as 0.3–0.65. The range of calculated water activities depends on whether crystalline quartz or amorphous silica is assumed to be formed from reaction (201). As Velbel et al. [1991] and Gooding [1986] note, these water activities are compatible with the presence of liquid water in brines or in thin films. In this regard we also note that Murrman [1973] demonstrated experimentally that cationic diffusion in frozen soil is surprisingly rapid relative to diffusion in the solid state. Specifically, Murrman found that for typical silt soils the diffusion coefficient for Na^+ is about 10^{-7} cm^2 sec^{-1} at 270 K. This is orders of magnitude faster than cationic diffusion in minerals at similar temperatures. Thus, cationic diffusion in the thin water films found in frozen rock and soil is relatively rapid.

Furthermore, the weathering process must have taken place within a geologically short period of time because studies of decaying cosmogenic nuclides show that the maximum time the Antarctic meteorites have been on the Earth is less than a million years [Nishiizumi et al., 1989]. However, as we discuss later, the specific weathering products studied by Velbel et al. [1991] are thermodynamically unstable under Martian conditions because of the much lower water vapor partial pressures in the Martian atmosphere. Also, the lower mean temperature of 215 K on Mars versus a mean temperature of 253 K in the Antarctic dry valleys, combined with the need for liquid water in some form, may mitigate against analogous reactions on Mars. Nevertheless, the work of Velbel et al. [1991] is a potentially important piece of evidence in favor of thermochemically driven gas–solid reactions on Mars.

We conclude that at present the role of thermochemical gas–solid reactions for chemical weathering on the Martian surface is probably limited, but that the type of reactions which may proceed is somewhat ambiguous because of a lack of kinetic data for many proposed reactions. In order to understand the possible nature of thermochemical weathering reactions on the Martian surface, we will review some of the thermodynamic modelling which has been done. This work

is important because it may provide a guide to the reactions which may occur if an energy source to provide the necessary activation energy is present. We will start off with a brief discussion of an observed process, CO_2 condensation onto the polar caps.

Carbon Dioxide Clathrate Hydrate. As mentioned earlier, Leighton and Murray [1966] proposed that the Martian polar caps contained CO_2 ice (dry ice). This proposal was apparently confirmed by the Mariner 7 infrared radiometer observations that showed temperatures of 148 K, the dry ice sublimation point under $\sim$ 6 mb of CO_2(g), at the Martian southern polar cap [Neugebauer et al., 1971]. Subsequent observations by Mariner 9 and *Viking* reinforced the idea that the residual southern polar cap is composed of dry ice [e.g., Jakosky and Haberle, 1991, and references therein].

However, an interesting alternative, CO_2 clathrate hydrate $CO_2 \cdot 6H_2O$, was proposed by Miller and Smythe [1970]. This phase is interesting for several reasons. Among these is the potential for storing large amounts of other volatiles (e.g., N_2, CO, and the noble gases) in the CO_2 clathrate hydrate [Musselwhite and Lunine, 1990].

Miller and Smythe experimentally measured the CO_2 equilibrium pressure for clathrate formation over the temperature range 152 – 193 K. Their results are given by

$$6H_2O(\text{ice}) + CO_2(g) = CO_2 \cdot 6H_2O(s) \qquad (202)$$

$$\log_{10} P_{CO_2} = 7.56 - 1338/T - 6.6 \times 10^{-3}T. \qquad (203)$$

Miller and Smythe pointed out that above $\sim$ 121 K, the CO_2 vapor pressure over dry ice, which is given by

$$\log_{10} P_{CO_2} = 8.34 - 1470/T - 4.1 \times 10^{-3}T, \qquad (204)$$

is greater than that over coexisting CO_2 clathrate + water ice. This is illustrated in Figure 25. Thus, they concluded that the Martian polar caps can consist of pure water ice, water ice + CO_2 clathrate, or dry ice + CO_2 clathrate. But, as they emphasized, water ice + dry ice are not thermodynamically stable together at the temperatures measured for the residual southern polar cap. Furthermore, Miller and Smythe [1970] stated that CO_2 clathrate formation from finely divided ice was rapid, taking only several hours at 150 K. However, their predicted compositions for the Martian polar caps are apparently contradicted by the observational evidence that the residual southern polar cap is composed of dry ice. How can this contradiction be resolved?

There are three alternatives for resolving this problem. One is that the Martian polar caps contain water ice + dry ice but are not in thermochemical equilibrium with atmospheric CO_2. The second alternative is that the polar caps contain water ice + dry ice and are indeed in equilibrium with atmospheric CO_2. However, this alternative requires that the laboratory data which indicate otherwise are incorrect. The third alternative is that the residual southern polar cap (and/or the seasonal polar caps) are CO_2 clathrate + water ice or CO_2 clathrate + dry ice and are in equilibrium with atmospheric CO_2, but the observational data

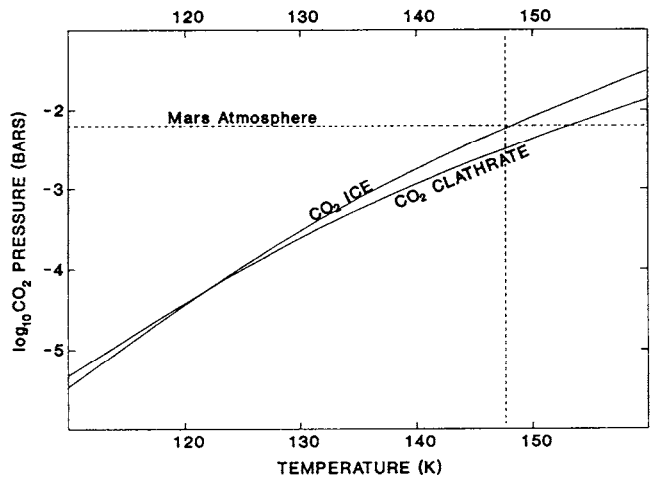

Fig. 25. A comparison of the CO_2 vapor pressure over CO_2 ice (dry ice) and over CO_2 clathrate hydrate ($CO_2 \cdot 6H_2O$) with the mean CO_2 pressure of the Martian atmosphere. The observed temperature of 148 K measured for the Martian south polar cap by the Mariner 7 infrared radiometer [Neugebauer et al., 1971] is indicated by the vertical dashed line. At this temperature, the vapor pressure over CO_2 ice and the observed CO_2 pressure of the Martian atmosphere are virtually identical, thus providing strong evidence that CO_2 ice is present in the polar caps as proposed by Leighton and Murray [1966]. Note that CO_2 clathrate hydrate, which has been proposed as a constituent of the Martian polar caps by Miller and Smythe [1970], is thermodynamically more stable than CO_2 ice (i.e., has lower CO_2 vapor pressures) at temperatures above $\sim$121 K.

cannot distinguish between CO_2 clathrate and water ice (or dry ice). This alternative has also been discussed by Dobrovolskis and Ingersoll [1975].

Unfortunately, at present it is not possible to distinguish which of these three alternatives is correct. With regard to the laboratory data, Miller and Smythe [1970] state that their measured dissociation pressures for CO_2 clathrate are consistent with prior work and they also state that equilibrium was approached from both higher and lower pressures. However, they do not present any data, such as diffraction patterns, to prove unambiguously that the solid phase they prepared was pure CO_2 clathrate and not a mixture of CO_2 clathrate + CO_2 adsorbed/absorbed on water ice. It is also impossible to determine the clathrate formation rate per cm^2 of exposed water ice because the ice grain size was not reported. However, these questions can be answered by appropriate laboratory studies.

The observational constraints are also somewhat ambiguous. As shown in Figure 25, there is excellent agreement between polar cap temperatures of $\sim$ 148 K and the dry ice sublimation point for $\sim$ 6 millibars of gaseous CO_2. However, as noted by Miller and Smythe [1970], a slightly higher temperature of $\sim$ 153 K also provides excellent agreement with the CO_2 pressure over CO_2 clathrate + water ice. The interpretation of spectroscopic data may also be somewhat ambiguous because Smythe [1975] showed that reflection

spectra of water ice and of CO_2 clathrate are indistinguishable in the 1 – 6 μm range. In this regard we note that the prior laboratory reflection spectroscopy of Kieffer [1970a,b] did not include CO_2 clathrate hydrate, but only physical mixtures of water ice + dry ice.

Thus, to summarize, laboratory data predict that CO_2 clathrate hydrate is thermodynamically stable at temperatures and pressures characteristic of the residual southern polar cap. However, observational constraints are sufficiently ambiguous that it is probably not possible to tell whether or not the CO_2 clathrate is actually present in the residual southern polar cap and/or the seasonal polar caps.

Carbonates. Although carbonate minerals are generally believed to be present on the Martian surface, the evidence for their presence is indirect and inferential. Furthermore, carbonates are apparently present only in minor amounts if at all. Earth-based reflection spectroscopy gives an upper limit of a few percent for the abundance of calcium carbonate on the Martian surface [e.g., Blaney and McCord, 1989]. Other recent observations by Pollack et al. [1990] suggest that carbonates comprise approximately 1 – 3% of Martian airborne dust. Also, Clark et al. [1990] recently presented evidence for HCO_3^--bearing scapolite on Mars. However, Encrenaz and and Lellouch [1990] have cautioned that the identification of scapolite by Clark et al. [1990] should be regarded as tentative because of possible spectral interferences from CO in the Martian atmosphere. The observations of Pollack et al. [1990] apparently do not have this problem, but do not uniquely identify any specific carbonate minerals.

Another line of evidence for the presence of carbonate minerals on Mars comes from studies of the SNC (Shergottite–Nakhlite-Chassignite) meteorites, which are related to one another and which are widely believed to have come from Mars [e.g., see Banin et al., 1991]. The basis for this belief is the similarity between the trapped gases found in a glassy inclusion of one SNC meteorite (the Antarctic meteorite EETA 79001) and the composition of the Martian atmosphere [e.g., Becker and Pepin, 1984]. Calcium carbonate grains, at least some of which are calcite, have been found in the shocked glassy inclusions in EETA 79001 [Gooding et al., 1988]. Isotopic analyses of the carbon and oxygen in the carbonate indicate that it is not a weathering product formed in the Antarctic, and support the contention that the carbonate is an extraterrestrial weathering product formed on the meteorite parent body [Clayton and Mayeda 1988; Wright et al., 1988]. Calcium carbonate has also been identified in Nakhla by Wentworth and Gooding [1989]. Again, isotopic measurements indicate that the carbonate is not terrestrial in origin [e.g., Watson et al., 1991; Carr et al., 1985].

Finally, a third line of evidence suggesting the presence of carbonates on the Martian surface comes from the *Viking* analyses of the Martian surface. Some of the CO_2 evolved by heating soil samples up to 500° C may be due to the partial decomposition of carbonates [Biemann et al., 1977; Toulmin et al., 1977]. Modelling of the *Viking* X-ray fluorescence (XRF) analyses of the Martian surface by Clark and Van Hart [1981] has also led to the suggestion that carbonates are present on the Martian surface. However, it is important to note that the *Viking* XRF instrument could not detect elements with atomic numbers less than 12 (Mg), and therefore could not detect carbonates directly.

Thermodynamic calculations show that carbonates are stable on the Martian surface [e.g., O'Connor, 1968a; Gooding, 1978; Sidorov and Zolotov, 1986]. However, as mentioned previously, atmospheric CO_2 is definitely not in equilibrium with carbonate–silicate mineral assemblages on the Martian surface. This point is illustrated in Figures 26 and 27 where the CO_2 equilibrium pressures for reactions (2) and (1) are plotted over a range of temperatures spanning the high and low values observed on the Martian surface. Over this entire range, the calculated pressures are several orders of magnitude lower than the observed CO_2 partial pressure in the Martian atmosphere. For example, at 215 K, the equilibrium pressures for reaction (2) and reaction (1) are about 10^{-13} bars and 10^{-10} bars, respectively. If equilibrium were reached in geologically short times, then CO_2 would be totally absent from the Martian atmosphere and the dominant gases would be N_2 and Ar. This is clearly not the case. The spectral evidence for only minor amounts of carbonates on the Martian surface also shows that the atmosphere and surface are not in chemical equilibrium.

Other potential carbonate minerals which have been discussed include siderite and rhodochrosite. Siderite formation could occur by reactions exemplified by

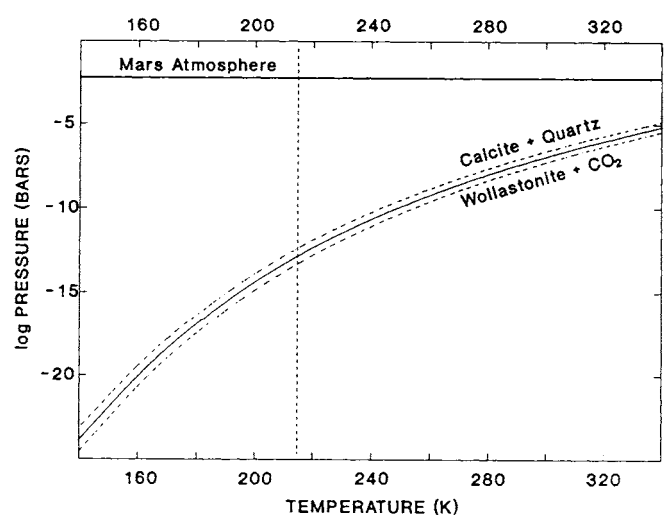

Fig. 26. A comparison of the mean CO_2 pressure in the Martian atmosphere with that calculated for reaction (2). The vertical dashed line indicates the mean Martian surface temperature of 215 K. The curved dashed lines represent the uncertainties in the calculated CO_2 pressure allowed by the uncertainties in the thermodynamic data for reaction (2). The observed CO_2 pressure is always significantly greater than that required to convert wollastonite to calcite.

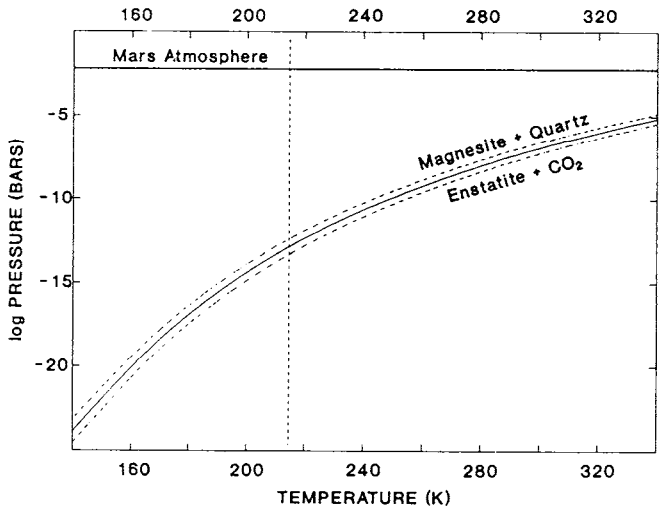

Fig. 27. As in Fig. 26 but for reaction (1). These two figures illustrate that the Martian surface is a potential sink for atmospheric CO_2 through carbonate formation, which is predicted to be thermodynamically favorable. However, as discussed in the text, gas–solid reactions such as carbonate formation may be kinetically inhibited.

$$FeSiO_3 + CO_2 = FeCO_3 + SiO_2 \quad (205)$$

$$\log_{10} P_{CO_2} = 8.46 - 3088(\pm 179)/T \quad (206)$$

$$Fe_2SiO_4 + 2CO_2 = 2FeCO_3 + SiO_2 \quad (207)$$

$$\log_{10} P_{CO_2} = 8.55 - 3111(\pm 130)/T. \quad (208)$$

Rhodochrosite formation could occur by the carbonation of rhodonite or tephroite. These reactions and the corresponding CO_2 equilibrium pressures are equations (14) to (19) discussed earlier. Rhodochrosite, like calcite and magnesite, is thermodynamically stable with respect to decarbonation, over the entire range of temperatures observed on the Martian surface. However, siderite displays qualitatively different behavior.

As illustrated in Figure 28, siderite is thermodynamically stable relative to ferrosilite + CO_2 up to 290±18 K. However, this is strictly an upper limit because as discussed previously, pure $FeSiO_3$ does not exist in nature. Instead it is dissolved in low-Ca pyroxene $(Mg,Fe)SiO_3$. In this case, the maximum temperature for siderite stability on the Martian surface is proportional to the $FeSiO_3$ thermodynamic activity in the low-Ca pyroxene. For a range of plausible $FeSiO_3$ activities of ~ 0.5 to ~ 0.1, the maximum temperature for siderite stability decreases from 282±18 K to 265±18 K. Siderite formation from fayalite and from fayalitic olivine [via reaction (207)] occurs at about the same CO_2 pressures and the maximum temperatures as a function of fayalite activity are identical to those just listed. Thus, thermodynamic constraints suggest that siderite may undergo decarbonation – carbonation cycles as the temperature increases and decreases on the Martian surface.

Finally, we want to point out that both siderite and rhodochrosite are thermodynamically unstable with respect to oxidation to Fe^{3+} and Mn^{4+} oxides by reactions such as

$$2FeCO_3 + \frac{1}{2}O_2 = Fe_2O_3 + 2CO_2 \quad (209)$$

$$\log_{10} K_{207} = 10.72 + 7192(\pm 229)/T \quad (210)$$

$$MnCO_3 + \frac{1}{2}O_2 = MnO_2 + CO_2 \quad (211)$$

$$\log_{10} K_{211} = 3.30 + 1288(\pm 86)/T. \quad (212)$$

In both cases the equilibrium oxygen fugacities are orders of magnitude below the observed value. If thermodynamics were the controlling factor, reactions (209) and (211) would probably convert all siderite and rhodochrosite on the Martian surface to hematite and pyrolusite. However, in the case of siderite it is more likely that the relative rates of the decarbonation and carbonation reactions on the one hand and the rate of hematite formation on the other hand will decide whether or not siderite is stable on the Martian surface. Likewise, in the case of rhodochrosite, it is likely that the relative rates of rhodochrosite formation (or exposure on the surface) and of pyrolusite formation will determine if $MnCO_3$ is present or not. The possible effects of photochemically driven reactions are also of interest in these two cases, but have not been studied experimentally.

Water Vapor, Liquid Water, and Water Ice. Observational data about the water vapor content of the Martian atmosphere and its temporal and spatial variations have recently been summarized by Jakosky and Haberle [1991]. A typical water vapor abundance in the Martian atmosphere is 15 ppt μm (equivalent to 5×10^{19} molecules cm^{-2} or 210 ppm by volume). The maximum observed water va-

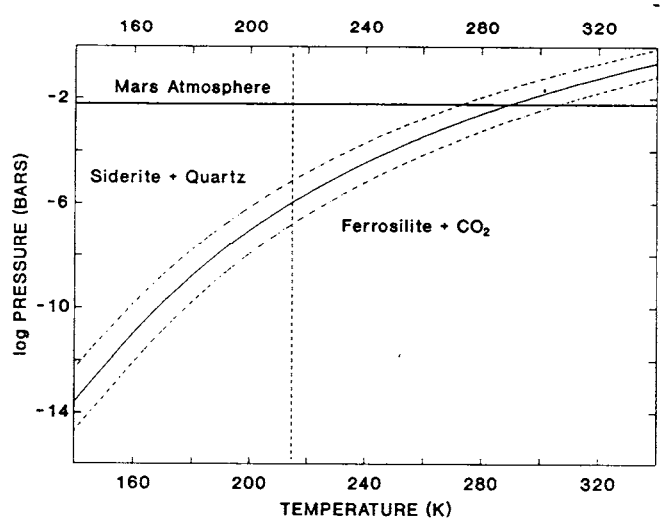

Fig. 28. As in Fig. 26 but for reaction (205). Siderite ($FeCO_3$) formation from fayalite is also thermodynamically favorable under average Martian surface conditions. Siderite becomes thermodynamically unstable at 290±18 K relative to pure $FeSiO_3$ and CO_2.

por abundance is about 90 ppt μm (~1260 ppm) during northern summer, and the minimum water vapor abundance drops below 1 ppt μm (14 ppm) during polar night.

Pure liquid water is unstable on the Martian surface because the water vapor pressure is always less than the triple point pressure of ~6 mbars. The thermodynamic stability of brines, concentrated aqueous salt solutions with water vapor pressures less than that of pure water, has been discussed by Brass [1980]. He finds that a water vapor pressure on the order of 10^{-5} bars (a water vapor mixing ratio of ~1670 ppm) is necessary to stabilize brines on the Martian surface. This is higher than the maximum observed value. Brass [1980] suggested that the required water vapor pressure may be found in pore spaces in the regolith. Thus, at best the occurrence of brines is probably limited to some subsurface regions. Brass [1980] and Clark and Van Hart [1981] have also concluded that the most likely brines are sulfate-rich and will precipitate salts at temperatures in the range of 269 to 272 K. However, at present there is no unambiguous evidence (e.g., from radar data) for the presence of brines on Mars [Zent et al., 1990].

Water ice is present in the polar caps, and may also be present in ground ice deposits at varying depths below the surface [e.g., Farmer and Dons, 1979; Fanale et al., 1986], and as adsorbed water on mineral grains in the regolith [e.g., Fanale and Cannon, 1974]. Consideration of these topics is beyond the scope of this review and we refer the reader to other papers such as Squyres [1989] and Jakosky and Haberle [1991] which summarize the relevant observational evidence and theoretical models. In this paper we are interested in comparing the thermodynamic stabilities of water ice and various hydrated phases on the surface of Mars. The vapor pressure equation for ice is

$$\log_{10} P_{H_2O} = 7.59 - 2678/T. \qquad (213)$$

This is plotted in Figure 29 where it is seen that temperatures of ~183 K and below are necessary for water ice condensation (e.g., as surface frost or ice crystals in the atmosphere).

Goethite. Goethite is a hydrated iron oxide [α-FeO(OH)] and is the principal constituent of limonite, a rock composed of a mixture of ferric oxides and hydroxides. Polarimetric measurements [e.g., Dollfus, 1961] and reflection spectroscopy data [e.g., see references summarized by Huguenin, 1974] have traditionally been interpreted as showing that limonite and goethite are present on the Martian surface. In the early 1960's it was believed that limonite and goethite were the principal constituents of the Martian surface. However, ferric oxides and hydroxides are now believed to be present at levels of approximately 6 to 8 % [e.g., Singer et al., 1979; Bell et al., 1990]. Two other polymorphs, lepidocrocite [γ-FeO(OH)] and feroxyhyte [δ-FeO(OH)] have also been suggested as being present on Mars. These proposals were made primarily as a result of the *Viking* magnetic properties experiment which indicated the presence of a strongly magnetic material in the Martian soil. Fuller and Hargraves

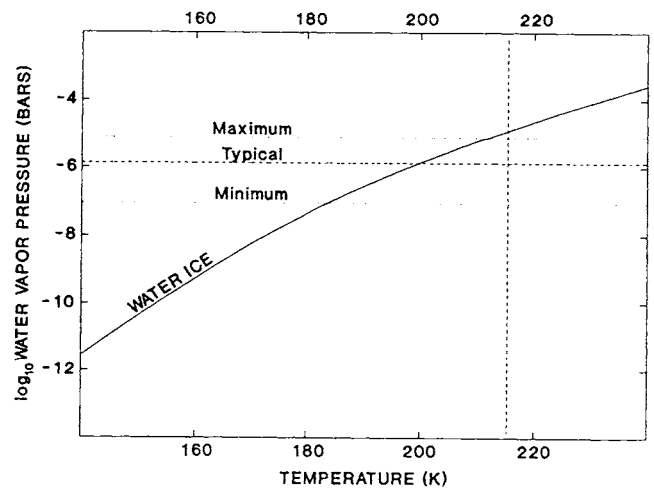

Fig. 29. The H_2O vapor pressure over ice is compared to the observed range of water vapor abundances in the Martian atmosphere. The values corresponding to the minimum, typical, and maximum water vapor abundances are 1 ppt μm, 15 ppt μm, and 90 ppt μm, respectively. The 1 ppt μm value is actually an upper limit to the true minimum, which is below this value. The vertical dashed line corresponds to a mean temperature of 215 K.

[1978] and Hargraves et al. [1979] suggested that maghemite (γ-Fe_2O_3) was the magnetic material. They also proposed that lepidocrocite, which dehydrates to maghemite, could also be present if its dehydration were kinetically inhibited. Alternatively, Burns [1980] suggested that feroxyhyte, δ-FeO(OH), which is ferrimagnetic, was the magnetic material. Although these suggestions cannot be quantitatively evaluated because no thermodynamic data are tabulated for these two polymorphs, it is likely that all three polymorphs have similar thermodynamic properties. Thus, an assessment of the stability of goethite should be a good guide to the stability of the other two FeO(OH) polymorphs as well.

The thermodynamic stability of goethite on the Martian surface was first considered by Adamcik [1963] who suggested that goethite was responsible for buffering the atmospheric water vapor pressure via equilibrium with hematite

$$2\alpha - \mathrm{FeO(OH)} = \mathrm{Fe_2O_3} + \mathrm{H_2O(g)}. \qquad (214)$$

However, the goethite thermodynamic data used by Adamcik [1963] have since been superseded by better data [e.g., Robie et al., 1979]. The equilibrium water vapor pressure for reaction (214) is

$$\log_{10} P_{H_2O} = 8.28 - 2727(\pm 104)/T. \qquad (215)$$

This is compared to the observed range of water vapor partial pressures in the Martian atmosphere in Figure 30. At the mean temperature of ~215 K and a typical water vapor abundance (15 ppt μm), goethite is thermodynamically unstable and should dehydrate to hematite. However, within the uncertainties of the thermodynamic data for reaction (214), goethite is apparently stable at temperatures of 185 K and below. This conclusion appears firm and was first

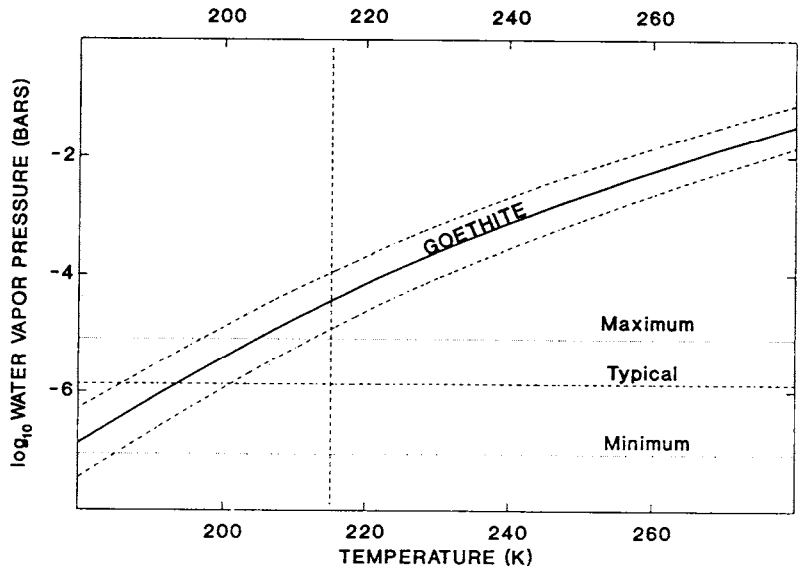

Fig. 30. The equilibrium H_2O dissociation pressure for goethite [FeO(OH)] dehydration to hematite is compared to the observed range of water vapor abundances in the Martian atmosphere. The curved dashed lines show the range of H_2O dissociation pressures allowed by the uncertainties in the thermodynamic data for reaction (214). The vertical and horizontal dashed lines are defined in the caption to Fig. 32.

stated by O'Connor [1968a] who noted that "Thermodynamic calculations of mineral stability fields under a range of predicted surface conditions for Mars indicate that goethite will be unstable except under the wettest and coldest parts ($P_{H_2O} \sim 10^{-6}$ atm, T < 200 K) of this range". Other workers also concluded that goethite is thermodynamically unstable on the Martian surface [e.g., Fish, 1966; Gooding, 1978]. Thus, there is an apparent conflict between the thermodynamic models predicting that goethite is unstable on the Martian surface and the spectral evidence for its presence.

A possible explanation for this problem was put forward by Pollack et al. [1970a,b]. They used literature data and their own experiments to estimate an activation energy of 92–140 kJ mole^{-1} for reaction (214). These values were then used to calculate that goethite dehydration under Martian surface conditions is kinetically inhibited over 10^9 year timescales. Pollack et al. [1970a,b] also proposed that goethite is thermodynamically stable slightly below the Martian surface where the temperature is constant. In their model physical mixing of this material onto the surface renews goethite which has dehydrated to hematite.

However, despite the intuitive appeal of the Pollack et al. model, there are several potential problems with their explanation. One problem is that the dehydration rate per unit area was not determined in the literature studies which Pollack et al. [1970a,b] used for their kinetic analysis. Thus, it is not clear if there is a critical value of grain size below which goethite dehydration is kinetically favorable. Another potential problem (as Pollack et al. note) is that the activation energy for reaction (214) was not well determined, and thus a range of possible values had to be considered. Finally, a third potential problem is that solar uv photochemically driven dehydration of goethite was neglected in their analysis. If effective, this process may increase the goethite dehydration rate on the Martian surface.

In fact, Andersen and Huguenin [1977] claimed that photochemically driven ($\lambda < 280$ nm) goethite dehydration was an efficient process in their laboratory experiments. However, their results have been challenged by Morris and Lauer [1981] who failed to observed any goethite dehydration in their own photochemical experiments of up to 420 hours duration. Scaling their laboratory results to UV fluxes on the Martian surface led Morris and Lauer [1981] to derive a lower limit of 10–100 years for the time required for goethite photo-dehydration on Mars. However, this is a geologically short time period and goethite photo-dehydration on a longer timescale cannot be ruled out on the basis of their experiments. We also note that neither study used surface sensitive analytical techniques to check for any dehydration. Furthermore, Huguenin [1982] noted that the light source used by Morris and Lauer [1981] gave short-wavelength UV fluxes that were $\leq 1\%$ of those used in his experiments at 200 nm. Huguenin therefore claimed that Morris and Lauer failed to observe any photo-dehydration because they did not run their experiment for long enough time periods. But we note that, Huguenin did not give an opinion on how long the experiments of Morris and Lauer should have been run to observe any reaction.

Thus, to summarize, thermodynamic models show that goethite is unstable on the Martian surface, where it has apparently been detected by polarimetric measurements and

reflection spectroscopy. The available kinetic studies of reaction (214) indicate that goethite dehydration is kinetically inhibited for long time periods under Martian surface conditions. As a result, goethite may be present on the Martian surface even though it is thermodynamically unstable. However, the conclusions of these kinetic studies are tempered by several potential problems with the experiments on the thermally driven dehydration reaction and by conflicting experimental results on the photochemically driven dehydration reaction. Thus, despite over 3 decades of study, it is still not possible to definitively state whether or not goethite is present on the Martian surface.

Hydrated Chlorides and Sulfates. Several investigators have also considered the possibility that hydrated salts may be thermodynamically stable on the Martian surface [e.g., Clark, 1978; Clark and Van Hart, 1981; Suleimenov et al., 1986; Zolotov, 1989]. The possibility that hydrated salts may undergo dehydration/rehydration cycles has also been discussed by Zolotov [1989]. These studies have concentrated on binary salts such as sodium, magnesium, and calcium sulfates and chlorides which are believed to be present in the Martian soil on the basis of the *Viking* X-ray fluorescence and gas chromatograph–mass spectrometer results. The former experiment indicated the presence of large amounts of sulfur and chlorine (e.g., see Table 12) and the latter experiment indicated the presence of 1–3% water in the samples analyzed. For the magnesium sulfates the relevant dehydration equilibria and the corresponding water vapor dissociation pressures are given by

$$MgSO_4 \cdot 7H_2O = MgSO_4 + 7H_2O(g) \quad (216)$$

$$\log_{10} P_{H_2O}(\text{epsomite}) = 7.76 - 3041(\pm 120)/T \quad (217)$$

$$MgSO_4 \cdot 6H_2O = MgSO_4 + 6H_2O(g) \quad (218)$$

$$\log_{10} P_{H_2O}(\text{hexahydrite}) = 7.62 - 3026(\pm 95)/T \quad (219)$$

$$MgSO_4 \cdot 4H_2O = MgSO_4 + 4H_2O(g) \quad (220)$$

$$\log_{10} P_{H_2O}(\text{leonhardtite}) = 7.82 - 3147(\pm 150)/T \quad (221)$$

$$MgSO_4 \cdot 2H_2O = MgSO_4 + 2H_2O(g) \quad (222)$$

$$\log_{10} P_{H_2O}(\text{sanderite}) = 7.87 - 3243(\pm 120)/T \quad (223)$$

$$MgSO_4 \cdot H_2O = MgSO_4 + H_2O(g) \quad (224)$$

$$\log_{10} P_{H_2O}(\text{kieserite}) = 8.03 - 4147(\pm 90)/T. \quad (225)$$

The dehydration equilibria and the corresponding water vapor dissociation pressures for the calcium sulfate hydrates are given by

$$CaSO_4 \cdot 2H_2O = CaSO_4 + 2H_2O(g) \quad (226)$$

$$\log_{10} P_{H_2O}(\text{gypsum}) = 7.67 - 2756(\pm 80)/T \quad (227)$$

$$CaSO_4 \cdot \frac{1}{2}H_2O = CaSO_4 + \frac{1}{2}H_2O(g) \quad (228)$$

$$\log_{10} P_{H_2O}(\text{bassanite}) = 7.49 - 2277(\pm 80)/T. \quad (229)$$

Finally, the dehydration equilibrium for decomposition of sodium sulfate decahydrate (mirabilite) to anhydrous sodium sulfate (thenardite) is given by

$$Na_2SO_4 \cdot 10H_2O = Na_2SO_4 + 10H_2O(g) \quad (230)$$

$$\log_{10} P_{H_2O}(\text{mirabilite}) = 7.54 - 2723(\pm 180)/T. \quad (231)$$

The calculated water vapor pressures for these sulfate hydrates and the range of values allowed by the uncertainties in the thermodynamic data are listed in Table 13. These results show that hydrated magnesium sulfates up to and including the hexahydrate will be thermodynamically stable under average Martian surface conditions of 215 K and ~210 ppm water vapor, and that the heptahydrate (epsomite) is probably also stable. However the formal uncertainties in the thermodynamic data indicate that as much as 249 ppm water vapor may be required to stabilize epsomite. This is slightly greater than the typical water vapor content of the Martian atmosphere. The temperature dependence of the dissociation pressure curve for epsomite is illustrated in Figure 31. It gives an idea of the temperatures at which epsomite is stable under different water vapor partial pressures in the Martian atmosphere. The other hydrated magnesium sulfates are more stable than epsomite and require smaller water vapor partial pressures to be stable at a given temperature. The data in Table 13 also show that hydrated calcium sulfates and hydrated sodium sulfate (mirabilite) will not be thermodynamically stable under these conditions. Either much more water vapor or colder temperatures are needed to stabilize these hydrated sulfates on the Martian surface.

The dehydration equilibria and the corresponding equi-

TABLE 13. Equilibrium Water Vapor Pressures for Hydrated Sulfates on the Martian Surface (215 K)*

Hydrated Sulfate	Mineral Name	Water Content(%)	Water Vapor Mixing Ratios and the Range of Values			
$MgSO_4 \cdot 7H_2O$	Epsomite	51%	69 ppm	(19 ppm	–	249 ppm)
$MgSO_4 \cdot 6H_2O$	Hexahydrite	47%	58 ppm	(21 ppm	–	162 ppm)
$MgSO_4 \cdot 4H_2O$	Leonhardtite	37%	25 ppm	(5 ppm	–	127 ppm)
$MgSO_4 \cdot 2H_2O$	Sanderite	23%	10 ppm	(3 ppm	–	37 ppm)
$MgSO_4 \cdot H_2O$	Kieserite	13%	0.9 ppb	(0.4 ppb	–	2 ppb)
$CaSO_4 \cdot 2H_2O$	Gypsum	21%	0.12%	(0.05%	–	0.28%)
$CaSO_4 \cdot \frac{1}{2}H_2O$	Bassanite	6%	13%	(6%	–	31%)
$Na_2SO_4 \cdot 10H_2O$	Mirabilite	56%	0.12%	(0.02%	–	0.86%)

*Calculated assuming a total pressure of 6 millibars.

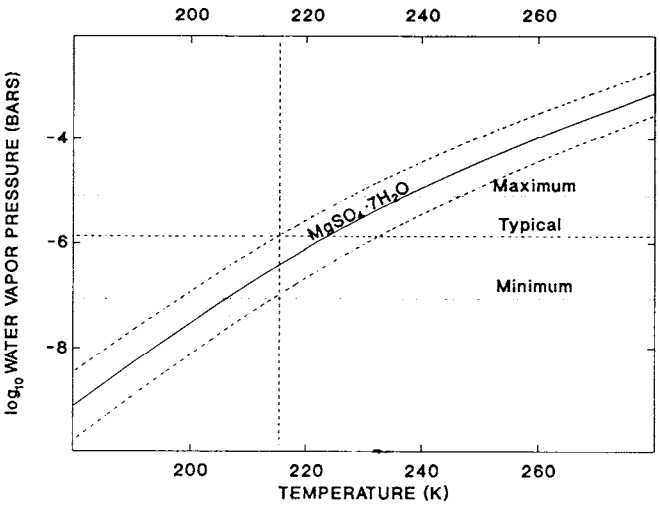

Fig. 31. As in Fig. 30, but for epsomite dehydration to $MgSO_4$. Within the uncertainties of the thermodynamic data, epsomite may not be stable under typical Martian surface conditions (249 ppm water vapor to stabilize epsomite vs. a typical value of ~210 ppm). However, all the lower hydrates of $MgSO_4$ are stable under these conditions.

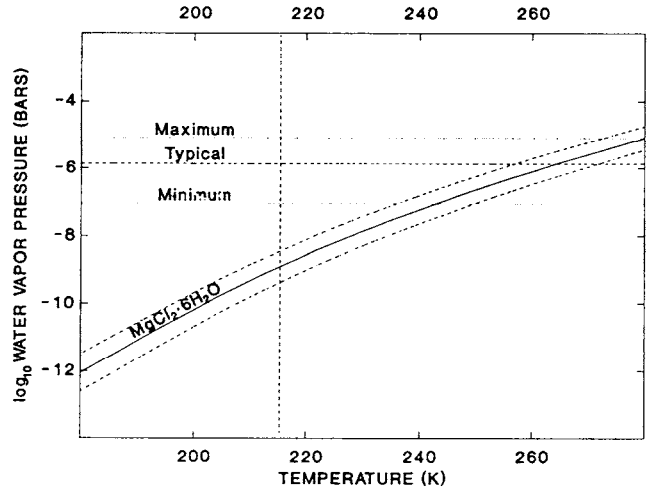

Fig. 32. As in Fig. 30, but for bischofite dehydration to $MgCl_2$. All lower hydrates of $MgCl_2$ are also stable under typical Martian surface conditions.

librium water vapor pressures for hydrated magnesium and calcium chlorides are given by

$$MgCl_2 \cdot 6H_2O = MgCl_2 + 6H_2O(g) \quad (232)$$

$$\log_{10} P_{H_2O}(\text{bischofite}) = 7.44 - 3510(\pm 100)/T \quad (233)$$

$$MgCl_2 \cdot 4H_2O = MgCl_2 + 4H_2O(g) \quad (234)$$

$$\log_{10} P_{H_2O} = 7.57 - 3732(\pm 90)/T \quad (235)$$

$$MgCl_2 \cdot 2H_2O = MgCl_2 + 2H_2O(g) \quad (236)$$

$$\log_{10} P_{H_2O} = 7.49 - 3946(\pm 80)/T \quad (237)$$

$$MgCl_2 \cdot H_2O = MgCl_2 + H_2O(g) \quad (238)$$

$$\log_{10} P_{H_2O} = 7.36 - 4167(\pm 80)/T \quad (239)$$

$$CaCl_2 \cdot 6H_2O = CaCl_2 + 6H_2O(g) \quad (240)$$

$$\log_{10} P_{H_2O}(\text{antarcticite}) = 7.39 - 3045(\pm 110)/T \quad (241)$$

$$CaCl_2 \cdot 4H_2O = CaCl_2 + 4H_2O(g) \quad (242)$$

$$\log_{10} P_{H_2O} = 7.50 - 3070(\pm 160)/T \quad (243)$$

$$CaCl_2 \cdot 2H_2O = CaCl_2 + 2H_2O(g) \quad (244)$$

$$\log_{10} P_{H_2O} = 7.44 - 3058(\pm 160)/T \quad (245)$$

$$CaCl_2 \cdot H_2O = CaCl_2 + H_2O(g) \quad (246)$$

$$\log_{10} P_{H_2O} = 7.32 - 3754(\pm 140)/T. \quad (247)$$

Table 14 lists the calculated water vapor dissociation pressures for these magnesium and calcium chloride hydrates and Figure 32 shows the temperature dependent dissociation pressure curve for bischofite, the least stable Mg chloride hydrate. These results show that the magnesium chloride hydrates, like the magnesium sulfate hydrates, are more stable than their Ca-bearing counterparts. However, it is also evident that the calcium chloride hydrates are much more stable than hydrated calcium sulfates. Thus, both hydrated magnesium and calcium chlorides are predicted to be thermodynamically stable under typical Martian surface conditions.

Hydrated Carbonates. As noted earlier, carbonates are believed to be present on the Martian surface. Also, Calvin and King [1991] have recently proposed that several features in the Mariner 6 and 7 spectrometer data are due to hydro-

TABLE 14. Equilibrium Water Vapor Pressures for Hydrated Chlorides on the Martian Surface (215 K)*

Hydrated Chloride	Mineral Name	Water Content(%)	Water Vapor Mixing Ratios and the Range of Values			
$MgCl_2 \cdot 6H_2O$	Bischofite	53%	0.2 ppm	(0.07 ppm	–	0.6 ppm)
$MgCl_2 \cdot 4H_2O$		43%	30 ppb	(10 ppb	–	70 ppb)
$MgCl_2 \cdot 2H_2O$		27%	2 ppb	(1 ppb	–	5 ppb)
$MgCl_2 \cdot H_2O$		16%	0.2 ppb	(0.07 ppb	–	0.4 ppb)
$CaCl_2 \cdot 6H_2O$	Antarcticite	49%	28 ppm	(9 ppm	–	91 ppm)
$CaCl_2 \cdot 4H_2O$		39%	28 ppm	(5 ppm	–	154 ppm)
$CaCl_2 \cdot 2H_2O$		25%	28 ppm	(5 ppm	–	152 ppm)
$CaCl_2 \cdot H_2O$		14%	10 ppb	(3 ppb	–	50 ppb)

*Calculated assuming a total pressure of 6 millibars.

magnesite and artinite, which are hydrated carbonates. We therefore also examined the thermodynamic stability of several common hydrated Ca and Mg carbonates for which data are available. The dehydration equilibria considered and the corresponding water vapor dissociation pressures are

$$CaCO_3 \cdot H_2O = CaCO_3(\text{calcite}) + H_2O(g) \quad (248)$$

$$\log_{10} P_{H_2O} = 7.87 - 2565(\pm 90)/T \quad (249)$$

$$MgCO_3 \cdot 3H_2O = MgCO_3 + 3H_2O(g) \quad (250)$$

$$\log_{10} P_{H_2O} = 7.59 - 2412(\pm 80)/T \quad (251)$$

$$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O = 4MgCO_3 + Mg(OH)_2 + 4H_2O(g) \quad (252)$$

$$\log_{10} P_{H_2O} = 7.51 - 2219(\pm 295)/T \quad (253)$$

$$Mg_2(OH)_2CO_3 \cdot 3H_2O = MgCO_3 + Mg(OH)_2 + 3H_2O(g) \quad (254)$$

$$\log_{10} P_{H_2O} = 8.04 - 2740(\pm 90)/T. \quad (255)$$

At 215 K, the water vapor pressure required for hydromagnesite to be stable is $\sim 1.6 \times 10^{-3}$ bars. This is about 1000 times higher than the typical water vapor content of the Martian atmosphere. The most stable of these four carbonates is artinite, which has a dissociation pressure of $\sim 2 \times 10^{-5}$ bars at 215 K. However, even in this case the maximum water vapor partial pressure observed in the Martian atmosphere is too low to stabilize artinite under typical Martian conditions. Thus, we conclude that hydrated carbonates are only thermodynamically stable under conditions cooler and wetter than on average for Mars. If further work confirms that hydromagnesite and/or artinite are present on the Martian surface, then they are probably fossil weathering products which owe their continued existence to kinetic barriers preventing their dehydration.

Photochemical Weathering Reactions

Hydrogen Peroxide and Other Photochemically Produced Species. As noted earlier, direct evidence for the importance of atmospheric photochemistry on Mars is provided by the observed abundances of O_2 and CO, which are many orders of magnitude larger than the thermochemical equilibrium values at Martian surface temperatures. In addition to their importance for interpreting the abundances of different gases (e.g., O_2, CO, O_3), theoretical models of Martian atmospheric photochemistry also suggest that photochemically driven chemical weathering may be an important process at the Martian surface [e.g., Parkinson and Hunten, 1972; Hunten, 1974; McElroy and Kong, 1976; Kong and McElroy, 1977; McElroy et al., 1977; Shimazaki and Shimizu, 1979]. For example the penetration of solar UV radiation with wavelengths as short as 195 nm to the Martian surface is predicted to lead to the production of significant amounts of several highly reactive species. One of these is hydrogen peroxide (H_2O_2), which is predicted to be produced by the photolysis of water vapor [e.g., Parkinson and Hunten, 1972; Barth et al., 1991]. As shown in Table 15 and Figure 33, the predicted H_2O_2 abundances from several photochemical models are in the range of 30 – 100 ppb. These values are several times smaller than the upper limit of a few times 10^{-7} reported by Bjoraker et al. [1987] from whole-disk spectra. The predicted abundances of some other photochemically produced species are also listed in Table 15. It is interesting to note that (except for O_2), the most abundant of these is H_2. However, molecular hydrogen is probably much less reactive than many of the other molecules produced. These are generally oxidants and may participate in the oxidation of Fe-bearing minerals on the Martian surface.

For example, the Gibbs free energy change for the reaction

$$2Fe_3O_4 + H_2O_2 \rightarrow 3Fe_2O_3 + H_2O \quad (256)$$

is about -326 kJ mole^{-1} at 215 K. Other reactions involving H_2O_2 oxidation of Fe^{2+}-bearing minerals are also energetically very favorable. However, despite the emphasis placed on using peroxides to simulate the results of the *Viking* life detection experiments [e.g., Huguenin, 1982], the oxidation of inorganic, transition metal-bearing minerals by H_2O_2 under Martian surface conditions has not been studied in the laboratory.

Photo-Oxidation of Magnetite. However, some experiments on photochemically driven oxidation of Fe-bearing minerals has been done. This work began in the early 1970's with experiments by Huguenin [1973a,b] on the photostimulated oxidation of magnetite. He reported that magnetite in a simulated Martian atmosphere was rapidly oxidized to hematite when irradiated with a xenon lamp which simulated the solar spectrum. Huguenin's work was later extended to the photostimulated formation of goethite and hydrated clay minerals on Mars [Huguenin, 1974], to the implications of photochemical weathering as a volatile sink [Huguenin, 1976], to the unusual chemical activity observed in the *Viking* biology experiments [Huguenin, 1982; Huguenin et al., 1979], and to heterogeneous catalysis of CO_2 regeneration on Fe-bearing minerals [Huguenin et al., 1977].

Despite Huguenin's claims, experimental studies of photochemical weathering by other investigators have led to mixed results. Some of this work [Morris and Lauer, 1981] was discussed earlier in connection with goethite dehydration on the Martian surface. Other experiments by Morris and Lauer [1980] also studied the effects of UV irradiation on magnetite in simulated Martian atmospheres, but were unable to reproduce Huguenin's results. In these experiments synthetic magnetite powders in pure O_2 ($\sim$100 torr pressure) were irradiated with unfiltered and filtered light from a high pressure xenon arc lamp. The extent of oxidation to hematite was determined from magnetic measurements made on the samples. Morris and Lauer [1980] found no oxidation in experiments run for up to 400 hours except when the unfiltered light from the xenon lamp heated the magnetite samples to temperatures above the threshhold temperature for thermal

TABLE 15. Predicted Abundances of Photochemically Produced Species at the Martian Surface*

Species	$\log_{10}$ Number Density (cm^{-3})	Mixing Ratio	References
H_2	12.5	17 ppm	Shimazaki & Shimizu 1979
H_2O_2	10.1	60 ppb	Shimazaki & Shimizu 1979
	9.7	30 ppb	McElroy et al. 1977
	10.3	100 ppb	Parkinson & Hunten 1972
O_3	9.7	30 ppb	McElroy et al. 1977
	8.3	20 ppb	Parkinson & Hunten 1972
HO_2	8.5	~2 ppb	Shimazaki & Shimizu 1979
			Parkinson & Hunten 1972
	8.1	0.6 ppb	McElroy et al. 1977
O	7.5	~0.2 ppb	McElroy et al. 1977
			Parkinson & Hunten 1972
OH	4.6	$10^{-12.7}$	McElroy et al. 1977
			Shimazaki & Shimizu 1979
	5.2	$10^{-12.1}$	Parkinson & Hunten 1972
H	6.3	$10^{-11.0}$	Parkinson & Hunten 1972
	5.2	$10^{-12.1}$	Shimazaki & Shimizu 1979
NO	7.2–8.9	0.08–4 ppb	Yung et al. 1977
NO_2	7.6	0.2 ppb	Yung et al. 1977

*Volume mixing ratios calculated assuming a total pressure of 6 millibars and a temperature of 215 K.

oxidation in an O_2 atmosphere. However, as noted above, Huguenin [1982] criticized their simulations on the grounds that Morris and Lauer did not run their experiments long enough for any effect to be observed. This criticism is based on Huguenin's claim that the filtered light used by Morris and Lauer has such a low intensity at short wavelengths that any UV driven photo-oxidation will take much longer than the duration of the experiments.

Likewise, Clark et al. [1979] also conducted photochemical weathering experiments that led to negative results. They exposed a variety of putative Martian crustal minerals (e.g., magnetite, basaltic glass, and smectite clay) to UV irradiation in simulated Martian atmospheres but found no evidence for any gaseous and/or solid reaction products different than the starting materials. In these experiments magnetite powders were irradiated in pure O_2 (600 – 730 torr) for up to 713 hours. Again a xenon arc lamp was used in the simulations. Despite the longer irradiation times no photo-oxidation was observed. However, the situation is further complicated by the experiments by M.W. Schaefer ("Low Temperature Oxidation of Magnetite by Ultraviolet Irradiation," unpublished manuscript, MIT, 1981). She also studied magnetite photo-oxidation, but used a Hg lamp instead of a xenon lamp. Mossbauer spectra of the synthetic magnetite sample both before and after the experiments showed an increased Fe^{3+}/Fe^{2+} ratio although the composition of the oxidized sample was uncertain. Thus, to summarize, experimental results on magnetite photo-oxidation are contradictory, although the available evidence suggests that the very rapid photo-oxidation reported by Huguenin [1973a,b] may have been partly due to thermal effects.

Other Photochemical Weathering Experiments. Two other interesting experiments are the work of Blackburn et al. [1979] who reported the photo-oxidation of pyrolusite (β-MnO_2) and the work of Booth and Kieffer [1978] who studied the effects of UV irradiation on carbonate formation. In the former experiments, pyrolusite was irradiated with a xenon arc lamp in either moist or dry CO_2-bearing atmospheres for 215 hours. At the end of this time the samples were tested for their ability to mimic the results of the *Viking* gas exchange experiment. The oxidation state of

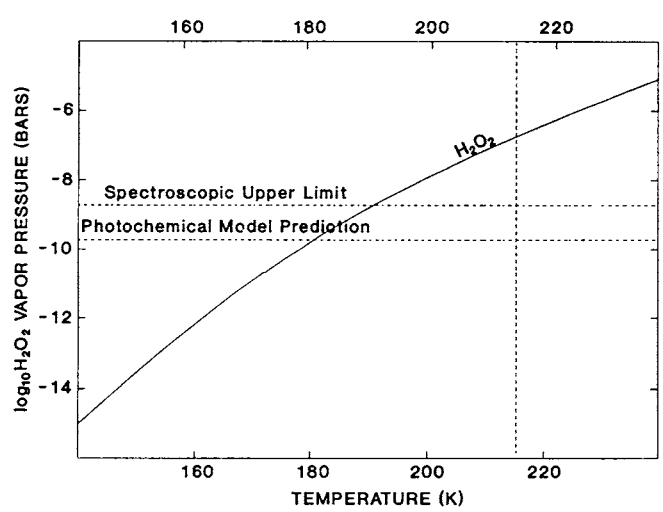

Fig. 33. A comparison of the vapor pressure over solid H_2O_2 with the spectroscopic upper limit from Bjoraker et al. [1987] and the photochemical model predictions of McElroy et al. [1977]. The vertical dashed line represents the mean temperature of 215 K. Hydrogen peroxide, which is predicted to be produced photochemically, may be sufficiently abundant to condense at temperatures of ~190 K and below on the Martian surface.

Mn on the sample surfaces was also studied by using X-ray photoelectron spectroscopy. Blackburn et al. [1979] found that samples irradiated in moist atmospheres could reproduce the O_2 release observed by *Viking* and that the reacted samples were partially oxidized to either Mn^{5+} or to Mn^{6+}.

Booth and Kieffer [1978] irradiated natural basaltic powders in both moist and dry CO_2-bearing gases for periods up to 54 hours. Experiments were also done in the absence of any UV irradiation. In this case a high pressure mercury arc lamp was the irradiation source. Booth and Kieffer concluded that UV irradiation did not measurably affect the carbonate formation rate which they determined as 10^{12-13} molecules cm^{-3} sec^{-1}. However, Stephens and Stevenson [1990] have criticized the work of Booth and Kieffer because the experimental simulations did not proceed long enough for the carbonate formation rate to enter the diffusion controlled regime. We also note that the intensity of short-wavelength ($\lambda < 200$ nm) used in these experiments is very low. This may partially account for the apparent absence of any effects on reaction rates due to UV irradiation.

SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

We have attempted to give a quantitative discussion as well as a critical review of the chemical interactions between the atmosphere and surface of Venus and to briefly contrast these interactions with those taking place between the atmosphere and surface of Mars. The results of our calculations have been used to predict stable minerals and mineral assemblages on the surface of Venus, to determine which, if any, atmospheric gases are being buffered by mineral assemblages on the surface, and to critically review and assess the extensive literature dealing with atmosphere–surface chemistry on Venus. We want to summarize this discussion by presenting what we feel are the important issues facing us today about atmosphere–surface chemistry on Venus and Mars, and to recommend specific experimental, observational, and theoretical studies which can improve our knowledge of these issues.

The important issues in atmosphere–surface chemistry on Venus and our recommendations for addressing these questions include the following:

(1) The mineralogical composition of the surfaces of Venus and Mars is presently unknown. This information is crucial to understanding the chemical interactions between the atmospheres and surfaces of these two planets and needs to be determined by spacecraft missions. We recommend development of a X-ray diffraction experiment suitable for spacecraft operations in order to address this issue. In this regard, we note that Vaniman et al. [1991] have recently discussed development of a combined X-ray diffraction and X-ray fluorescence spacecraft instrument. Many of the questions currently facing us about gas–solid reactions on these two planets can be solved with a knowledge of the presence and abundance of the major rock-forming minerals.

(2) As noted by other authors such as Lewis, the CO_2 pressure on Venus is identical within the uncertainties in the thermodynamic data to the CO_2 equilibrium partial pressure developed by the calcite + wollastonite + quartz assemblage at the mean Venus surface temperature of 740 K. However, the rate of this reaction under Venusian surface conditions is not known and needs to be measured experimentally to determine if this important reaction is indeed capable of buffering CO_2 on Venus. These measurements need to be made so that the dependence of the reaction rate on important variables (e.g., temperature, mineral surface area, water vapor partial pressure, etc.) is determined and can be extrapolated and/or interpolated to Venusian surface conditions. The rate and mechanism of both the decarbonation and carbonation reactions need to be studied.

(3) Several authors [e.g., Florensky et al., 1977; Nozette and Lewis 1982] have proposed that a combination of chemical and physical weathering on mountaintops can provide to the lowlands regions on Venus the calcium-rich mineral assemblages theoretically predicted to be necessary for buffering reactions such as the calcite + wollastonite + quartz equilibrium. However, essentially no information is available on the efficiency of physical weathering for removing the chemically reacted outer layers from mineral grains under Venusian surface conditions. We recommend experimental studies using facilities such as the Venus Wind Tunnel at the NASA Ames Research Center to measure quantitatively these efficiencies.

(4) Chemical equilibrium calculations using the published thermodynamic data on scapolite minerals predict that meionite (CO_3^{2-}–bearing scapolite) and sulfate meionite are unstable on the surface of Venus but that marialite (Cl^-–bearing scapolite) is stable on the surface. However, the Semenov et al. [1981] thermodynamic data on marialite cannot be accepted uncritically and we recommend calorimetric measurements of the low temperature heat capacity, high temperature heat content, and the heat of formation of well characterized natural mineral samples having a known ordering state. These measurements could be supplemented by retrieval of the thermodynamic properties of marialite from phase equilibrium experiments.

(5) The f_{O_2} of the Venusian lower atmosphere and surface is controlled by the CO/CO_2 ratio, and is inside the magnetite stability field. However, as argued by Pieters et al. [1986], spectral reflectivity measurements made by several Venera spacecraft imply that hematite is present on the surface of Venus. This apparent inconsistency with the thermodynamic predictions may reflect kinetic inhibition of the hematite→magnetite conversion or the existence of a stable Fe^{3+}–bearing mineral on the surface of Venus. These questions can be answered by experimental measurements under the appropriate conditions of the rate of the hematite→magnetite conversion and of the kinetics and mechanism of olivine oxidation in CO/CO_2 gas mixtures.

(6) No pure hydrated silicates for which thermodynamic data are available are predicted to be thermodynamically stable on the Venusian surface. The possible exceptions are tremolite and phlogopite which may be stable at altitudes

higher than those observed by the Pioneer Venus radar altimetry experiment. The question of tremolite and phlogopite stability can be clarified by improved measurements of their thermodynamic properties in order to decrease the large uncertainties in the existing thermodynamic data. The recent work by Jenkins et al. [1991] on the thermodynamic properties of synthetic tremolite is an important step in this direction. The question of stabilities of other hydrated silicates can be clarified by experimental studies of the thermodynamic properties of some amphibole and hornblende minerals that are believed to be more stable than the hydrated silicates for which data are available. The amphiboles and hornblendes which we recommend studying are edenite, some members of the richterite family, and some alkali amphiboles [e.g., see Gilbert et al., 1982].

(7) The chemical interactions of sulfur gases and sulfur-bearing minerals on the Venusian surface is still only poorly understood. However, it is nevertheless clear that chemical equilibrium models are inapplicable to sulfur gas–solid chemistry on Venus. Observational data indicate that atmospheric abundance of SO_2 is significantly higher than the predicted chemical equilibrium value. Laboratory reaction rate measurements for one reaction, anhydrite formation from SO_2 + calcite, show that it is too slow to reduce the SO_2 abundance down to the chemical equilibrium value, thus providing a possible explanation for the observations. However, no quantitative kinetic data are available for the reactions of SO_2 with calcium-bearing igneous minerals on the Venusian surface. We recommend experimental measurements of the kinetics and mechanisms of the reactions of SO_2 with diopside, anorthite, and wollastonite under appropriate conditions to enable extrapolation and/or interpolation of the laboratory rate data to Venusian surface conditions.

(8) Radar observations from Earth-based sites, the Pioneer Venus spacecraft, and the Magellan spacecraft show the presence of radar "bright" low emissivity regions in the highland areas of Venus. These areas have been suggested to be pyrite [e.g., Pettengill et al., 1982] and subsequent work suggested a volumetric abundance of ~10–15% [Pettengill et al., 1988]. However, preliminary data on the rate of pyrite and pyrrhotite chemical weathering under Venusian surface conditions [Fegley and Treiman, 1990; Treiman and Fegley, 1991] indicate that these minerals are rapidly weathered on the Venusian surface, and are thus unlikely to be present for extended time periods. In order to resolve this apparent discrepancy we recommend several types of studies. One of these is further laboratory studies of the kinetics of iron sulfide (e.g., pyrite, pyrrhotite) weathering under Venusian surface conditions. Another study is a laboratory investigation of the radar properties of possible analogs to the radar "bright" low emissivity regions on Venus. On the basis of the estimated volumetric abundance of pyrite in radar "bright" low emissivity regions on Venus, analog materials are probably natural samples rich in iron-bearing oxides and sulfides such as lunar basalts rich in ilmenite, magmatic sulfides from terrestrial deposits, and magnetite-rich terrestrial basalts. However, other high dielectric constant phases (e.g., perovskite), which are common accessory minerals in alkaline rocks, carbonatites, and kimberlites should also be considered.

(9) The abundances of HCl and HF in the Venusian atmosphere are probably buffered by mineral assemblages on the Venusian surface, although the assemblages suggested previously in the literature [Lewis, 1970a] are incorrect because they involve thermodynamically unstable or metastable assemblages. We recommend experimental studies of the thermodynamics and kinetics of the new buffers proposed in this paper. All these buffers involve stable mineral assemblages observed in different rock types on the Earth, and thus any experimental studies will yield information relevant to terrestrial petrology as well as to Venus.

The important issues in atmosphere–surface chemistry on Mars and our recommendations for addressing these questions include the following:

(10) Qualitative considerations and the extrapolation of high temperature kinetic data for some gas–solid reactions indicate that thermochemical weathering reactions are probably kinetically inhibited under Martian surface conditions. Furthermore, it is clear that CO_2, the dominant atmospheric gas on Mars, is not in thermochemical equilibrium with pyroxene minerals apparently detected by reflection spectroscopy on the Martian surface. If this were the case, then the Martian atmosphere would be devoid of any CO_2 and the dominant gases would be N_2 and Ar. However, studies of chemical weathering in Antarctic soils and studies of terrestrial weathering products on Antarctic meteorites qualitatively suggest that some thermochemical weathering reactions may occur under Martian surface conditions. We recommend experimental studies of the kinetics for several proposed thermochemical weathering reactions which may occur under Martian conditions. Some candidate reactions include goethite dehydration, siderite oxidation, rhodochrosite oxidation, and formation and dehydration of different hydrated sulfate and chloride minerals.

(11) Theoretical models of Martian atmospheric photochemistry predict that highly reactive species such as H_2O_2, HO_2, OH, and O_3 will be produced at the surface of Mars. The predicted abundance of H_2O_2, which is potentially interesting for oxidation of transition metal-bearing minerals, is slightly less than the current spectroscopic upper limit. We recommend new observations designed to search for H_2O_2 at the predicted abundance levels of 30-100 ppb predicted from these models.

(12) Laboratory studies of photochemical weathering reactions, such as the putative photo-oxidation of magnetite and the putative photo-dehydration of goethite have given both positive and negative results that both support and contradict theoretical expectations that photochemical gas–solid reactions will be important on the Martian surface. We recommend further experimentation, perhaps using surface sensitive analytical techniques, to resolve these ques-

tions. Some candidate reactions include the two mentioned above and possible photochemical oxidation of other transition metal-bearing oxides and silicates.

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