Venus Surface Mineralogy: Observational and Theoretical Constraints

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We utilize Earth-based, Earth-orbital, and spacecraft observations of the atmosphere and surface of Venus, thermodynamic models of atmosphere-lithosphere interactions, and where available kinetic data on relevant gas-solid reactions to place constraints on the mineralogy of the surface of Venus. We discuss which minerals and mineral assemblages are stable on the surface of Venus and which, if any, of these minerals are involved in controlling the abundances of reactive gases in the atmosphere of Venus. We conclude by identifying key issues facing us today about the mineralogy and geochemistry of the surface of Venus and suggest experimental, observational, and theoretical studies that can improve our knowledge of these important questions.

1. INTRODUCTION

The nature of the surface of Venus, Earth's sister planet, has been the subject of much debate and speculation during the past four decades. This debate arose in large part because the surface of Venus is obscured from our view by the global sulfuric acid cloud cover. Thus, during the 1950s and early 1960s, when available data about Venus was limited to Earth-based remote sensing, a wide range of views about the conditions prevailing on the venusian surface were put forward in the scientific literature. As noted by *Lewis* (1971b), these views of Venus ranged from a planet covered by global oceans of carbonic acid, to a planet with 10-km-thick water-ice polar caps and boiling hot equatorial regions, to an extremely hot, dry, wind-swept planet covered by global deserts (e.g., see *Menzel and Whipple,* 1955; *Libby,* 1968a,b; *Öpik,* 1961, respectively, for discussions of these three models).

With the continuing improvements in Earth-based remote sensing and with the advent of space probes that successfully landed on the surface of Venus (e.g., Venera 9, which returned the first pictures of the venusian surface in October 1975), it became clear that many of these early models had to be discarded. We now know that conditions on the surface of Venus are characterized by a high global mean surface temperature of about 740 K, by a high global mean surface pressure of about 95 bar, and by extremely dry conditions with the amount of water vapor at the surface being only ~20 ppm by volume, orders of magnitude lower than the 1-4% by volume water vapor content of the terrestrial troposphere.

However, despite the great advances in our knowledge about conditions on the surface of Venus, many important questions about the nature of the surface still remain unanswered. For example, although radar observations provide evidence for global variations in surface properties (e.g., *Pettengill et al.,* 1982), we still have no direct observations of the mineralogy of the surface of Venus and have only limited information about

the geochemistry at a handful of sites on the surface. Likewise, our knowledge of how the surface chemistry and mineralogy are affected by chemical reactions with the hot, dense, venusian atmosphere, which contains reactive gases such as HF, HCl, and SO_2, is also incomplete. These uncertainties are partially due to a lack of relevant observations, but also arise from conflicts between some of the existing observations.

In this paper we will review work relevant to these fundamental issues about the geochemistry and mineralogy of the surface of Venus. We will use constraints derived from Earth-based, Earth-orbital, and spacecraft observations of the atmosphere and surface of Venus to discuss which minerals and mineral assemblages are stable on the surface of Venus and to determine which, if any, of these minerals are involved in regulating the abundances of reactive gases in the venusian atmosphere. Throughout our discussion we will use chemical thermodynamic models to interpret the observational data. A detailed discussion of chemical thermodynamic modeling of atmosphere-lithosphere interactions on Venus has recently been given by *Fegley and Treiman* (1991) and we therefore make use of their results in this paper. Finally, we will conclude by identifying key issues facing us today about the geochemistry and mineralogy of the surface of Venus and will suggest theoretical, experimental, and observational studies that can improve our knowledge of these important questions.

2. CARBONATE MINERALS

We will start by considering observational constraints on carbonate minerals, which frequently have been proposed to be present on Venus (e.g., *Adamcik and Draper,* 1963; *Khodakovsky et al.,* 1979; *Lewis,* 1968, 1970, 1971a; *Mueller,* 1963, 1964a; *Vinogradov and Volkov,* 1971).

The most direct information on the geochemistry of the surface of Venus, the trace-element and major-element analyses performed by the Soviet Venera and Vega spacecraft, provide

only weak evidence for the presence of carbonates. As Table 1 shows, seven different spacecraft have performed analyses at different surface sites. Four analyses, done by γ-ray spectroscopy, only give abundances for K, U, and Th (Table 2), while three other analyses, done by X-ray fluorescence (XRF) spectroscopy, give major-element abundances (Table 3). The major-element compositions in Table 3 have been compared to terrestrial rock types (e.g., *Barsukov et al.*, 1986; *Volkov et al.*, 1986). The possible correspondence of the Venera 13 analysis with terrestrial alkaline rocks (e.g., olivine basalt) and the Venera 14 analysis with more common terrestrial rock types (e.g., MORB) is given in Table 3. The Venera and Vega XRF experiments were sensitive only to elements heavier than Mg, and were not able to detect C. Thus, the normative compositions derived from these elemental analyses (Table 4) do not contain any carbonate.

Because of the instrumental limitations, the XRF analyses at best provide indirect evidence for the presence of carbonates. None of the analyses in Table 3 total 100%, even after the Na abundances calculated by *Surkov et al.* (1984, 1986) are taken into account. Carbon is the only other major element lighter than Mg that is a plausible constituent of minerals on the venusian surface. Nitrogen can be ruled out because conditions are too hot for either ammonium or nitrate minerals to be stable and are too oxidizing for nitride minerals to be stable (*Fegley and Treiman*, 1991). Likewise, as we discuss later, hydrated minerals can be ruled out because no hydrated minerals (e.g., amphiboles, micas, clays, etc.) are stable under venusian surface conditions. Thus, taking the mass deficits in Table 3 at face value leads to the conclusion that several percent by mass of carbonate is present on the venusian surface. For example, if calcite ($CaCO_3$) were present, then ~25% of all Ca in the Venera 13 analysis, ~12% of all Ca in the Venera 14 analysis, and ~58% of all Ca in the Vega 2 analysis would have to be in $CaCO_3$ to account for the observed mass deficits. However, mass deficits may plausibly result from sampling techniques rather than the presence of carbonates.

A second independent, but also indirect, line of evidence for carbonates on Venus comes from the interpretation of Magellan radar observations of fluvial-like geologic features on Venus. *Kargel et al.* (1991) have proposed carbonatite magmas as one possible phase responsible for producing these features. Kimberlite magmas, which also contain carbonate (e.g., *Mitchell*, 1986), have been suggested by *Head et al.* (1991) to account for other geologic features observed by the Magellan spacecraft.

The most persuasive, albeit indirect, evidence for the presence of carbonates on Venus comes from comparisons of the observed CO_2 pressure at the surface of Venus with the CO_2 pressures generated by different carbonate-silicate chemical equilibria. As Table 5 shows, CO_2 is the major gas in the atmosphere of Venus, and it would be somewhat surprising if CO_2 were not involved in chemical reactions with reactive minerals on the hot surface of the planet. In fact, *Urey* (1952, 1959) proposed that carbonate-silicate equilibria could regulate the CO_2 pressure in a planetary atmosphere. However, he

TABLE 1.   Locations of space probes performing geochemical analyses of the surface of Venus[*].

Probe	Latitude (°)	Longitude (°)	Altitude (km)[†]
Venera 8	-10	335	0.4 ± 0.1
Venera 9	31.7	290.8	1.6 ± 0.4
Venera 10	16.0	291.0	1.0 ± 0.6
Venera 13	-7.6	303.5	0.9 ± 0.3
Venera 14	-13.2	310.1	0.5 ± 0.3
Vega 1	8.1	176.7	-0.3 ± 0.1
Vega 2	-7.2	179.4	0.8 ± 0.4

[*] Modified from *Garvin et al.* (1984).
[†] Relative to a median radius of 6051.5 km.

TABLE 2.   Gamma ray analyses of the surface of Venus (*Surkov et al.*, 1987).

Probe	K (%)	U (ppm)	Th (ppm)	K/U Ratio
Venera 8	4.0 ± 1.2	2.2 ± 0.7	6.5 ± 0.2	$18,200^{+16,500}_{-8500}$
Venera 9	0.47 ± 0.08	0.60 ± 0.16	3.65 ± 0.42	$7,800^{+4700}_{-2700}$
Venera 10	0.30 ± 0.16	0.46 ± 0.26	0.70 ± 0.34	$6,500^{+16,500}_{-4600}$
Vega 1	0.45 ± 0.22	0.64 ± 0.47	1.5 ± 1.2	$7,000^{+32,400}_{-4900}$
Vega 2	0.40 ± 0.20	0.68 ± 0.38	2.0 ± 1.0	$5,900^{+14,100}_{-4000}$

TABLE 3.   Composition of the surface of Venus (*Surkov et al.*, 1984, 1986) and comparisons to terrestrial rock types (data from *Carmichael et al.*, 1974).

Component	Chemical Composition (Mass % ± 1σ)				
	Venera 13	Venera 14	Vega 2[*]	MORB	Alkali Olivine Basalt
SiO_2	45.1 ± 3.0	48.7 ± 3.6	45.6 ± 3.2	49.02	46.29
TiO_2	1.59 ± 0.45	1.25 ± 0.41	0.2 ± 0.1	1.46	1.90
Al_2O_3	15.8 ± 3.0	17.9 ± 2.6	16 ± 1.8	18.04	17.17
FeO	9.3 ± 2.2	8.8 ± 1.8	7.7 ± 1.1	7.8	12.83
MnO	0.2 ± 0.1	0.16 ± 0.08	0.14 ± 0.12	0.13	0.19
MgO	11.4 ± 6.2	8.1 ± 3.3	11.5 ± 3.7	7.85	6.95
CaO	7.1 ± 0.96	10.3 ± 1.2	7.5 ± 0.7	11.51	7.31
Na_2O[†]	2.0 ± 0.5	2.4 ± 0.4	2.0	2.92	3.90
K_2O	4.0 ± 0.63	0.2 ± 0.07	0.1 ± 0.08	0.08	1.48
SO_3	1.62 ± 1.0	0.88 ± 0.77	4.7 ± 1.5	—	—
Total	98.1%	98.7%	95.4%	98.81	98.52

[*] The Vega 2 analysis also has the following upper limits: <0.3% Cl, Cu, Pb; <0.2% Zn; <0.1% Sr, Y, Zr, Nb, Mo; <0.08% As, Se, Br.
[†] Not detected; calculated by Surkov et al.

TABLE 4. Normative mineral compositions (*Barsukov et al.*, 1986; *Surkov et al.*, 1984).

Mineral	Venera 13	Venera 14	Vega 2
Orthopyroxene	—	18.2	25.4[*]
Clinopyroxene	—	—	2.5[†]
Diopside	10.2	9.9	—
Olivine	26.6	9.1	13.9[‡]
Anorthite	24.2	38.6	38.3
Albite	3.0	20.7	18.9
Orthoclase	25.0	1.2	0.5
Nepheline	8.0	—	—
Ilmenite	3.0	2.3	0.5
Total	100.0	100.0	100.0

[*] The orthopyroxene is 75 mol% enstatite.
[†] The clinopyroxene is 1.2 mol% wollastonite, 0.9 mol% enstatite, and 0.4 mol% ferrosilite.
[‡] The olivine is 75 mol% forsterite.

TABLE 5. Composition of the lower atmosphere of Venus[*].

Gas	Abundance	References and Notes
CO_2	96.5 ± 0.8%	*Adams and Dunham* (1932)
		Von Zahn et al. (1983)
N_2	3.5 ± 0.8%	*Von Zahn et al.* (1983)
	4.0 ± 2.0%	0-22 km; *Hoffman et al.* (1980a,b)
	4.0 ± 0.3%	0-22 km; *Istomin et al.* (1979)
	3.54 ± 0.04%	42 km; *Oyama et al.* (1980)
	3.41 ± 0.01%	22 km; *Oyama et al.* (1980)
	2.5 ± 0.3%	22-42 km; *Gel'man et al.* (1979)
SO_2	185 ± 43 ppm	22 km; *Oyama et al.* (1980)
	130 ± 35 ppm	≤42 km; *Gel'man et al.* (1979)
	(30-50) ppm	25-40 km; *Berto et al.* (1987)
H_2O	150 ppm	42 km; *Moroz et al.* (1979)
	60 ppm	22 km; *Moroz et al.* (1979)
	20 ppm	0 km; *Moroz et al.* (1979)
	40 ppm	35-45 km; *Bézard et al.* (1990)
CO	45 ± 10 ppm	cloud top; *Connes et al.* (1968)
	51 ppm	cloud top; *Young* (1972)
	30 ± 18 ppm	42 km; *Oyama et al.* (1980)
	20 ± 3 ppm	22 km; *Oyama et al.* (1980)
	28 ± 7 ppm	36-42 km; *Gel'man et al.* (1979)
	17 ± 1 ppm	12 km; *Marov et al.* (1989)
	45 ppm	35-45 km; *Bézard et al.* (1990)
H_2S[†]	3 ± 2 ppm	<20 km; *Hoffman et al.* (1980a,b)
HDO	1.3 ± 0.2 ppm	*DeBergh et al.* (1991)
HCl	0.6 ± 0.12 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	35-45 km; *Bézard et al.* (1990)
COS	0.3 ppm	35-45 km; *Bézard et al.* (1990)
S_{1-8}	20 ppb	≤50 km; *Moroz et al.* (1980)
		≤50 km; *San'ko* (1980)
	(2-10) ppm	25-40 km; *Berto et al.* (1987)
SO	20 ± 10 ppb	cloud top; *Na et al.* (1990)
HF	$5^{+5}_{-2.5}$ ppb	cloud top; *Connes et al.* (1967)
	10 ppb	cloud top; *Young* (1972)
	4.5 ppb	35-45 km; *Bézard et al.* (1990)

[*] Excluding the noble gases.
[†] Reported as a preliminary value. *Oyama et al.* (1980) reported an upper limit of 2 ppm at ≤22 km altitude.

dismissed the importance of this mechanism for Venus because the low surface temperature accepted at that time for Venus led to large disagreements between the equilibrium CO_2 pressures from the chemical reactions and the observed CO_2 pressure in the atmosphere of Venus.

After spacecraft measurements proved the existence of high surface temperatures on Venus, this disagreement disappeared because the CO_2 pressures generated by reactions such as

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2 \qquad (1)$$

$$\log_{10} P_{CO_2} \text{ (bar)} = 7.97 - 4456(\pm 98)/T \qquad (2)$$

$$MgCO_3 + MgSiO_3 = Mg_2SiO_4 + CO_2 \qquad (3)$$
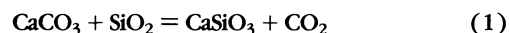
$$\log_{10} P_{CO_2} \text{ (bar)} = 8.85 - 4903(\pm 120)/T \qquad (4)$$

$$2CaMg(CO_3)_2 + SiO_2 = 2CaCO_3 + Mg_2SiO_4 + 2CO_2 \qquad (5)$$

$$\log_{10} P_{CO_2} \text{ (bar)} = 8.95 - 4735(\pm 122)/T \qquad (6)$$

at temperatures of 660-740 K are similar to the observed CO_2 pressure at the surface of Venus (e.g., see Figs. 1-3). This correspondence led several theorists (e.g., *Adamcik and Draper*, 1963; *Lewis*, 1968, 1970; *Mueller*, 1963, 1964a) to propose that the CO_2 pressure in the atmosphere of Venus was regulated by chemical reactions between mineral assemblages on the surface of Venus. In fact, *Mueller* (1963) noted that the temperature on the surface of Venus "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."
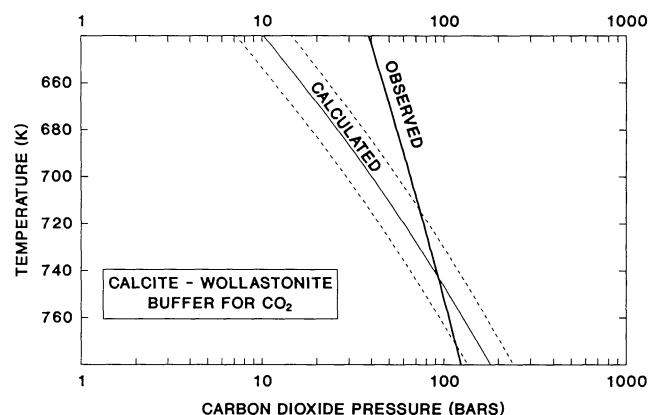

Fig. 1. A comparison of the observed and calculated CO_2 pressures at the surface of Venus. The observed CO_2 partial pressure is simply 0.965 times the total pressure from *Seiff* (1983). The calculated CO_2 pressure is for reaction (1). The dashed lines show the range of calculated CO_2 pressures allowed by the uncertainties in the thermodynamic data. The calculated and observed curves intersect at 740 ± 30 K (0 ± 4 km). Refer to Fig. 4 to relate temperatures to altitudes on the surface of Venus. From *Fegley and Treiman* (1991).
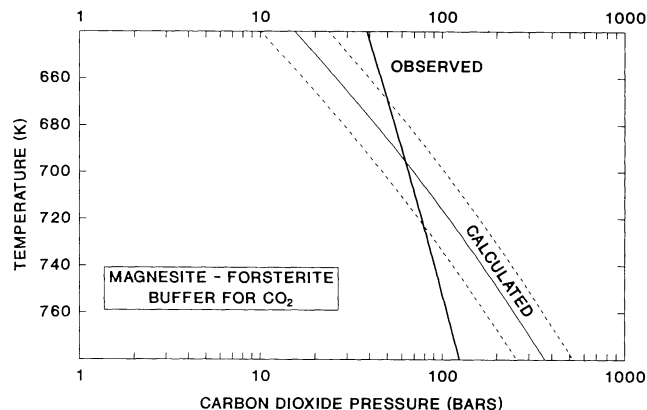
Fig. 2. A comparison of the CO_2 pressure calculated for reaction (3) with the observed CO_2 pressure at the surface of Venus. The dashed lines show the range of calculated CO_2 pressures allowed by the uncertainties in the thermodynamic data. The two curves intersect at 700 ± 30 K (5 ± 4 km). Magnesite is apparently stable only at cooler temperatures (higher altitudes) than calcite, although their stability fields overlap within the formal uncertainties of the thermodynamic data. From *Fegley and Treiman* (1991).
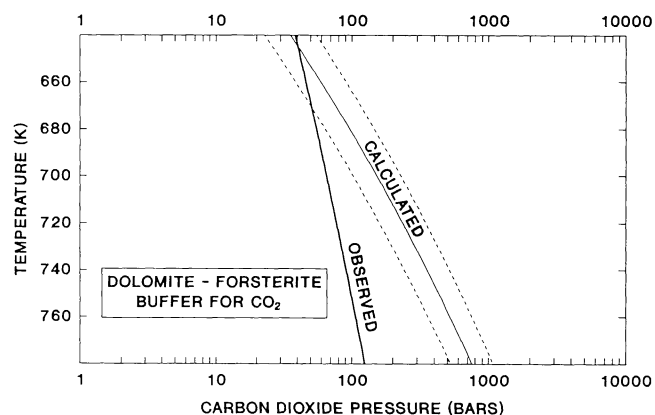
Fig. 3. Same as in Fig. 2 but for reaction (5). The intersection of the two curves is at 645 ± 25 K (12 ± 3 km). Dolomite is probably restricted to only the coolest temperatures (highest altitudes) on Venus. From *Fegley and Treiman* (1991).

As Fig. 4 shows, the range of temperatures considered in Figs. 1-3 corresponds to the range of temperatures at different altitudes on the surface of Venus. Thus, calcite is predicted to be stable over almost the entire surface of Venus. In contrast, magnesite ($MgCO_3$) and dolomite [$CaMg(CO_3)_2$] are apparently stable only at higher altitudes, which make up a much more limited fraction of the total surface area. However, as shown in Figs. 1-3, the uncertainties in the thermodynamic data translate into large uncertainties in the altitude ranges within which the different carbonate minerals first become stable.
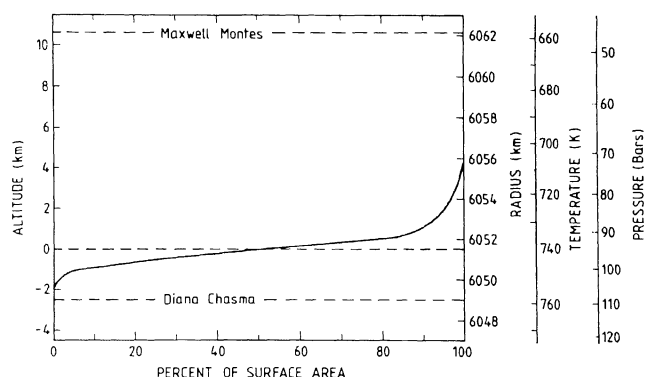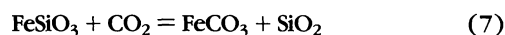

Fig. 4. Surface area distribution on Venus as a function of altitude. The vertical scales indicate the altitude from the median planetary radius of 6051.5 km and the atmospheric temperature and pressure. The highest (Maxwell Montes) and lowest (Diana Chasma) points observed by Pioneer Venus are also 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. From *Fegley and Treiman* (1991).

The altitude-dependent, or hypsometric, control of mineral stabilities on the surface of Venus was probably first discussed by *Florensky et al.* (1977) and later studied quantitatively by *Nozette and Lewis* (1982), who considered a few reactions involving carbonates, hydrated silicates, and halogen-bearing minerals. The basis of this concept is simply that the variations in temperature and pressure over the surface of Venus (from about 740 K and 95 bar in the lowlands to about 660 K and 50 bar at the top of Maxwell Montes) will lead to different thermodynamic stability fields for different minerals. As we shall see later, the hypsometric control of mineral stabilities may play an important role in the origin of the high-radar-reflectivity regions found at high altitudes on Venus. However, it is also important to note that the altitude-dependent temperature variations over the surface of Venus may also lead to kinetic control of mineral stabilities because of the exponential dependence of reaction rates on temperature. Thus for sufficiently large activation energies, chemical weathering reactions, such as equations (3) and (5) above, will proceed much more slowly in the cooler highlands than in the hotter plains.

At present, these qualitative considerations cannot be quantified because the required kinetic data have not been measured under appropriate conditions. Several kinetic studies have in fact been done on the calcite-wollastonite reaction (e.g., *Jander*, 1927; *Repa*, 1954; *Gordon*, 1971; *Kridelbaugh*, 1973; *Tanner et al.*, 1985), but none of the studies measured the specific reaction rate (molecules cm^{-2} s^{-1}) required to calculate how fast the reaction will take place on the venusian surface. In some cases (e.g., *Jander*, 1927) the experiments were done under conditions that allowed the formation of

several other calcium silicates in addition to wollastonite, while in other cases (e.g., *Repa*, 1954) only qualitative data were reported. The more recent studies by *Gordon* (1971), *Kridelbaugh* (1973), and *Tanner et al.* (1985) do not have these problems. However, with the exception of the work of *Kridelbaugh* (1973), the kinetic studies have been done with binary CO_2-H_2O mixtures containing percent levels of H_2O, far above the amounts actually present in the lower atmosphere of Venus. Unfortunately, *Kridelbaugh's* (1973) study, which was done under anhydrous conditions, has been questioned by *Tanner et al.* (1985) on several grounds, and is probably also inappropriate for our purposes. Thus new kinetic studies are necessary before questions about the kinetic control of carbonate mineral stability in the venusian highlands can be quantitatively addressed.

At this point we discuss whether or not other carbonates in addition to calcite, magnesite, and dolomite are to be expected on the surface of Venus. *Lewis* (1970) considered the stability of siderite ($FeCO_3$) and *Fegley and Treiman* (1991) considered the stability of rhodochrosite ($MnCO_3$). These carbonates are interesting because Fe and Mn compounds are potential candidates for the high-radar-reflectivity materials seen at high altitudes on Venus (e.g., *Pettengill et al.*, 1988; *Garvin et al.*, 1985a,b). Siderite and rhodochrosite could form by reactions such as

$$FeSiO_3 + CO_2 = FeCO_3 + SiO_2 \qquad (7)$$

$$\log_{10}P_{CO_2} (bar) = 8.46 - 3088(\pm179)/T \qquad (8)$$

$$Fe_2SiO_4 + 2CO_2 = 2FeCO_3 + SiO_2 \qquad (9)$$

$$\log_{10}P_{CO_2} (bar) = 8.55 - 3111(\pm130)/T \qquad (10)$$

$$MnSiO_3 + CO_2 = MnCO_3 + SiO_2 \qquad (11)$$
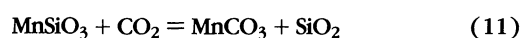
$$\log_{10}P_{CO_2} (bar) = 8.84 - 4405(\pm119)/T \qquad (12)$$

$$Mn_2SiO_4 + 2CO_2 = 2MnCO_3 + SiO_2 \qquad (13)$$

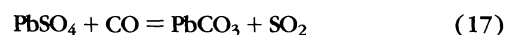$$\log_{10}P_{CO_2} (bar) = 8.79 - 4388(\pm119)/T \qquad (14)$$

The lowest equilibrium CO_2 pressures required for siderite and rhodochrosite to be stable will occur if pure Fe silicates and Mn silicates are available for reaction. Of course, this is unrealistic because ferrosilite ($FeSiO_3$) is unstable in nature and fayalite (Fe_2SiO_4), rhodonite ($MnSiO_3$), and tephroite (Mn_2SiO_4) are expected to be present in solid solution in olivine. However, even in this idealized case, comparison of the equilibrium CO_2 pressures for these reactions with the observed CO_2 pressure at the surface of Venus shows that neither siderite nor rhodochrosite are thermodynamically stable on the venusian surface.

Other potential carbonate-forming elements such as Pb, Sr, and Zn are present at low levels in average venusian rocks and soil (e.g., see the Vega 2 analysis in Table 3), and their carbonates would not normally be expected to be important even if stable. However, because cerussite ($PbCO_3$) has a room-temperature dielectric constant of ~20 at frequencies of 100-1000 MHz (*Church et al.*, 1988; *Young and Frederikse*, 1973), its stability was also evaluated by using the reactions

$$PbSiO_3 + CO_2 = PbCO_3 + SiO_2 \qquad (15)$$
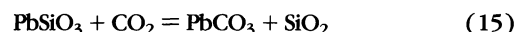
$$\log_{10}P_{CO_2} (bar) = 7.92 - 3727(\pm241)/T \qquad (16)$$

$$PbSO_4 + CO = PbCO_3 + SO_2 \qquad (17)$$

$$\log_{10}K_{17} = 1.72 - 1803(\pm99)/T \qquad (18)$$

where the thermodynamic data were taken from *Robie et al.* (1979) and the JANAF Tables (*Chase et al.*, 1985). In the case of reaction (15), when we assume that pure $PbSiO_3$ is present, which leads to the lowest equilibrium CO_2 pressure, we find that $PbCO_3$ is unstable anywhere on the surface of Venus. At high altitudes (T ~ 660 K) the equilibrium CO_2 pressure is about 190 bar, or almost four times higher than the observed value, and in the lowlands at 740 K the discrepancy is even worse. In the case of reaction (17), which is considered because anglesite ($PbSO_4$) is a common Pb-bearing mineral on the Earth, we also find that $PbCO_3$ is unstable over the entire surface of Venus.

In summary, we conclude that the only carbonates that are likely to be found on the surface of Venus are calcite, at almost all altitudes, and magnesite and dolomite, but only at higher altitudes.

3. IRON-BEARING MINERALS

We next consider the types of Fe-bearing minerals that may be present on the surface of Venus. Not surprisingly, the Venera 13, Venera 14, and Vega 2 XRF analyses of the surface of Venus showed that Fe is one of the major elements present at levels of a few mass percent. Unfortunately, these analyses provide very little information about the actual Fe-bearing minerals or about the oxidation state of Fe in these minerals. Additional constraints derived from other spacecraft measurements and from thermodynamic models of atmosphere-lithosphere interactions must be used in order to deduce which Fe-bearing minerals are likely to be present.

3.1. Iron Oxides

In an attempt to obtain information about the oxidation state of Fe minerals on the surface of Venus, *Pieters et al.* (1986) combined data from the Venera 9/10 wide-angle photometer and the Venera 13/14 camera to produce a reflection spectrum of the venusian surface in the 0.54-1.0-μm region. Their results, reproduced in Fig. 5, show that at visible wavelengths the spectral reflectance of the venusian surface is not diagnostic about the Fe oxidation state, with either Fe^{2+}- or Fe^{3+}-bearing phases being acceptable. However, at longer wavelengths in the near-infrared, the high reflectance apparently requires Fe^{3+}-bearing minerals such as hematite (Fe_2O_3). This conclusion is somewhat surprising because other spacecraft measurements and thermodynamic equilibrium predictions indicate that the f_{O_2} at the surface of Venus is more reducing than that at the magnetite-hematite (MH) phase boundary.
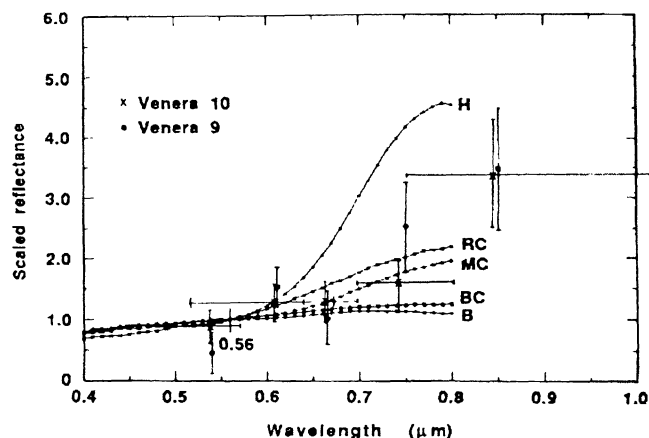
Fig. 5. Reflection spectra of the venusian surface at the Venera 9/10 sites are compared with the reflection spectra of terrestrial mineral and rock samples. H is hematite, RC is red cinder, MC is maroon cinder, B is basalt, and BC is black cinder. From *Pieters et al.* (1986).

For example, the "Contrast" experiment on Venera 13/14 (*Florensky et al.,* 1983; *Volkov et al.,* 1986) qualitatively measured the f_{O_2} at the surface of Venus from the color change that took place on an indicator plate as a result of the chemical reactions

$$Na_4V_2O_7 + CO_2 + CO = V_2O_4 + 2Na_2CO_3 \qquad (19)$$

$$Na_4V_2O_7 + 2CO = V_2O_3 + 2Na_2CO_3 \qquad (20)$$
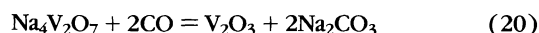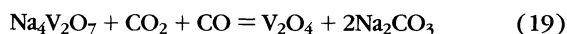
This experiment indicated $f_{O_2} \leq 10^{-21}$ bar, which (as illustrated by Fig. 6) is inside the magnetite stability field.

The qualitative measurement by the "Contrast" experiment is in good agreement with the f_{O_2} calculated from the observed CO/CO_2 ratio in the lower atmosphere of Venus. *In situ* measurements of the CO abundance in the lower atmosphere of Venus have been made by the Pioneer Venus and Venera 11 and 12 spacecraft. These data, which are summarized in Table 5, show that the CO abundance in the lower atmosphere ranges from about 30 ppm at 42 km altitude to about 17 ppm at 12 km altitude. 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 about 13 ppm, which corresponds to $f_{O_2} \sim 10^{-21.2}$ bar. Essentially the same oxygen fugacity is calculated by simply assuming that the CO abundance is constant at 20 ppm from 22 km down to the surface. (Within the stated uncertainties, the Pioneer Venus measurement of 20 ± 3 ppm CO at 22 km and the Venera 11/12 measurement of 17 ± 1 ppm CO at 12 km are identical, thus supporting this assumption.) In this case the temperature-dependent expression for the oxygen fugacity is

$$\log_{10} f_{O_2} = 18.57 - 29621(\pm 19)/T \qquad (21)$$

and the calculated f_{O_2} at the surface of Venus is $\sim 10^{-21.5}$ bar.

Thus, qualitative measurements of the f_{O_2} at the surface of Venus and quantitative measurements of the CO/CO_2 ratio in the lower atmosphere of Venus both indicate that the surface of Venus lies within the magnetite stability field. How then can we explain the apparent discrepancy with the results of *Pieters et al.* (1986)?

One possibility suggested by *Pieters et al.* (1986) is the existence of a more oxidizing environment at the surface of Venus. This explanation requires us to reject the results of the "Contrast" experiment; it also requires that the CO mixing ratio be reduced to ~4 ppm at the surface of Venus. This explanation appears unlikely but cannot be quantitatively evaluated until either the CO mixing ratio or the oxygen fugacity has been measured quantitatively in the 0-12-km-altitude region.

A second possibility, also originally proposed by *Pieters et al.* (1986), is that the surface mineralogy of Venus may be incompletely equilibrated with the overlying atmosphere. This suggestion is plausible for reactions with sufficiently large activation energies, but at present cannot be quantitatively evaluated for Fe-bearing minerals because the required kinetic data are unavailable. However, we point out that the magnetite → hematite conversion is known to be a sluggish reaction below 1000 K on a laboratory timescale (*O'Neill,* 1988; *Hemingway,* 1990).

A third possibility, suggested by *Fegley and Treiman* (1991), is that a stable Fe^{3+} mineral may be produced as a result of chemical weathering reactions on the surface of Venus. *Fegley*
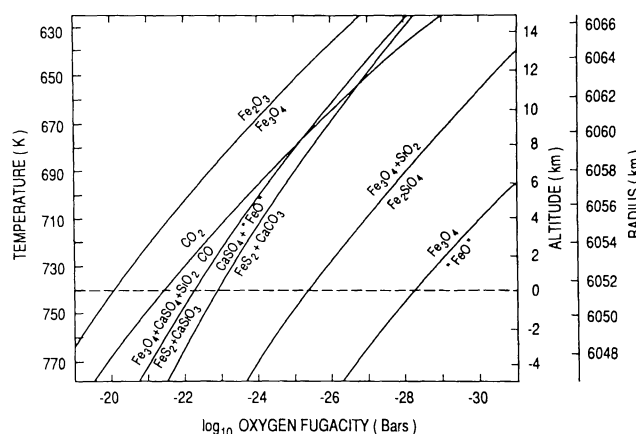

Fig. 6. The temperature-dependent oxygen fugacity (CO/CO_2) in the lower atmosphere of Venus is compared to the oxygen fugacities buffered by different iron-bearing mineral assemblages that may exist on the surface of Venus. Mineral assemblages to the right of the Venus atmosphere curve (CO/CO_2) are 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 ($Fe_{0.947}O$) 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. From *Fegley and Treiman* (1991).

and Treiman (1991) used the available thermodynamic data for common ferric minerals [acmite $NaFe^{3+}Si_2O_6$, magnesioferrite $MgFe_2^{3+}O_4$, and epidote $Ca_2Fe^{3+}Al_2Si_3O_{12}(OH)$] to test this idea, but found that none of these three minerals would be stable. Unfortunately, no thermodynamic data are available to calculate the stabilities of many other ferric minerals. *Fegley and Treiman* (1991) also pointed out that laihunite (ideally $Fe^{2+}Fe_2^{3+}Si_2O_8$) is an interesting candidate mineral. Laihunite is a nonstoichiometric distorted olivine-type mineral found in nature and is produced by the oxidation in air of synthetic fayalite (*Kitamura et al.*, 1984; *Kondoh et al.*, 1985). Laihunite might be produced on Venus by reactions such as

$$6Fe_2^{2+}SiO_4 + 4CO_2 = 3Fe^{2+} Fe_2^{3+}Si_2O_8 + Fe_3O_4 + 4CO \quad (22)$$
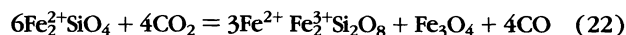
but no experimental or theoretical data are available to assess this suggestion at present.

3.2. Iron-bearing Silicates

Ferromagnesian silicates (such as Fe-bearing olivine and low-Ca pyroxene) on the surface of Venus can react with the CO_2 and CO in the overlying atmosphere. As a result, the amount of Fe_2SiO_4 dissolved in olivine and $FeSiO_3$ dissolved in low-Ca pyroxene can vary as a function of altitude on the planet because reactions exemplified by

$$2CO_2 + 3Fe_2SiO_4 = 2Fe_3O_4 + 3SiO_2 + 2CO \quad (23)$$

$$CO_2 + 3FeSiO_3 = Fe_3O_4 + 3SiO_2 + CO \quad (24)$$
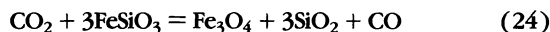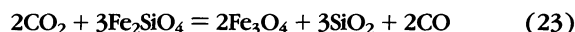
will distribute Fe between magnetite and the silicate minerals. Using thermodynamic data for the pure endmember minerals and activity-composition models from the literature (*Robie et al.*, 1979; *Helgeson et al.*, 1978; *Wood*, 1987), *Fegley and Treiman* (1991) calculated the following equations for the temperature-dependent variations in the fayalite (X_{Fa}) and ferrosilite (X_{Fs}) mole fractions in olivine and low-Ca pyroxene on the surface of Venus

$$\log_{10}a_{Fa} = -2.76 + 1060(\pm160)/T \quad (25)$$

$$\log_{10}a_{Fa} = \log_{10}X_{Fa}^2 + (1 - X_{Fa})^2(1 + 2X_{Fa}) \cdot 438/T \quad (26)$$

$$\log_{10}a_{Fo} = \log_{10}X_{Fo}^2 + (1 - X_{Fo})^2(1 - X_{Fo}) \cdot 874/T \quad (27)$$

$$\log_{10}a_{Fs} = \log_{10}X_{Fs} = -1.326 + 496(\pm146)/T \quad (28)$$

Their results, displayed in Table 6, 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 of Venus than in the lowland regions. Thus, in the lowland plains at a temperature of ~740 K, olivine containing up to 9-15 mol% fayalite and low-Ca pyroxene containing up to 14-35 mol% ferrosilite are predicted to be stable, while at the top of Maxwell Montes where T ~ 660 K, olivine containing up to 13-17 mol% fayalite and low-Ca pyroxene containing up to 16-44 mol% ferrosilite are predicted to be stable. Parenthetically we also note that the normative olivine composition with 25 mol% fayalite that was calculated for the Vega 2 XRF analysis (Table 4) is thermodynamically unstable at that site (~0.8 km) and would oxidize to a mixture of magnetite + more forsteritic olivine.

3.3. Iron Sulfides

In the early 1980s, radar observations by the Pioneer Venus spacecraft apparently provided evidence for the presence of iron sulfides on Venus (*Pettengill et al.*, 1982). It was observed that high-altitude regions on Venus displayed significantly higher radar reflectivities and backscatter than the venusian lowlands (e.g., see Table 7). Pettengill and colleagues modeled the radar observations in a series of papers (*Pettengill et al.*, 1982, 1983, 1988; *Ford and Pettengill*, 1983) and suggested that the high-reflectivity regions consisted of inclusions of high dielectric material(s) embedded in a rocky matrix. They also derived the bulk dielectric constant and corresponding volume fraction of the conductive phase for different regions on Venus. As shown in Table 7, the bulk dielectric constant ϵ for the venusian lowlands is about 5 and only a small amount of a conductive phase is required. However, at altitudes of 4 km and above, dielectric constants of ~20-40 and ~10-15% of a conductive phase are implied by the radar data. (It is interesting to note that even if all S in the Venera 13, Venera 14, or Vega 2 analyses is arbitrarily assumed to be present as pyrrhotite or as pyrite, not enough is present to produce this large volume fraction of conductive phase.)

TABLE 6. Predicted composition of olivine and pyroxene on the surface of Venus (*Fegley and Treiman*, 1991).

Altitude (km)	Temperature (K)	$\log_{10}f_{O_2}$ (bars)	Olivine Mole % Fa and Range		Pyroxene Mole % Fs and 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)

TABLE 7.   Electromagnetic properties of the surface of Venus (*Pettengill et al.*, 1988).

Location	Altitude (km)	Radar Reflectivity (ρ_0)	Radio Emissivity (e)	Dielectric Permittivity (ϵ)	Volume % of Conductive Phase
Average Lowlands	0	0.14 ± 0.03	0.86 ± 0.04	5.0 ± 0.9	$0.0(+0.7)$
Thetis Regio	4	0.37 ± 0.08	0.60 ± 0.07	20.5 ± 9.0	8.6 ± 3.5
Ovda Regio	5	0.39 ± 0.05	0.55 ± 0.06	24.3 ± 8.8	10.0 ± 3.0
Ozza Mons	5	0.40 ± 0.05	0.61 ± 0.04	21.6 ± 6.2	9.0 ± 2.3
Rhea Mons	5	0.35 ± 0.04	0.70 ± 0.06	—	—
Theia Mons	5	0.43 ± 0.05	0.61 ± 0.04	22.8 ± 6.4	9.5 ± 2.3
Maat Mons	6	0.40 ± 0.05	0.76 ± 0.07	21.6 ± 7.2	9.0 ± 2.7
Maxwell Montes	9	>0.4	0.50 ± 0.07	38.7 ± 15.0	13.8 ± 3.7

More recently, the initial Magellan radar observations of Venus have provided additional information about high-radar-reflectivity regions at high altitudes on Venus. For example, *Pettengill et al.* (1991) reported that some areas around Maxwell Montes have emissivities of 0.35 and dielectric constants as high as 87. Also, *Tyler et al.* (1991) report that most regions above an altitude of 6055 km show low emissivities.

As mentioned above, *Pettengill et al.* (1982) interpreted the radar data as evidence for pyrite FeS_2 at high altitudes on Venus. However, other phases such as magnetite, hematite, ilmenite, Mn minerals, and pyrrhotite ($Fe_{1-x}S$) have also been suggested as potential candidates for the high dielectric material(s). Magnetite is in fact predicted to be stable on the surface of Venus. But how likely are iron sulfides?

The chemistry of iron sulfides on Venus was recently reviewed by *Fegley and Treiman* (1991) and we shall make use of their results in the subsequent discussion. As Fegley and Treiman noted, *Mueller* (1965) presented the first theoretical models of S chemistry on Venus. However, he neglected to include the important gas COS in his calculations and thus obtained incorrect results concerning the stability of iron sulfides on Venus. Furthermore at the time of his work, no observations of or upper limits for sulfur gases (e.g., COS, H_2S, SO_2, S_x) were available for comparison with his results. The first complete models of sulfide chemistry on Venus were done shortly afterward by *Lewis* (1968, 1970, 1971b, 1974), who included all the relevant gaseous species and was able to compare his results to the upper limits set by Earth-based spectroscopy (*Cruikshank*, 1967; *Anderson et al.*, 1969; *Kuiper*, 1971). Lewis' models were the first to show that at the mean Venus surface temperature of ~740 K, iron sulfides should react spontaneously with the CO_2 and CO in the overlying atmosphere to produce the reduced sulfur gas COS. This result has been reproduced by later workers (e.g., *Barsukov et al*, 1980, 1982; *Khodakovsky*, 1982; *Nozette and Lewis*, 1982; *Volkov et al.*, 1986; *Zolotov*, 1991).

The chemical weathering of pyrite and pyrrhotite is predicted to proceed via reactions such as

$$3FeS_2 + 2CO + 4CO_2 = 6COS + Fe_3O_4 \qquad (29)$$

$$\log_{10}K_{29} = 7.48 - 19334(\pm441)/T \qquad (30)$$

$$3FeS + 4CO_2 = 3COS + CO + Fe_3O_4 \qquad (31)$$

$$\log_{10}K_{31} = -1.56 - 11533(\pm311)/T. \qquad (32)$$

At temperatures of ~660-740 K on the surface of Venus, pyrite and pyrrhotite chemical weathering yields COS mixing ratios of ~5-30 ppm for pyrite and ~10-70 ppm for pyrrhotite. The higher COS mixing ratios are produced at higher temperatures (i.e., in lowland regions) and the lower COS mixing ratios are produced at lower temperatures (i.e., in highland regions).

In other words, pyrite on the surface of Venus will continue to be oxidized by the CO_2 and CO in the overlying atmosphere until either all pyrite is exhausted or until the equilibrium COS mixing ratio is generated; the same is true for pyrrhotite on the surface of Venus.

The results of the pyrite chemical weathering calculations are illustrated in Fig. 7 where they are compared to the observed COS abundance of ~0.3 ppm in the lower atmosphere of Venus (*Bézard et al.*, 1990). The observed COS abundance is much lower than the abundance required for pyrite to be stable on the surface of Venus. A similar conclusion also holds for pyrrhotite, which requires even larger COS mixing ratios in order to be stable. However, the COS observations of *Bézard et al.* (1990) are for the 35-45-km region of the venusian atmosphere, and may not be representative of the COS abundance lower in the atmosphere.
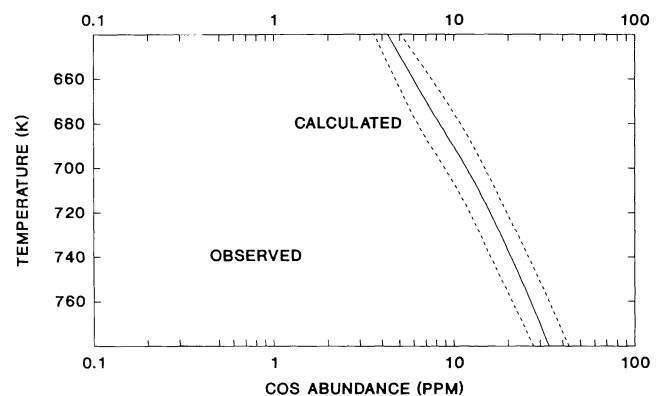

Fig. 7. A comparison of the COS abundance calculated from pyrite chemical weathering with the observed COS abundance in the 35-45-km region of the lower atmosphere of Venus (*Bézard et al.*, 1990). The dashed lines show the range of COS abundances allowed by the uncertainties in the thermodynamic data. As discussed in the text, the COS abundances expected near the surface of Venus from equilibrium with S_2 and CO are also significantly lower than those required for pyrite stability on Venus. From *Fegley and Treiman* (1991).

Luckily we can check this possibility by making use of the gas-phase equilibrium between COS and S_2

$$2CO + S_2 = 2COS \qquad (33)$$

$$\log_{10}K_{33} = -8.30 + 9591(\pm116)/T \qquad (34)$$

As mentioned earlier, the Venera 11/12 and Pioneer Venus spacecraft made measurements of the CO/CO_2 ratio in the 12-22-km region of the venusian atmosphere. The Venera 11/12 spacecraft also measured light absorption in the 0-30-km region (*Moroz et al.*, 1979, 1980) and these measurements provide information on the S_2 mixing ratio in this region of the atmosphere (*San'ko*, 1980; *Zolotov*, 1985). The derived S_2 mixing ratio is ~20 ppb and is constant with altitude from 0 to 20 km. We therefore used the measured CO and S_2 abundances in the near-surface atmosphere of Venus to calculate the equilibrium COS mixing ratios. The results show that the COS mixing ratio varies from ~60 ppb at 740 K to ~0.5 ppm at 660 K. These results confirm that pyrite and pyrrhotite are thermodynamically unstable everywhere on the surface of Venus because the equilibrium COS mixing ratios in the near-surface atmosphere are significantly lower than the values needed to stabilize these two sulfide minerals.

We note that J. A. Wood and colleagues (*Wood and Hashimoto*, 1991; *Wood and Klose*, 1991) recently proposed that pyrite and pyrrhotite are stable over most of the surface of Venus. Our results presented above predict exactly the opposite. This contradiction apparently exists because Wood and colleagues neglected COS gas in their calculations and considered only metastable equilibria involving SO_2 (*Wood and Hashimoto*, 1991).

3.4. Pyrite and Pyrrhotite Chemical Weathering Kinetics

In order to test how long iron sulfides could remain on the surface of Venus, *Fegley and Treiman* (1990) and *Treiman and Fegley* (1991) started experimental studies of the rates of pyrite and pyrrhotite chemical weathering. The experiments were done using basically the same techniques utilized by *Fegley and Prinn* (1989) in a kinetic study of anhydrite formation from calcite + SO_2. Well-characterized natural pyrite and pyrrhotite samples with known surface areas were heated isothermally in 1 bar of pure CO_2 or in CO_2-H_2 gas mixtures for different time periods. The samples were then quenched in the cool furnace gas by rapidly being raised out of the hot zone of the furnace. The rate of reaction was determined by measuring the weight change of the samples after reaction. The purity of the starting materials was checked by X-ray diffraction, by instrumental neutron activation analysis, and by calculations of sample densities. These techniques showed that the starting materials were pure FeS_2 and $Fe_{0.95}S$. The reacted samples were also examined by X-ray diffraction, optical microscopy, and scanning electron microscopy.

The preliminary experimental results indicate 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 derived rate equation for the pyrite → pyrrhotite conversion is

$$R = 10^{26.09(\pm0.34)}\exp[-17,038(\pm640)/T] \qquad (35)$$

and the activation energy is 141.7 ± 5.3 kJ mole^{-1}. The units on the rate equation are sulfur atoms cm^{-2} s^{-1}. For comparison we note that *Schwab and Philinis* (1947), who studied pyrite decomposition in pure CO_2 from 873-973 K, reported an apparent activation energy of 145 kJ mole^{-1}, in good agreement with the preliminary results of *Fegley and Treiman* (1990).

The preliminary results of the pyrrhotite oxidation experiments indicate that this also is a complex process that proceeds through at least two steps. The first step, which follows an Arrhenius-type relation, may involve the growth of a critical number of magnetite nuclei. This behavior is consistent with that exhibited by many reactions involving solids (e.g., *Brown et al.*, 1980). The second step involves the oxidation process and displays a dependence on time $t^{1/4}$. While this is unusual behavior, it is confirmed by the data of *Asaki et al.* (1983) on troilite oxidation in Ar-O_2 gas mixtures that also exhibited a $t^{1/4}$ dependence in the later stage.

The experiments indicate that pyrrhotite oxidation to magnetite is also a rapid reaction, although it is apparently slower than the pyrite → pyrrhotite conversion. It appears unlikely that either pyrite or pyrrhotite could survive on the venusian surface for geologically long time periods, although this conclusion must be tempered by the fact that only preliminary experimental results applicable to short time periods are available. However, it is important to realize that the volume change for the pyrrhotite → magnetite conversion is negative (-7%), so the oxide coating that is formed will be porous and will not present a barrier to gaseous diffusion. At present, the kinetic data imply that, if pyrite (or pyrrhotite) is responsible for the high radar reflectivity observed in the venusian highlands, then fresh sulfides will be constantly needed to replenish the material that has been chemically weathered.

4.   TITANIUM-BEARING MINERALS

4.1.   Ilmenite

Ilmenite ($FeTiO_3$) has also been suggested as a candidate for the high dielectric material believed to be present in the venusian highlands (e.g., *Garvin*, 1985; *Garvin and Head*, 1985; *Garvin et al.*, 1985a,b; *Head et al.*, 1985). We first examine the thermodynamic constraints on ilmenite stability on Venus and then review laboratory data on dielectric constant measurements of ilmenite-bearing lunar samples in order to determine if ilmenite is a likely candidate for the high dielectric material on Venus.

Ilmenite stability on Venus is probably controlled by its oxidation to magnetite and rutile

$$3FeTiO_3 + \tfrac{1}{2}O_2 = Fe_3O_4 + 3TiO_2 \qquad (36)$$
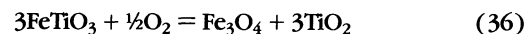
$$\log_{10}K_{36} = -5.70 + 12143(\pm322)/T \qquad (37)$$

We calculated the stability fields of ilmenite and of magnetite + rutile as a function of oxygen fugacity, and the results are displayed in Fig. 8 along with the oxygen fugacity for 20 ppm CO in the lower atmosphere of Venus. The two curves intersect at ~755 K, and ilmenite is unstable at all lower temperatures over the surface of Venus. However, the uncertainties in the thermodynamic data (*Robie et al.,* 1979) are sufficiently large that this intersection may occur anywhere from ~660 K to ~850 K. A more firm thermodynamic constraint on ilmenite stability would require improved thermodynamic data for reaction (36).

Ilmenite is the most abundant oxide mineral in lunar rocks and forms as much as 15-20 vol% of many Apollo 11 and 17 mare basalts. It commonly occurs as bladed crystals up to a few millimeters long. The volumetric abundance of ilmenite in some lunar samples is in the same range (10-15%) as that estimated by *Pettengill et al.* (1988) for the volumetric abundance of the high dielectric phase in the venusian highlands. Furthermore, the occurrence of ilmenite in lunar samples as small inclusions in a rocky matrix is very similar (if not identical) to the loaded dielectric model proposed by *Pettengill et al.* (1982, 1988) for Venus. Thus, the extensive measurements of the relative dielectric permittivities of lunar samples should provide a test of the hypothesis that ilmenite is the high dielectric phase in the venusian highlands.

Heiken et al. (1991) summarize the results of dielectric constant measurements on lunar samples. The largest value of the relative dielectric permittivity measured was 11 for an Apollo 11 mare basalt containing ~16% ilmenite. However, most permittivity values were less than 7. Furthermore, as illustrated in Fig. 9, there is no correlation between the ilmenite content of lunar samples and the relative dielectric permittivity. However, there is a correlation with the loss tangent, which increases with increasing ilmenite content.

Thus, ilmenite appears to be an unlikely candidate for the high dielectric phase in the venusian highlands, and other suitable minerals must be sought.
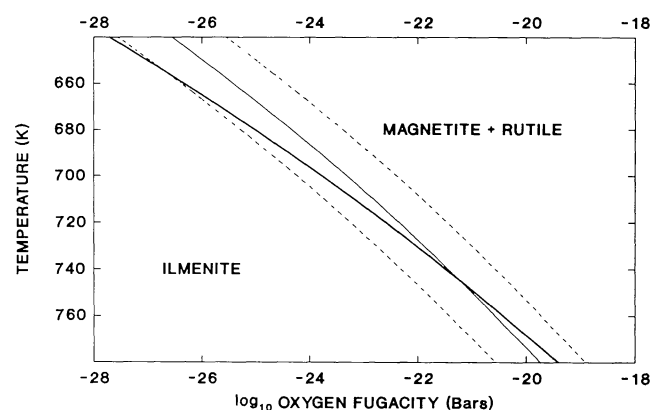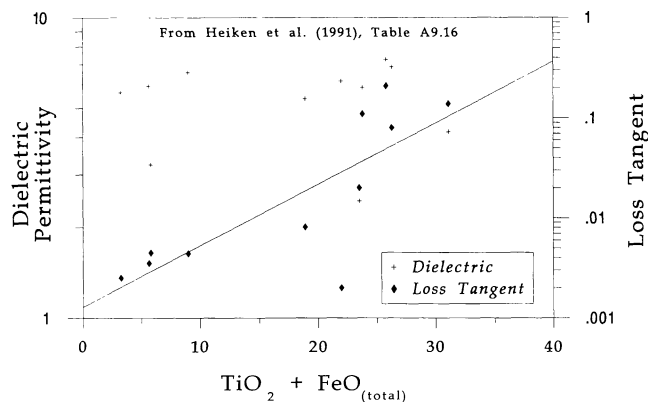

Fig. 9. Results of dielectric constant measurements on lunar samples at 450 MHz from *Heiken et al.* (1991, Table A9.16). The dielectric constants for all samples are less than 10 and do not correlate with the ilmenite content. The diagonal line is a least-squares fit showing the correlation of the loss tangent with the ilmenite content.

4.2. Perovskite

A combination of factors make perovskite, ideally $CaTiO_3$, an intriguing candidate for the high dielectric phase(s) in the venusian highlands. One factor is the relatively high dielectric constant of $CaTiO_3$. For example, laboratory measurements of synthetic calcium titanate ceramics (at 298 K) show dielectric constants of ~165-170 over frequencies of 10^2 to 10^{10} Hz, and ~155-160 over frequencies of 10^2 to 10^7 Hz at a slightly higher temperature of 355 K (*Von Hippel,* 1954). The laboratory measurements also show that $CaTiO_3$ is a low-loss material (*Young and Frederikse,* 1973; *Von Hippel,* 1954).

Another factor is the occurrence of perovskite as a characteristic accessory mineral in some types of alkaline rocks (e.g., *Deer et al.,* 1963; *Sørensen,* 1974; *Johannsen,* 1937). For example, ~2.5-9 vol% perovskite is found in melilite-rich alkaline rocks in localities such as the Kola Pennisula, the Oka Hills, Quebec, and South Africa. Comparable amounts (5-9%) of perovskite are found in leucite-rich rocks from Uganda and in nepheline-rich rocks from Colorado (*Johannsen,* 1937). Rarer rock types associated with alkaline rocks on Earth are even richer in perovskite. For instance, magnetite-perovskite dikes in the Powderhorn alkaline complex, Colorado, contain 50% perovskite in addition to 41% magnetite, 8% ilmenite, and 1% apatite (*Larsen,* 1942).

Although alkaline rocks are a rare terrestrial rock type, several arguments suggest that alkaline rocks are present on Venus and play an important role in atmosphere-surface interactions. The γ-ray-spectroscopy data for U, Th, and K at the Venera 8 site (*Vinogradov et al.,* 1973; *Surkov,* 1977) and the X-ray fluorescence data for major rock-forming oxides at the Venera 13 site have been interpreted as high-potassium alkaline basalts (*Volkov et al.,* 1986; *Barsukov et al.,* 1986). These interpretations are consistent with thermodynamic calculations that show that the assemblage of sodalite + nepheline ±

Fig. 8. A comparison of the ilmenite and magnetite + rutile stability fields with the oxygen fugacity defined by the CO/CO_2 ratio in the lower atmosphere of Venus. The dotted lines indicate the range of uncertainties from the thermodynamic data for this reaction.

albite, which is common in terrestrial alkaline rocks such as nepheline-syenites and related types (*Deer et al.,* 1963; *Johannsen,* 1937), can buffer the HCl abundance in the venusian atmosphere at the observed value (*Fegley and Treiman,* 1991). In addition, mineral assemblages involving fluorphlogopite, which is common in ultrabasic rocks (e.g., *Deer et al.,* 1963), can buffer the HF abundance in the venusian atmosphere at the observed value (*Lewis,* 1970; *Fegley and Treiman,* 1991). Furthermore, several types of alkaline rocks such as the ijolites, melteigites, and urtites (rocks composed predominantly of feldspathoids and clinopyroxene) also contain the assemblage calcite + wollastonite (*Sørensen,* 1974; *Johannsen,* 1937), which is generally believed to buffer the CO_2 pressure in the venusian atmosphere (e.g., *Mueller,* 1963, 1964a; *Lewis,* 1970; *Vinogradov and Volkov,* 1971). Thus, observational data on the composition of the venusian surface and theoretical models of atmosphere-surface chemistry on Venus both suggest the presence of alkaline rocks and characteristic accessory minerals such as perovskite.

Perovskite is predicted to be inert with respect to gas-solid reactions involving HCl in the overlying atmosphere because the observed HCl abundance is significantly lower than the equilibrium abundance required for hydrophilite formation. This reaction, which yields rutile, is

$$CaTiO_3 + 2HCl = CaCl_2 + TiO_2 + H_2O \qquad (38)$$
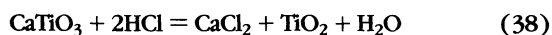
$$\log_{10}K_{38} = -6.46 + 7164(\pm 114)/T \qquad (39)$$

Evaluating equation (39) at 740 K, the mean surface temperature on Venus, shows that ~11 ± 2 ppm HCl, or about 20 times more than the observed value of ~0.5 ppm, are needed for hydrophilite, $CaCl_2$, to form. The equilibrium abundance of HCl decreases with decreasing temperature, but at 660 K, the approximate temperature at the top of Maxwell Montes, ~4 ± 1 ppm HCl are still required for hydrophilite formation. Thus, perovskite is predicted to be resistant to attack by HCl in the venusian atmosphere over the entire venusian surface.

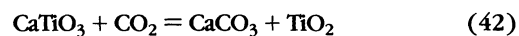However, a different situation may occur for the reaction of perovskite with HF to form fluorite

$$CaTiO_3 + 2HF = CaF_2 + TiO_2 + H_2O \qquad (40)$$

$$\log_{10}K_{40} = -7.01 + 10,995(\pm 137)/T \qquad (41)$$

Evaluation of equation (41) at 740 K shows that ~55 ± 11 ppb HF, or about 5-10 times more than the observed value of 5-10 ppb, are needed for fluorite formation, so perovskite will not be attacked by HF over most of the venusian surface. However, at 660 K the equilibrium abundance is only ~10 ± 2 ppb, which overlaps the observed HF abundance. These results indicate that within the combined uncertainties of the thermodynamic data and observed HF abundance, perovskite can be converted to fluorite + rutile at the highest altitudes on the venusian surface (e.g., at the very summit of Maxwell Montes).

It is also interesting to note that reactions with two less-corrosive gases in the venusian atmosphere, CO_2 and SO_2, can also destroy perovskite by forming calcite and anhydrite respectively. The net reactions and their equilibrium constants are

$$CaTiO_3 + CO_2 = CaCO_3 + TiO_2 \qquad (42)$$

$$\log_{10}P_{CO_2} = 8.45 - 5019(\pm 129)/T \qquad (43)$$

$$CaTiO_3 + \tfrac{1}{2}O_2 + SO_2 = CaSO_4 + TiO_2 \qquad (44)$$

$$\log_{10}K_{44} = -14.86 + 21,919(\pm 243)/T \qquad (45)$$

However, in contrast to fluorite formation, both calcite formation and anhydrite formation are predicted to be thermodynamically favorable over the entire venusian surface. The thermodynamic favorability of fluorite formation at the highest altitudes on Venus, coupled with the higher reactivity of HF relative to that of CO_2 and SO_2, may lead to the following situation.

At the highest altitudes, such as on the top of Maxwell Montes, perovskite is converted to fluorite + rutile at a rate that is rapid with respect to production of fresh perovskite-bearing material (e.g., by volcanism or by exposure of unreacted rock). At slightly lower altitudes, where fluorite formation is not thermodynamically favorable, the rates of formation of calcite + rutile and/or anhydrite + rutile are slow on a geologic timescale. However, at the lowest altitudes on Venus, where the temperature is 740 K or higher, the rates of calcite and anhydrite formation are faster and perovskite destruction is rapid once again.

We feel that this scenario is interesting for several reasons. One reason is that the Ca-bearing weathering products formed from perovskite have lower dielectric constants than perovskite itself. Thus, the weathered material should have a different radar signature, presumably more like that of the "average" venusian surface. We note that rutile, which is also formed in these reactions, does have a fairly high dielectric constant of ~80-100, dependent somewhat on the crystal orientation relative to the electric field and ambient temperature (e.g., *Von Hippel,* 1954; *Young and Frederikse,* 1973). However, we question whether or not these ε values are high enough for rutile itself to yield the observed ε ~ 87 derived for Maxwell Montes (*Pettengill et al.,* 1991) and to do so when present at a volume fraction of only ~15% as indicated by the earlier Pioneer Venus radar data (*Pettengill et al.,* 1988).

In this regard we note that studies have been done of the dielectric constant of two-phase mixtures composed of TiO_2 dispersed in low dielectric matrixes (e.g., *Kingery et al.,* 1976). A mixture of 85 vol% polystyrene + 15% TiO_2 had a dielectric constant of only ~5, about 20 times lower than the value of 100 observed for the pure TiO_2. Furthermore, data presented in *Kingery et al.* (1976) also demonstrate that the dielectric constant of TiO_2 drops rapidly as the amount of porosity in a polycrystalline TiO_2 ceramic increases. Presumably the rutile formed as a weathering product of perovskite will be more porous than the initial crystal [as was the case for anhydrite formed as a weathering product of calcite in the experiments of *Fegley and Prinn* (1989)] and thus would be expected to have a lower dielectric constant than fully dense rutile. In fact,

the volume change of -44% that occurs in the perovskite → rutile conversion indicates that substantial porosity will be formed. As a consequence, the weathering products may also be more easily abraded than the initial perovskite so they can be more easily removed by aeolian weathering and mass wasting. If so, then the rutile can be blown into the lowlands where it can either undergo further reactions such as $MgTiO_3$ formation

$$TiO_2 + Mg_2SiO_4 = MgTiO_3 + MgSiO_3 \qquad (46)$$
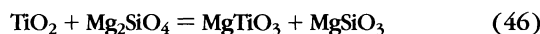
$$log_{10}K_{46} = -0.04 + 224(\pm 138)/T \qquad (47)$$

or simply be dispersed at such a low concentration that no substantial dielectric constant enhancements can be seen.

Finally, we note that the different chemical reactions involved in perovskite destruction on Venus may provide an explanation for the initial Magellan observations that indicated that the high dielectric phase(s) are not always present at the highest elevations on the venusian surface (e.g., *Arvidson et al.,* 1991; *Pettengill et al.,* 1991). This apparently paradoxical situation cannot be explained by the other candidates for the high dielectric materials on Venus. If these initial observations by the Magellan spacecraft are confirmed, then laboratory studies of the kinetics of fluorite, calcite, and anhydrite formation from perovskite via reactions (40), (42), and (44) would be of interest.

5.   HYDRATED SILICATES

The presence of hydrated silicates on the surface of Venus was probably first suggested by *Mueller* (1964a,b). He specifically proposed that phlogopite $[KMg_3AlSi_3O_{10}(OH)_2]$ would be present but could not test his prediction quantitatively because of the lack of data about phlogopite thermodynamics and water vapor partial pressure at the surface of Venus.

Subsequently, many other investigators tried to calculate the stabilities of hydrated silicates on the surface of Venus (e.g., *Lewis,* 1968, 1970; *Mueller,* 1970; *Lewis and Kreimendahl,* 1980; *Khodakovsky et al.,* 1979; *Barsukov et al.,* 1980; *Nozette and Lewis,* 1982; *Volkov et al.,* 1986; *Khodakovsky,* 1982). This literature is full of contradictory predictions about hydrated silicate stabilities on Venus because of unavailable or unreliable thermodynamic data and uncertainties about the actual water vapor content of the near-surface atmosphere of Venus.

Fegley and Treiman (1991) used the latest available thermodynamic data to calculate the water-vapor dissociation pressures of common hydrated minerals and compared their results to the spacecraft measurements of the water vapor abundance in the lower atmosphere of Venus. The latter data are also somewhat contradictory (e.g., see *Von Zahn et al.,* 1983, and *Fegley and Treiman,* 1991, for reviews) but the most reliable data indicate a water vapor abundance of only 20 ppm at the surface of Venus (*Moroz et al.,* 1979, 1980, 1983); this is equivalent to a water vapor pressure of ~0.002 bar at the surface of Venus.

TABLE 8.   Dissociation pressures for hydrated silicates on the surface of Venus (*Fegley and Treiman,* 1991)[*].

Mineral Name	Ideal Formula	Dissociation Pressure
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	0.09 bar
Phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$	0.1 bar
Talc	$Mg_3Si_4O_{10}(OH)_2$	2 bar
Epidote	$Ca_2FeAl_2Si_3O_{12}(OH)$	4 bar
Pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	13 bar
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	23 bar
Paragonite	$NaAl_2Si_3O_{10}(OH)_2$	110 bar
Glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$	230 bar
Margarite	$CaAl_4Si_2O_{10}(OH)_2$	240 bar
Chrysotile	$Mg_3Si_2O_5(OH)_4$	310 bar
Anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	510 bar
Prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	610 bar
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	620 bar
Kaolinite	$Al_2Si_2O_5(OH)_4$	890 bar
Annite	$KFe_3AlSi_3O_{10}(OH)_2$	12,600 bar

[*] At 740 K.

A summary of the results obtained by *Fegley and Treiman* (1991) is given in Table 8. They found that none of the hydrated silicates considered are stable anywhere on the surface of Venus. The two most stable hydrated minerals were tremolite and phlogopite, but even these two had water vapor dissociation pressures about 50 times larger than the observed water vapor pressure at the venusian surface. All the other hydrated silicates for which thermodynamic data are available have markedly higher water vapor dissociation pressures. As noted by *Fegley and Treiman* (1991), no thermodynamic data are available for some amphiboles and hornblendes such as edenite, some members of the richterite family, and some alkali amphiboles. Thus it is possible that if these minerals are more stable than tremolite they may exit on the venusian surface. However, at present it appears that the surface of Venus is too hot (even in the highland regions) and too dry for any hydrated minerals to exist there.

6.   SULFATE MINERALS

Measurements by the Pioneer Venus and Venera 11/12 spacecraft summarized in Table 5 show that SO_2 is the major sulfur gas in the lower atmosphere of Venus. This can react with Ca-bearing minerals on the surface to form anhydrite ($CaSO_4$) via reactions such as

$$SO_2 + CaCO_3 = CaSO_4 + CO \qquad (48)$$
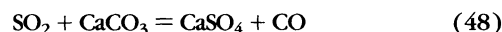
$$log_{10}K_{48} = -1.82 + 2092(\pm 230)/T \qquad (49)$$

However, the analogous reactions with Mg-bearing minerals, for example, the reaction with magnesite

$$SO_2 + MgCO_3 = MgSO_4 + CO \qquad (50)$$
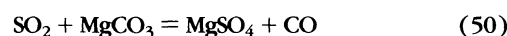
$$log_{10}K_{50} = -1.18 - 558(\pm 74)/T \qquad (51)$$

are thermodynamically unfavorable because they require SO_2 pressures higher than the observed values in the venusian atmosphere.

As illustrated in Fig. 10, the equilibrium SO_2 pressure for the formation of anhydrite from calcite is about 100 times lower than the observed SO_2 pressure on Venus. This implies that reaction (48) is a sink for SO_2 on Venus. In fact, the Venera 13/14 and Vega 2 analyses of the surface of Venus (Table 3) show that the CaO/SO_3 ratio is less than that expected if all Ca were present as anhydrite. Thus, the present-day surface of Venus is still a sink for SO_2 via anhydrite formation. It also implies that the rate of anhydrite formation is a slow process.

Kinetic measurements of the rate of reaction (48) have been made by isothermally heating high-purity natural calcite crystals with known surface areas and weights in 1 bar of CO_2-SO_2 for varying time periods. The rate of anhydrite formation was measured by several methods such as chemical analysis for sulfate, weight gain, and scanning electron microscopy. The latter method was used to measure the porosity and thickness of the anhydrite layers formed on the reacted crystals (e.g., Fig. 11). The experimental techniques used are described by *Fegley and Prinn* (1989), who derived the rate equation

$$R = 10^{19.64(\pm 0.28)}\exp[-15,248(\pm 2970)/T] \qquad (52)$$

which has units of SO_2 molecules $cm^{-2}s^{-1}$. The corresponding activation energy is 126.8 ± 24.7 kJ mole^{-1}.

The global mean rate of anhydrite formation on the surface of Venus, which is calculated from the rate equation by taking into account the temperature variation with altitude on Venus,
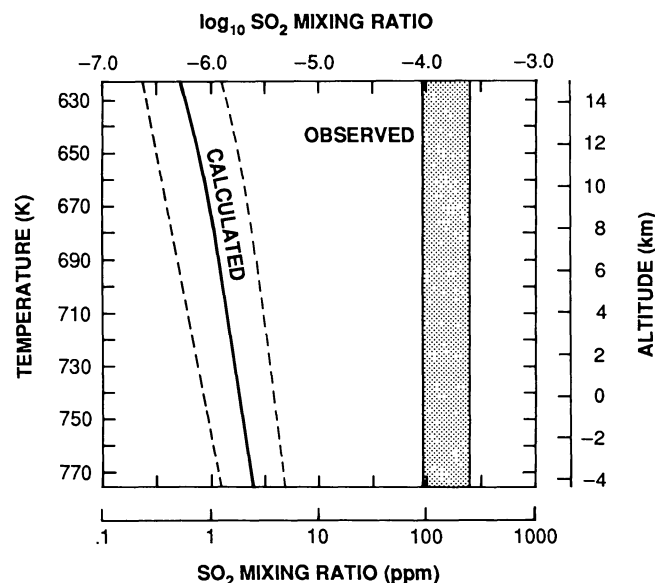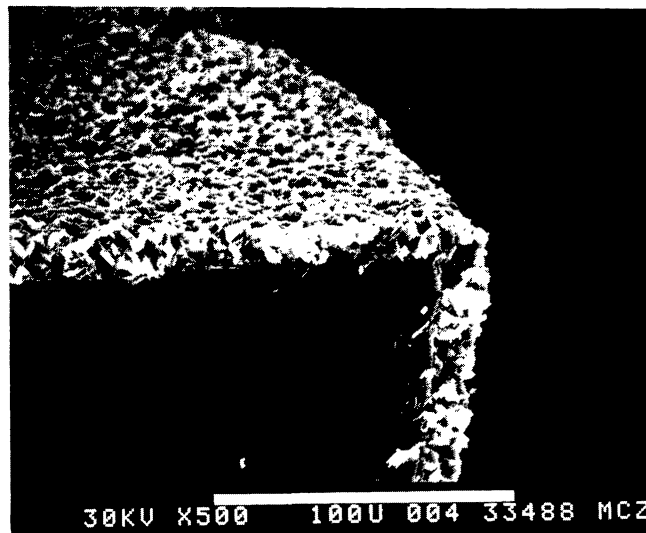

Fig. 11. A scanning electron micrograph of the fracture surface of a calcite crystal that has partially reacted with a gas mixture having the nominal composition 1% SO_2 + 99% CO_2. The outer surfaces of the crystal are coated with anhydrite $CaSO_4$. The reaction conditions were 850°C for 192 hr. The scale bar is 100 μm long. Photo from *Fegley and Prinn* (1989).

Fig. 10. A comparison of the SO_2 abundance calculated for reaction (48) 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 ~1 ppm. The dichotomy suggests that sulfur gases in the atmosphere of Venus are not in equilibrium with the surface of Venus. From *Fegley and Treiman* (1991).

is $\sim$4.6 $\times$ 10^{10} molecules $cm^{-2}s^{-1}$. This is equivalent to about 1 μm of anhydrite deposition per year. *Fegley and Prinn* (1989) and *Fegley and Treiman* (1991) have applied these data to a discussion of the volcanism rate on Venus by using a steady-state model for SO_2 on Venus and the plausible assumption that volcanism is a source of sulfur.

Here we merely note that about 1.9 Ma are required for reaction (48) to reach equilibrium on the surface of Venus. Thus, the anhydrite + calcite assemblage on the surface of Venus cannot be buffering SO_2 in the atmosphere of Venus. Preliminary kinetic data (*Fegley and Prinn*, 1989) show that other possible anhydrite formation reactions, such as the reaction of SO_2 with diopside, are at least as slow as the reaction of SO_2 with calcite. Thus this reaction cannot be buffering SO_2 on Venus, as recently suggested by *Wood and Hashimoto* (1991).
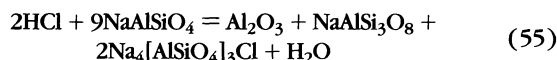
7. HALOGEN-BEARING MINERALS

Finally, we consider the implications of the observations of HF and HCl in the atmosphere of Venus for the mineralogy of the surface. As shown in Table 5, HF is present at about 5 ppb by volume and HCl at about 0.5 ppm by volume. Shortly after the discovery of HF and HCl in the atmosphere of Venus, *Lewis* (1968, 1970) and *Mueller* (1968, 1969) proposed that the atmospheric abundances of the two hydrogen halides were regulated, or buffered, by chemical equilibria between halogen-bearing minerals and other silicates on the surface of Venus. The highly reactive nature of HCl and HF, which is used to

etch glass, intuitively suggests that this explanation is reasonable. It is further supported by the essentially identical abundances of HF and HCl observed above the clouds by *Connes et al.* (1967) and below the clouds by *Bézard et al.* (1990). This would not be expected if the abundances of HF and HCl were controlled by episodic phenomena such as volcanism unless their average reaction rates were identical and slow over this period.

Fegley and Treiman (1991) critically evaluated the reactions proposed as HCl and HF buffers by *Lewis* (1970) and considered new reactions for buffering these two gases. They found that several different equilibria are potential candidates for buffering HCl and HF in the atmosphere of Venus. In the case of HCl, the two best buffers were found to be

$$12HCl + 6CaSiO_3 + 5Na_4[AlSiO_4]_3Cl = 17NaCl + 6CaAl_2Si_2O_8 + 3NaAlSi_3O_8 + 6H_2O \tag{53}$$

$$\log_{10}K_{53} = -20.17 + 49{,}384(\pm 4884)/T \tag{54}$$

$$2HCl + 9NaAlSiO_4 = Al_2O_3 + NaAlSi_3O_8 + 2Na_4[AlSiO_4]_3Cl + H_2O \tag{55}$$

$$\log_{10}K_{55} = -13.56 + 16{,}150(\pm 2259)/T \tag{56}$$

which are illustrated in Figs. 12 and 13 respectively. Reaction (53) involves the mineral assemblage wollastonite + sodalite + halite + anorthite + albite, while reaction (55) involves the mineral assemblage nepheline + corundum + albite + sodalite. Both these buffers involve mineral assemblages found in alkaline rocks such as nepheline-syenites (*Deer et al.*, 1963) and argue for the presence of alkaline rocks on the surface of Venus.
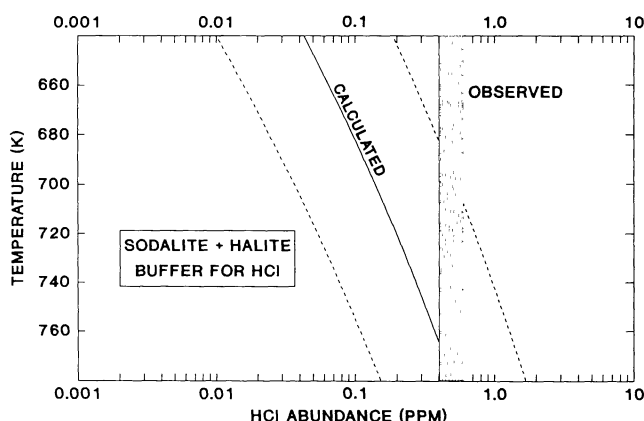

Fig. 13. A comparison of the HCl abundance calculated for reaction (55) with the observed HCl abundance (*Bézard et al.*, 1990; *Connes et al.*, 1967; *deBergh et al.*, 1989) in the atmosphere of Venus. The dashed lines indicate the range of HCl values allowed by the uncertainties in the thermodynamic data. Refer to Fig. 4 to relate temperatures to altitudes on the surface of Venus. From *Fegley and Treiman* (1991).
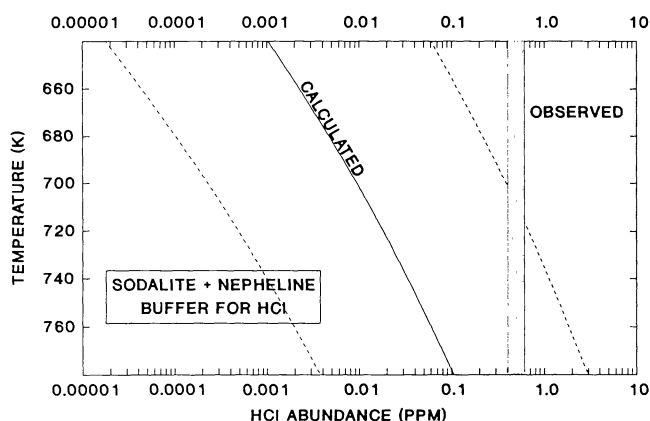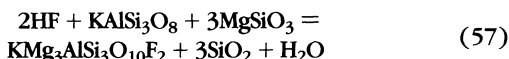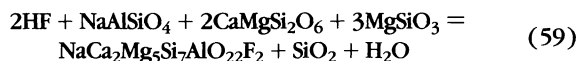
In the case of HF the two best buffers were found to be

$$2HF + KAlSi_3O_8 + 3MgSiO_3 = KMg_3AlSi_3O_{10}F_2 + 3SiO_2 + H_2O \tag{57}$$

$$\log_{10}K_{57} = -5.53 + 10{,}765(\pm 1848)/T \tag{58}$$

$$2HF + NaAlSiO_4 + 2CaMgSi_2O_6 + 3MgSiO_3 = NaCa_2Mg_5Si_7AlO_{22}F_2 + SiO_2 + H_2O \tag{59}$$

$$\log_{10}K_{59} = -6.88 + 12{,}098(\pm 1120)/T \tag{60}$$

Reaction (57) was originally proposed by *Lewis* (1970) but probably involves microcline instead of sanidine as he proposed, because K-feldspar is probably totally ordered at venusian surface temperatures. Reaction (59), involving the mineral assemblage nepheline + diopside + enstatite + fluoredenite + quartz, governs the stability of fluoredenite in felsic rocks. Figures 14 and 15 illustrate how the HF abundances produced by these two reactions compare to the observed HF abundance in the venusian atmosphere.

Thus, the high reactivity of HF and HCl coupled with the high temperature of the venusian surface suggests that these two gases are in chemical equilibrium with minerals on the surface of Venus. The virtually identical HF and HCl abundances observed 20 years apart in two different regions of the atmosphere of Venus support this concept. The mineral assemblages that apparently are in equilibrium with the observed HCl abundance include sodalite + nepheline ± albite and are assemblages found in alkaline rocks on the Earth. The mineral assemblages that apparently are in equilibrium with the observed HF abundance involve fluorphlogopite in some cases and fluoramphiboles such as fluoredenite and fluortremolite in other cases (*Fegley and Treiman*, 1991).
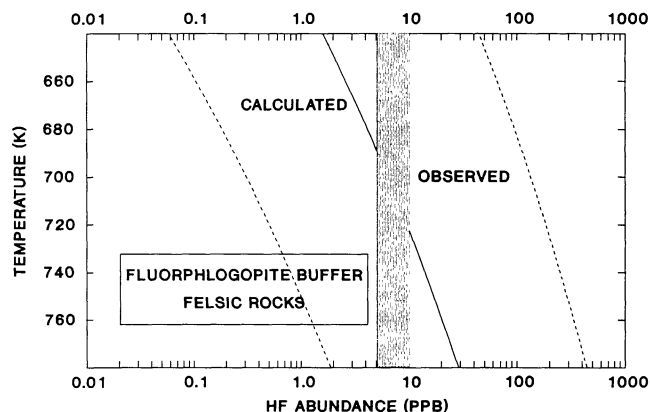

Fig. 12. A comparison of the HCl abundance calculated for reaction (53) with the observed HCl abundance (*Bézard et al.*, 1990; *Connes et al.*, 1967; *deBergh et al.*, 1989) in the atmosphere of Venus. The dashed lines indicate the range of HCl values allowed by the uncertainties in the thermodynamic data. Refer to Fig. 4 to relate temperatures to altitudes on the surface of Venus. From *Fegley and Treiman* (1991).

Fig. 14. A comparison of the HF abundance calculated for reaction (57) 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* (1970). Refer to Fig. 4 to relate temperatures to altitudes on the surface of Venus. From *Fegley and Treiman* (1991).
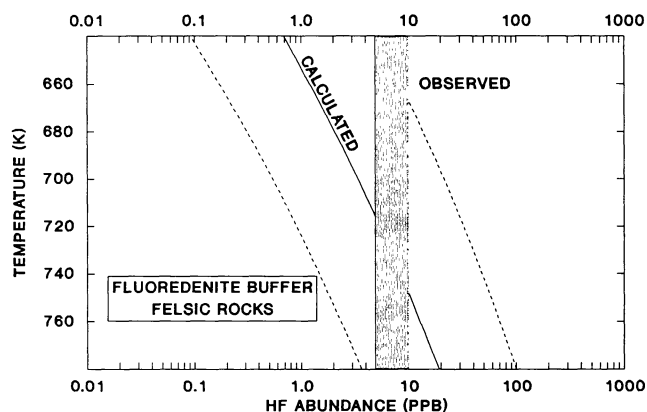

Fig. 15. A comparison of the HF abundance calculated for reaction (59) with the observed HF abundance (*Bézard et al.*, 1990; *Connes et al.*, 1967) in the atmosphere of Venus. The dashed lines indicate the range of HF values allowed by the uncertainties in the thermodynamic data. Refer to Fig. 4 to relate temperatures to altitudes on the surface of Venus. From *Fegley and Treiman* (1991).

8. SUMMARY

In this paper we have given a brief review of how constraints derived from Earth-based, Earth-orbital, and spacecraft observations can be combined with chemical thermodynamic models and other laboratory measurements (e.g., kinetic data, dielectric constant measurements) to make deductions about the mineralogy of the surface of Venus. At this point we want to conclude by identifying the key issues facing us today about the geochemistry and mineralogy of the surface of Venus and making some recommendations for future work in this area.

First, it is important to remember that no direct information is available about the mineralogy of the surface of Venus. The geochemical analyses that have been done are limited to a handful of sites at low elevations and only give data on major-element abundances in three cases and K, U, and Th abundances in four other cases. Furthermore, even these data are limited because some major elements of interest (e.g., C and F) could not be detected because of limitations in the spacecraft instrumentation. We recommend development of an X-ray diffraction experiment suitable for spacecraft operations in order to get direct information about the mineralogy of Venus (e.g., see *Vaniman et al.*, 1991). Failing this, we also recommend elemental analysis of highland regions of Venus by an X-ray fluorescence instrument. This would at least provide elemental compositions for regions believed to be enhanced in Fe, S, and Ti. These data would potentially provide constraints on models of altitude-dependent mineralogy on Venus.

Another unresolved question is the presence of carbonates on the surface of Venus. Although the most direct way to address this question is to search for calcite, dolomite, and magnesite (e.g., by X-ray diffraction), another important area of study is the kinetics of the different carbonate-silicate equilibria believed to occur on Venus. At present we do not know if these equilibria can be established on reasonable timescales or if geologically long time periods are involved. This question can be answered by suitably designed laboratory experiments that can then be extrapolated and/or interpolated to venusian surface conditions. An important factor in these experiments is to determine the dependence of the reaction rate on parameters such as the temperature, total pressure, mineral surface area, etc. Maintenance of anhydrous conditions is also important.

The presence of hematite on the surface of Venus is also an open question that could potentially be resolved by laboratory experimentation. This is another case where kinetic data are needed. The relevant spacecraft measurements needed to address this issue are the oxygen fugacity and/or CO mixing ratio in the 0-12-km region of the atmosphere of Venus.

However, perhaps the most actively debated question at present is the nature of the high-radar-reflectivity regions in the highland regions of Venus. These areas have been suggested to contain ~10-15 vol% of pyrite (*Pettengill et al.*, 1982, 1983, 1988). However, as discussed earlier, iron sulfides are predicted to be thermodynamically unstable over the entire surface of Venus and should be oxidized to magnetite and COS gas. The observed abundance of COS in the lower atmosphere of Venus is significantly lower than the amount required for iron sulfides to be stable on the venusian surface. Furthermore, preliminary kinetic data on pyrite and pyrrhotite chemical weathering under venusian surface conditions indicate that these minerals are rapidly weathered and are unlikely to be present for geologically long time periods. In order to resolve this apparent discrepancy we suggest several types of laboratory studies. One is further studies of the rates of iron sulfide chemical weathering under venusian surface conditions. Another is a laboratory investigation of the radar properties of possible analogs to the high-radar-reflectivity regions on Venus. Possible analogs are magnetite-rich terrestrial basalts, magmatic sulfides from terrestrial deposits, and perovskite-rich alkaline rocks.

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