

GEOCHEMISTRY OF SURFACE-ATMOSPHERE INTERACTIONS ON VENUS

B. FEGLEY, Jr.
Washington University

G. KLINGELHÖFER
Institut für Kernphysik, Darmstadt

K. LODDERS
Washington University

and

T. WIDEMANN
Service d'Aéronomie du CNRS

We review the consequences of atmosphere-surface interactions for the geochemistry of Venus. Earth-based, Earth-orbital, and spacecraft observations of the atmosphere and surface are combined with experimental studies of reaction rate kinetics and theoretical models of thermochemical equilibria to discuss mineral buffering of CO₂, HCl, and HF in the atmosphere; the evidence for carbonatites and related alkaline igneous rocks on the surface; the oxidation state of the surface of Venus, the sulfur geochemical cycle; and the origin of low radar emissivity regions on the surface of Venus. Although available experiments, observations, and theory provide important constraints on atmosphere-surface interactions, some of the key issues that remain unresolved include (1) the mineralogy of the surface of Venus, (2) the chemical composition of the lower 22 km of the atmosphere of Venus, (3) the oxidation state of the surface of Venus, and (4) the identity of the high dielectric phase(s) present in low radar emissivity regions. These issues can be best addressed by *in-situ* measurements of atmospheric composition and surface mineralogy on future spacecraft missions.

I. INTRODUCTION

Venus is a natural laboratory for studying thermochemical interactions between a planetary surface and the overlying atmosphere (Fegley and Treiman 1992). The temperature is ~740 K and the global surface pressure is about 95.6 bar (at the modal planetary radius of 6051.4 km (Fórd and Pettengill 1992), which is taken as 0 km altitude in this chapter). Chemically reactive and highly corrosive gases such as HF, HCl, H₂SO₄, SO₂, and supercritical CO₂ are present in Venus' atmosphere at abundances orders of magnitude

[591]

In *Venus II* (1997), S. W. Bougher, D. M. Hunten, and R. Phillips, Eds. University of Arizona Press, pp. 591-636.

greater than in the Earth's atmosphere and therefore indicate the lower atmosphere of Venus is probably reacting with the surface. Only a few percent of the incident solar flux penetrates to below the clouds and the short-wavelength ultraviolet sunlight that photolyzes CO_2 is stopped at high altitudes above the clouds. Thus, photochemically driven atmosphere-surface reactions are less important than thermochemically driven atmosphere-surface reactions.

In the 1960s the microwave radiometer on the Mariner 2 mission (Barath et al. 1964) confirmed the earlier Earth-based microwave observations (Mayer et al. 1958) of high brightness temperatures for Venus. The Mariner 2 observations led Mueller (1963) to realize that the deduced surface temperature of ~ 700 K "corresponds with those [temperatures] 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."

Mueller's hypothesis of chemical equilibrium formed the basis for theoretical work by many investigators who explored the consequences for the geochemistry and mineralogy of the surface and the composition of the atmosphere (see, e.g., the review by Fegley and Treiman 1992). Despite these theoretical studies and the great advances in Earth-based, Earth-orbital, and spacecraft observations of Venus many important questions about the nature of the surface remain unanswered.

In this chapter we use constraints derived from observations of the surface and atmosphere of Venus; from chemical equilibrium models of atmosphere-lithosphere chemical reactions; and from laboratory studies of the kinetics of some important gas-solid reactions to discuss three fundamental issues about the geochemistry and mineralogy of the surface of Venus:

1. What are the major minerals, and rock types that are present on the surface of Venus? Related questions involve the possible hypsometric control of mineralogy and whether or not chemical reactions between the atmosphere and surface are kinetically or thermodynamically controlled.
2. What is the oxidation state of the surface of Venus? Is magnetite (Fe_3O_4) stable on the surface of Venus, or is hematite (Fe_2O_3) stable on the surface of Venus, or are both oxides stable? Related questions involve whether or not the gases in the near-surface atmosphere of Venus are in thermochemical equilibrium with each other and with minerals present on the surface.
3. What plausible phases are responsible for the low radar emissivity regions on the surface? Related questions are whether or not the low radar emissivity regions reflect altitude-dependent chemical weathering reactions (see point 1 above), whether or not pyrite (FeS_2) is stable on the surface of Venus, or if volatile metal compounds analogous to those commonly observed around volcanic vents and fumaroles on the Earth are found on Venus.

After discussing these issues we conclude by identifying key questions about the geochemistry and mineralogy of the surface of Venus and suggest Earth-based observations, spacecraft and laboratory experiments, and theoretical studies that can improve our knowledge.

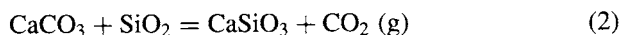
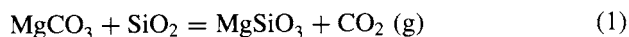
II. MINERALOGY OF THE SURFACE OF VENUS

We begin by considering constraints on the presence of carbonates on the surface of Venus. Because we have no direct information on the mineralogy of the surface, the question of whether or not carbonates are present on Venus is a long-standing and controversial issue (see, e.g., Barsukov et al. 1980,1982; Fegley and Treiman 1992; Fegley et al. 1992; Klose et al. 1992; Lewis 1968,1970,1971; Mueller 1963,1964; Orville 1974; Vinogradov and Volkov 1971; Volkov et al. 1986). We then discuss halogen-bearing minerals, which can buffer HCl and HF in the atmosphere. We conclude this section by discussing possible high dielectric constant phases present in low radar emissivity areas on the surface.

A. Thermochemical Calculations of Carbonate Stability on Venus

As Table I shows, CO₂ is the major gas in the atmosphere of Venus, and is a supercritical fluid under Venus' surface conditions. Carbon dioxide is involved in terrestrial metamorphic reactions which take place at temperatures of several hundred degrees, and it would be somewhat surprising if CO₂ were not also involved in chemical reactions with reactive minerals on the hot surface of Venus. Although unsuitable for providing kinetic data relevant to Venus (see, e.g., Fegley and Treiman 1992), laboratory experiments show that (even under anhydrous conditions) CO₂(g), quartz (SiO₂), calcite (CaCO₃), and wollastonite (CaSiO₃) react within hours at 830 to 900°C and CO₂ pressures of 1 to 68 bars (Kridelbaugh 1973).

Urey (1952) suggested that carbonate-silicate reactions such as



could regulate or buffer the CO₂ pressure in a planetary atmosphere. But when Urey (1952) proposed this concept, the low surface temperature accepted at that time for Venus led him to dismiss reactions (1) and (2) as irrelevant to Venus because the equilibrium CO₂ pressures at low temperatures are much smaller than the CO₂ pressure in the atmosphere of Venus.

However, the situation changed dramatically after the Mariner 2 microwave radiometer observations confirmed Venus' high surface temperature. Mueller (1963,1964) and others (see, e.g., Lewis 1968,1970) revived Urey's concept that carbonate-silicate equilibria are CO₂ buffers. Apparent discrepancies between observations by the American Mariner 5 flyby and Soviet

TABLE I

Abundances of Chemically Reactive Gases in the Lower Atmosphere of Venus^{a,b}

Gas	Abundance	References and Notes	
CO ₂	96.5±0.8%	Uncertainty due to uncertainty in N ₂ ; von Zahn et al. (1983)	
N ₂	3.5±0.8%	Recommended value from von Zahn et al. (1983)	
SO ₂	150 ppm	52 km; Bertaux et al. (1996) Vega 1 UV spectroscopy	
	65 ppm	52 km; Bertaux et al. (1996) Vega 2 UV spectroscopy	
	125 ppm	42 km; Bertaux et al. (1996) Vega 1 UV spectroscopy	
	200 ppm	42 km; Bertaux et al. (1996) Vega 2 UV spectroscopy	
	130±35 ppm	≤42 km; Gel'man et al. (1979) Venera 11/12 GC data	
	130±40 ppm	35–45 km; Bézard et al. (1993) Earth-based IR spectra	
	180±70 ppm	42 km; Pollack et al. (1993) Earth-based IR spectra	
	185±43 ppm	22 km; Oyama et al. (1980) Pioneer Venus GC data	
	38 ppm	22 km; Bertaux et al. (1996) Vega 1 UV spectroscopy	
	25±12 ppm	12 km; Bertaux et al. (1996) Vega 1 UV spectroscopy	
	H ₂ O	150 ppm	42 km; Moroz et al. (1979) Venera 11/12 Vis-IR spectrophotometry ^c
		60 ppm	22 km; Moroz et al. (1979) Venera 11/12 Vis-IR spectrophotometry ^c
		40 ppm	35–45 km; Bézard et al. (1990) Earth-based IR spectra
30±10 ppm		10–40 km; Pollack et al. (1993) Earth-based IR spectra	
30±10 ppm		15–25 km; de Bergh et al. (1995) Earth-based IR spectra	
30±15 ppm		0–15 km; de Bergh et al. (1995) Earth-based IR spectra	
20 ppm		0 km; Moroz et al. (1979) Venera 11/12 Vis-IR spectrophotometry ^c	
CO	45±10 ppm	Cloud top; Connes et al. (1968) Earth-based IR spectra	
	51 ppm	Cloud top; Young (1972) re-analysis of Connes et al. (1968) data	
	45 ppm	35–45 km; Bézard et al. (1990) Earth-based IR spectra	
	23±5 ppm	36 km; Pollack et al. (1993) Earth-based IR spectra	
	30±18 ppm	42 km; Oyama et al. (1980) Pioneer Venus GC data	
	28±7 ppm	36–42 km; Gel'man et al. (1979) Venera 11/12 GC data	
	20±3 ppm	22 km; Oyama et al. (1980) Pioneer Venus GC data	
	17±1 ppm	12 km; Marov et al. (1989) Venera 11/12 GC data	
H ₂ S	3±2 ppm	<20 km; Hoffman et al. (1980 ^{a,b}) Pioneer Venus MS data ^d	
HCl	0.6±0.12 ppm	Cloud top; Connes et al. (1967) Earth-based IR spectra	
	0.4 ppm	Cloud top; Young (1972) re-analysis of Connes et al. (1967) data	
	0.4 ppm	Cloud top; de Bergh et al. (1989) Earth-based IR spectra	
	0.5 ppm	35–45 km; Bézard et al. (1990) Earth-based IR spectra	
	0.48±0.12 ppm	23.5 km; Pollack et al. (1993) Earth-based IR spectra	
OCS	4.4±1.0 ppm	33 km; Pollack et al. (1993) Earth-based IR spectra	
	40±20 ppm	29–37 km; Mukhin et al. (1983) Venera 13/14 GC data	
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) re-analysis of Connes et al. (1967) data	
	4.5 ppb	35–45 km; Bézard et al. (1990) Earth-based IR spectra	
	1–5 ppb	33.5 km; Pollack et al. (1993) Earth-based IR spectra	

^a Modified from Fegley et al. (1992). ^bExcluding the noble gases and isotopically substituted species. ^cRe-analysis of these data by Young et al. (1984) gives a constant H₂O abundance of 20 to 30 ppm if only the 1.13 μm band is considered. ^dReported by Hoffman et al. (1980^{a,b}) as a preliminary value. Oyama et al. (1980) reported an upper limit of 2 ppm at ≤22 km altitude.

Venera 4-6 entry missions caused the temperature and pressure at the surface of Venus to remain a matter of debate until the early 1970s (Lewis 1968,1969,1970). However, it was generally accepted that the CO₂ pressure from reaction (2) at ~700 to 740 K was comparable to the CO₂ pressure at the surface of Venus.

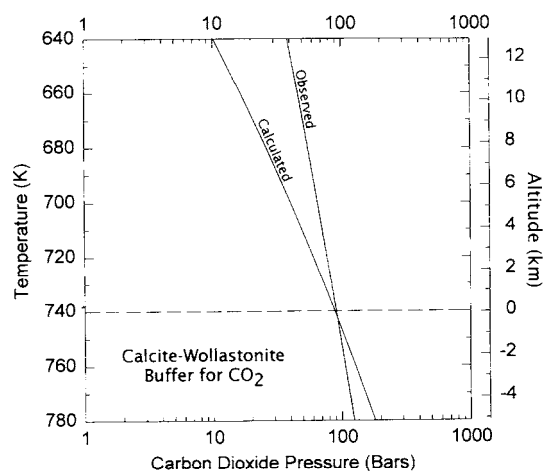


Figure 1. A comparison of the observed and calculated CO₂ pressures on Venus. The observed CO₂ pressure is 0.965 times the total pressure from Seiff (1983). The calculated CO₂ pressure is for the calcite-quartz-wollastonite buffer. The dashed lines are for 2 sigma uncertainties in the thermodynamic data. The observed and calculated curves intersect at 740 ± 30 K (0 ± 4 km altitude) (based on calculations presented in Fegley and Treiman 1992).

This point is illustrated by Fig. 1 which shows that the equilibrium CO₂ pressure buffered by the coexistence of quartz, calcite, and wollastonite intersects the observed CO₂ pressure in the lower atmosphere of Venus at 740 ± 30 K (0 ± 4 km altitude). This agreement is better than that for any other carbonate-silicate buffer (Fegley and Treiman 1992), and for over two decades has been regarded as evidence that reaction (2) is buffering the CO₂ pressure on Venus (Lewis 1970). (The details of thermodynamic calculations for this buffer, and other gas-solid reactions are discussed by Fegley and Treiman [1992].)

Equilibria similar to reactions (1) and (2) have been used to predict the thermodynamic stability of other carbonates on the surface of Venus. Lewis (1970) considered reactions involving dolomite (CaMg(CO₃)₂), magnesite (MgCO₃), and siderite (FeCO₃). He showed that only calcite was stable at 740 K. Fegley and Treiman (1992) calculated the hypsometric control of carbonate stability on Venus initially proposed by Florensky et al. (1977a). They showed that dolomite and magnesite could be stable at lower temperatures and higher altitudes where the equilibrium CO₂ pressures are equal to or less

than the CO₂ partial pressure in the atmosphere of Venus. Their results are summarized in Table II.

TABLE II
Carbonate Stability on the Surface of Venus^a

Reaction ^a	Stability Field ^b	
	T _{max} (K)	Z _{min} (km)
CaCO ₃ + SiO ₂ = CaSiO ₃ + CO ₂ (g)	740±30	0±4
MgCO ₃ + MgSiO ₃ = Mg ₂ SiO ₄ + CO ₂ (g)	700±30	5±4
CaMg(CO ₃) ₂ + 4MgSiO ₃ = 2Mg ₂ SiO ₄ + CaMgSi ₂ O ₆ + 2CO ₂ (g)	660±70	10±9
2CaMg(CO ₃) ₂ + SiO ₂ = 2CaCO ₃ + Mg ₂ SiO ₄ + 2CO ₂ (g)	645±25	12±3

^a Thermodynamic data sources are given in Fegley and Treiman (1992).

^b The maximum temperature and minimum altitude at which the carbonate-bearing mineral assemblage is stable.

Fegley and Treiman (1992) and Fegley et al. (1992) also calculated the stability of siderite, rhodochrosite (MnCO₃), and cerussite (PbCO₃) as a function of altitude because these minerals were potential candidates for high dielectric constant phases on Venus (Garvin and Head 1985; Pettengill et al. 1988). However, the pure carbonates are predicted to be unstable on Venus. Other potential carbonate-forming elements, such as Ba, Sr, and Zn are present at very low abundance in Venusian rocks. Their pure carbonates would not be important, even if stable.

However, the relevance of carbonate-silicate equilibria to Venus has been questioned by several authors (Orville 1974; Klose et al. 1992), who argued that calcite is absent on the surface of Venus. Because of the importance of carbonates for atmosphere-surface reactions on Venus, and in order to guide the design of geochemical experiments on future spacecraft missions to Venus, it is worth examining these arguments in some detail.

B. Geochemical Arguments For and Against Carbonates on Venus

1. Calcite Paragenesis. On the Earth calcite is generally, but not exclusively, found in sedimentary and metamorphic rocks (Deer et al. 1963). As noted by Fegley and Treiman (1992) and discussed in more detail by Fegley et al. (1992) and Kargel et al. (1994), calcite also typically is found at the level of a few percent in many alkaline igneous rocks such as nepheline-syenites, melilite-nephelinites, okaites, ijolites, and melteigites (Johannsen 1937). Calcite is also a major phase in kimberlites (Mitchell 1986) and some carbonatites (Woolley and Kempe 1989). Wollastonite occurs with calcite in many of the same alkaline igneous rocks. Kargel et al. (1994) pointed out that wollastonite occurs with quartz in carbonatites (Deer et al. 1963; Sorensen 1974; Hogarth 1989). As discussed in Sec. II.C below, the XRF and γ -ray analyses of the surface of Venus by several Venera and Vega spacecraft provide indirect evidence for the presence of calcite-bearing rocks on Venus. The XRF data and geomorphological evidence also suggest that carbonatites

and related alkaline igneous rocks, while rare on Earth, are apparently more common on Venus (Kargel et al. 1993,1994). Several other arguments also suggest the presence of calcite on Venus. We mention these points here, and discuss some of them in more detail with hydrogen halide buffers in Sec. II.D.

2. *Geomorphology.* Kargel et al. (1991,1994) argued that carbonatite magmas, which normally have water-like rheological properties, could be responsible for the canali, outflow channels, and associated volcanic deposits seen in Magellan radar images. Kargel and colleagues point out that these features on Venus more closely resemble fluvial landforms than common volcanic features made by basaltic magmas on the Earth and Mars.

3. *Hydrogen Halide Buffers.* These geological and geophysical arguments are consistent with independent geochemical arguments that carbonatites and related types of alkaline rocks provide the necessary mineral assemblages to buffer the observed HCl and HF abundances in the atmosphere of Venus (Fegley et al. 1992; Kargel et al. 1994). As discussed later in Sec. II.D, mineral assemblages containing wollastonite + sodalite ($\text{Na}_4[\text{AlSiO}_4]_3\text{Cl}$) or nepheline (NaAlSiO_4) give the best agreement between the calculated and observed HCl pressure in the atmosphere of Venus. Nepheline is widespread and abundant in alkaline igneous rocks and carbonatites. Wollastonite and sodalite also occur in these rock types but typically are not as widespread and abundant as nepheline. The best agreement between calculated and observed HF pressures in the atmosphere of Venus is provided by assemblages involving feldspathoids and fluoramphiboles or feldspar and fluorphlogopite. These mineral assemblages are also found in alkaline igneous rocks and carbonatites.

4. *Dielectric and Ferroelectric Minerals.* Carbonatites and associated alkaline igneous rocks also contain perovskites and pyrochlores, which are high dielectric phases, that may explain the low radar emissivity on Venus (Pettengill et al. 1982,1988; chapter by Pettengill). The observed abundances of perovskites and pyrochlores in terrestrial alkaline rocks and carbonatites are consistent with the amounts of ferroelectrics required to increase the bulk dielectric constant of rocks on Venus. Perovskites are common minor and trace phases, found at abundances of a few percent, in terrestrial carbonatites and igneous alkaline rocks (Hogarth 1989; Semenov 1974). For example, ~2 to 9% (by volume) perovskite is found in melilite-rich alkaline rocks from the Kola peninsula, the Oka hills in Quebec, and in South Africa and 5 to 9% (by volume) perovskite is found in leucite-rich rocks from Uganda and in nepheline-rich rocks from Colorado (Johannsen 1937; Deer et al. 1963; Sorensen 1974). Pyrochlores ($\text{A}_{16-x}\text{B}_{16}\text{O}_{48}(\text{O},\text{OH},\text{F})_{8-y}$), with a wide variety of compositions, are also common minor and trace minerals present at percent levels in carbonatites and associated alkaline igneous rocks (Hogarth 1989; Semenov 1974).

Synthetic perovskite (CaTiO_3) has dielectric constants of 165 to 170 at radar frequencies (Von Hippel 1954) and some natural perovskites have dielectric constants of 1100 to 2200 at 10 kHz (Timco 1977). Fegley et al. (1992) calculated the stability of pure CaTiO_3 against chemical weathering

by CO_2 , SO_2 , HCl , and HF on Venus. At the highest elevations (e.g., 10 km at the summit of Maxwell Montes), CaTiO_3 is converted to fluorite+rutile at a rate that exceeds the production of fresh, perovskite-bearing rock. Thus, the top of Maxwell displays normal radar emissivity because it is perovskite poor. Along the flanks of Maxwell, at slightly lower elevations, fluorite formation is thermodynamically unfavorable and the rate of CaTiO_3 weathering by the less reactive gases CO_2 and SO_2 is slow enough that perovskite can persist on a geologic time scale. These regions display low radar emissivity because they are perovskite rich. At the base of Maxwell, the temperatures are sufficiently high that chemical weathering of CaTiO_3 by CO_2 and SO_2 proceeds fast enough to destroy perovskite in a geologically short time. As a result, the low altitude regions also display normal radar emissivity.

Kargel et al. (1994) expanded on this model by noting that the variations in the critical elevation (where low emissivity regions begin) are plausibly due to variations in the compositions, and hence, reactivities, of natural perovskites. They also pointed out that some regions within the perovskite metastability zone (at intermediate altitudes) that show normal emissivity, may simply not contain any perovskite-bearing rocks.

Other perovskites, in particular Nb-rich ones, are ferroelectric phases with even higher dielectric constants (Lines and Glass 1977). Many synthetic pyrochlores studied in the laboratory are also ferroelectric phases. Figure 2 in Shepard et al. (1994) dramatically illustrates that the variation of dielectric constant with temperature for a typical ferroelectric compound almost exactly reproduces the altitude dependent emissivity variations that are observed at Ovda Regio. Arvidson et al. (1994) also showed that the ferroelectric model can reproduce the emissivity vs altitude curves for 13 areas in geologically different regions on the surface of Venus.

Using theoretical models for the bulk dielectric constant of a binary mixture, Shepard et al. (1994) showed that only 0.09% (by volume) of ferroelectric phases with dielectric constants of 100,000 can raise the bulk dielectric constant of Venus surface rock from values of ~ 4 to 5 to a dielectric constant of 65. Larger amounts of ferroelectrics would yield even larger bulk dielectric constants. Shepard et al. (1994) also showed that ferroelectrics of slightly different composition can plausibly explain the observed trend of emissivity vs altitude and the observed variations in the critical elevation from region to region on Venus.

Although the phases studied in the laboratory are generally not the same minerals found in carbonatites and alkaline igneous rocks, there are important similarities which suggest that it is important to measure electrical properties of appropriate minerals and rocks to test the model before it can be uncritically accepted or arbitrarily dismissed.

5. *Ancient Sedimentation or High Altitude Weathering.* Calcite could also be produced by other processes that operated on Venus in the past or operate on Venus today. If water were present on Venus in the past, as the high atmospheric D/H ratio suggests (see, e.g., Donahue et al. 1982), then

sedimentary calcite formation may have taken place. Alternatively, as proposed by Florensky et al. (1977a) and Nozette and Lewis (1982), chemical weathering of rocks at high elevations could produce calcite (and other carbonates) that are then abraded and blown into the hotter lowlands below where these fine-grained carbonate weathering products react with quartz to form wollastonite and establish the calcite-quartz-wollastonite buffer.

None of these arguments for or against the presence of calcite on Venus can be proven or disproven at the present time. However, alkaline igneous rocks, with or without associated carbonatites, provide the minerals involved in the calcite-quartz-wollastonite buffer, several petrologically plausible buffers for HCl and HF, plausible high dielectric constant phases to explain the origin of low radar emissivity regions, and also plausibly explain the observed variations of emissivity with altitude and location. As discussed below, elemental analyses of the surface of Venus are compatible with the presence of alkaline igneous rocks on Venus.

C. Evidence for Carbonates from X-ray Fluorescence and Gamma Ray Spectroscopy on Venera and Vega Landers

Table III lists the seven Venera and Vega missions which made geochemical analyses of the surface of Venus. Descriptions of these experiments are given in the Appendix on the CD-ROM (CDP4C4A1). Magellan radar imagery, interpretations of the γ -ray spectroscopy data for K, U, and Th (Table IV), and interpretations of the X-ray fluorescence (XRF) major element data (Tables V and VI) indicate that several different rock types were sampled by these geochemical analyses (see, e.g., Basilevsky et al. 1992; Barsukov et al. 1986; Kargel et al. 1993; Volkov et al. 1986).

For example, Kargel et al. (1993) interpreted the Venera 9, 10, 14, and Vega 1 and 2 landing sites as tholeiitic basalts, the Venera 13 site as a weathered olivine leucitite, and the Venera 8 site as a leucitite, rhyolite, or monzonite. These interpretations are not unique but the other groups cited above have come to similar conclusions. Of particular interest here are the interpretations (Basilevsky et al. 1992; Barsukov et al. 1986; Volkov et al. 1986) of the Venera 8 γ -ray and the Venera 13 XRF analyses indicating that alkaline igneous rocks on Venus (Tables III and V), may be more abundant than on the Earth (see, e.g., Kargel et al. 1993).

The mass deficits in the XRF elemental analyses (Table V) were interpreted by Fegley et al. (1992) and Kargel et al. (1994) as evidence for carbonates on Venus. The Venera and Vega XRF instruments (Surkov et al. 1983, 1984, 1986), like those flown on the Viking landers (Clark et al. 1977), were sensitive only to Mg and heavier elements, and could not detect C and other light elements with atomic numbers $Z < 12$. The Venera 13, 14, and Vega 2 XRF elemental analyses, show mass deficits of ~ 4 to 7% (Table V), before the addition of ~ 2 to 2.5% Na_2O , that was estimated on the basis of petrochemical trends (Barsukov et al. 1986; Surkov et al. 1984). Similar mass deficits of ~ 7 to 10% occur in the Viking XRF analyses (see, e.g., Clark et al.

TABLE III
Geochemical Analyses and Imaging on the Surface of Venus^a

Probe	Latitude ^b (deg)	Longitude ^b (deg)	Altitude ^c (km)	Location and Suggested Rock Types/ Lamprophyres? rhyolite?	Experiment	Reference(s)
Venera 8	-10.7	335.25	0.4±0.2	Mottled volcanic plains east of Navka Planitia; leucitite?	γ-ray	Vinogradov et al. 1973
Venera 9	31.0	291.64	1.2±0.5	NE slope of Beta Regio, lander site has 15 to 20° slope with decimeter-size rock fragments with soil between them, MORB-like basaltic tholeiite?	γ-ray TV image ^e Photometry ^d	Surkov 1977 Florensky et al. 1977a,b Ekonomov et al. 1980
Venera 10	15.42	291.51	0.7±0.6	Lowlands near SE edge of Beta Regio, lander site has soil between 10 to 15 cm high outcrops of bedrock, MORB-like basaltic tholeiite?	γ-ray TV image ^e Photometry ^d	Surkov 1977 Florensky et al. 1977a,b Ekonomov et al. 1980
Venera 13	-7.55	303.69	0.7±0.3	Navka Planitia at east end of Phoebe Regio rise, landscape similar to Venera 10 site, mafic alkaline rocks such as weathered olivine leucitite?, nephelinite?	XRF Redox experiment TV imaging ^{d,e}	Surkov et al. 1984 Florensky et al. 1983a Selivanov et al. 1983
Venera 14	-13.05	310.19	0.8±0.3	Southern Navka Planitia on flank of a volcano, landing site is a plain dominated by layered bedrock and minor amount of soil, weathered MORB-like tholeiite?	XRF Redox experiment TV imaging ^{d,e}	Surkov et al. 1984 Florensky et al. 1983a Selivanov et al. 1983
Vega 1	8.10	175.85	-0.2±0.1	Rusalka Planitia, north of Aphrodite Terra, no TV panoramas, MORB-like tholeiite?	γ-ray	Surkov et al. 1987a,b
Vega 2	-7.14	177.67	1.1±0.2	Transitional zone between Rusalka Planitia and E. edge of Aphrodite Terra rise, no TV panoramas, MORB-like tholeiite?	γ-ray XRF	Surkov et al. 1987a,b Surkov et al. 1986

^a Positional and elevation data are from Basilevsky et al. (1992); R. A. Brackett (personal communication, 1995).

^b Typical uncertainties on latitude and longitude are ±1.5° (Basilevsky et al. 1992).

^c Relative to a mean radius of 6051.5 km with one standard deviation uncertainties.

^d Also see Florensky et al. (1983b); Garvin et al. (1984) and Pieters et al. (1986) for interpretations of photometric data and imaging.

^e Black and white TV image for Venera 9 and 10; Red-green-blue TV imaging for Venera 13 and 14.

^f Suggested rock types are taken from the literature and are discussed in more detail in the text.

TABLE IV
Gamma Ray Analyses of the Surface of Venus^a

Lander	K (wt%)	U (ppm)	Th (ppm)
Venera 8	4.0±1.2	2.2±0.7	6.5±2.2
Venera 9	0.47±0.08	0.60±0.16	3.65±0.42
Venera 10	0.30±0.16	0.46±0.26	0.70±0.34
Vega 1	0.45±0.22	0.64±0.47	1.5±1.2
Vega 2	0.40±0.20 ^b	0.68±0.38	2.0±1.0

^a Table from Surkov et al. (1987a,b).

^b Compare to 0.1±0.08 wt% from XRF analysis on Vega 2.

TABLE V
Major Element Composition of the Surface of Venus and
of Some Terrestrial Rocks

Oxide	Mass Percent (±1σ)					
	Venera 13 ^a	Venera 14 ^a	Vega 2 ^{b,c}	N-MORB ^f	Leucitite ^g	Lamprophyre ^h
SiO ₂	45.1±3.0	48.7±3.6	45.6±3.2	48.77	46.2	46.3
TiO ₂	1.59±0.45	1.25±0.41	0.2±0.1	1.15	1.2	2.6
Al ₂ O ₃	15.8±3.0	17.9±2.6	16±1.8	15.90	14.4	13.5
FeO ^c	9.3±2.2	8.8±1.8	7.7±1.1	9.82	8.09	11.0
MnO	0.2±0.1	0.16±0.08	0.14±0.12	0.17	0.0	0.21
MgO	11.4±6.2	8.1±3.3	11.5±3.7	9.67	7.0	9.1
CaO	7.1±0.96	10.3±1.2	7.5±0.7	11.16	13.2	10.7
Na ₂ O ^d	2±0.5	2.4±0.4	2	2.43	1.6	3.1
K ₂ O	4.0±0.63	0.2±0.07	0.1±0.08	0.08	6.4	2.9
SO ₃	1.62±1.0	0.88±0.77	4.7±1.5			
Cl	<0.3	<0.4	<0.3			
Total	98.1	98.7	95.4	99.15 ^f	98.09	99.41

^a Surkov et al. (1984).

^b Surkov et al. (1986).

^c All Fe reported as FeO for all analyses.

^d Calculated by Surkov et al. (1984,1986).

^e In addition to Cl, Surkov et al. (1986) also report the following upper limits (in mass %): Cu, Pb<0.3; Zn<0.2; Sr, Y, Zr, Nb, Mo<0.1; As, Se, Br<0.08.

^f N-type, or normal MORB (Wilson 1989). Also contains 0.09% P₂O₅ and 0.30% H₂O.

^g Leucitite, an alkaline basalt (Philpotts 1990). Also contains 0.4% P₂O₅.

^h Lamprophyre, which is an ultrapotassic rock (Wilson 1989). Also contains 0.9% P₂O₅, 2.6% H₂O, and 2.5% CO₂.

1977,1982; Toulmin et al. 1977). The Na content of Martian soil was either estimated by assuming that enough Na was present to balance the measured Cl and S (Toulmin et al. 1977) or from analyses of the SNC meteorites (Banin et al. 1992).

As discussed by Toulmin et al. (1977), the mass deficits in the Viking

TABLE VI
Normative Mineralogy of the Venera and Vega Landing Sites^a

Mineral		CIPW Norm (Mass %)		
		Venera 13 _{1,2}	Venera 14 _{1,3}	Vega 2
Orthopyroxene	En	20.8	0.0	14.2
	Fs	9.2	0.0	10.1
Clinopyroxene	Wo	0.8	9.4	5
	En	0.5	5.8	2.8
Olivine	Fs	0.2	3.0	2.0
	Fo	7.4	16.2	2.6
	Fa	3.6	9.3	2.1
Plagioclase	Ab	17	0.0	17.0
	An	39.3	13.1	40.6
K-feldspar	Or	0.7	10.2	1.2
Feldspathoids	Lc	0.0	11.2	0.0
	Ne	0.0	18.8	0.0
Oxides	Il	0.4	3.0	2.4
Total		99.9	100.0	100.0

^a Calculated by Kargel et al. (1993) on a volatile-free basis. En: enstatite; Fs: ferrosilite; Wo: wollastonite; Fo: forsterite; Fa: fayalite; Ab: albite; An: anorthite; Lc: leucite; Ne: nepheline; Il: ilmenite.

XRF analyses, and by analogy in the Venera and Vega XRF analyses, must be attributed to some or all of the following factors: (1) analytical error, (2) the presence of low *Z* elements, and (3) the sum of smaller amounts of heavier elements that are individually below their respective detection limits. Toulmin et al. (1977) discuss why it is unlikely that analytical errors account for the observed mass deficits in the Viking XRF analyses. Based on descriptions of the Venera and Vega XRF experiments, the data processing procedures and algorithms (Surkov et al. 1983,1984,1985,1986,1987c), and the similar uncertainties in individual elemental abundances in the Viking, and Venera/Vega XRF analyses, it is unlikely that analytical errors can account for all of the observed mass deficits in the Venera 13,14 and Vega 2 XRF elemental analyses. The amounts of heavier elements that are individually below their respective detection limits are also probably insufficient to account for the remaining mass deficit. As emphasized by Toulmin et al. (1977) for the Viking XRF data, the cosmochemical abundances of other high *Z* elements (Anders and Grevesse 1989) and geochemical considerations suggest that the other undetected, high *Z* elements are not present in large enough amounts to contribute significantly to the mass deficit. The possible exceptions are Ni and Mn (Toulmin et al. 1977). However, Mn is already included in the Venera and Vega XRF analyses (Table III), and by analogy with the Earth's crust, the average Ni content of the surface of Venus would be ~0.003 to 0.02%.

As with the Viking XRF analyses, the most plausible explanation for

the mass deficits in the Venera and Vega XRF analyses is the presence of compounds formed by low Z elements. Some low Z elements (Li, Be, B) and their compounds can be ruled out as major contributors to the mass deficits because of their low cosmochemical and geochemical abundances. Oxygen and Na, which are not directly measured, are already considered in the XRF analyses. Nitrogen, in the form of nitrides and nitrates can be ruled out because these compounds are not stable on the surface of Venus (Fegley and Treiman 1992). Dissolved N in minerals is probably only a few ppm by mass. Fegley and Treiman (1992) concluded that hydrated silicates are unstable on the surface of Venus. Recent Earth-based infrared observations of H_2O in Venus' near-surface atmosphere and more recent thermodynamic data for hydrated minerals strengthen this conclusion. Thus, the mass deficits are most plausibly due to compounds formed by fluorine and carbon. Although F-bearing minerals are probably present on the surface, their abundance is unlikely to account for the entire mass deficit (as also argued by Toulmin et al. [1977] for the Viking XRF analyses). Assuming that the mass deficit is indeed due to carbonates, Kargel et al. (1994) calculated that calcite made up $\sim 4\%$ (by mass) of the Venera 13 sample, $\sim 3\%$ of the Venera 14 sample, and $\sim 10\%$ of the Vega 2 sample. In principle, these inferred carbonate abundances can be tested by future Venus landers equipped with low Z sensitive analytical experiments such as an APX (α -proton-X-ray) analyzer or with infrared reflection spectrometers.

D. HCl and HF Mineral Buffers

Table I shows that HCl and HF are only trace constituents of the Venusian atmosphere. However, they are still many times more abundant on Venus than on Earth. The HCl mixing ratio of ~ 0.5 ppm corresponds to a column density of $\sim 7 \times 10^{20}$ HCl molecules cm^{-2} . On Earth, the total Cl mixing ratio ($CH_3Cl + 2CF_2Cl_2 + 3CFCl_3 + 3CH_3CCl_3 + 4CCl_4 + HCl$) in the nonurban terrestrial troposphere is ~ 2.7 ppb (Fegley 1995). This is equal to a total Cl column density of $\sim 6 \times 10^{16}$ Cl atoms cm^{-2} , or about 0.009% of the Cl column density in the atmosphere of Venus. The Cl content of the terrestrial troposphere is dominated by man-made compounds such as chlorofluorocarbons, while volcanic HCl, sea spray, and some biogenic halocarbons comprise a smaller percentage of the chlorine in the Earth's troposphere. Thus, the Cl content of the terrestrial troposphere would be much smaller if the anthropogenic, biogenic, and oceanic components were removed.

Likewise, the 1 to 5 ppb of HF in the atmosphere of Venus corresponds to an HF column density of $\sim (1-7) \times 10^{18}$ cm^{-2} . The total F mixing ratio ($2CF_2Cl_2 + CFCl_3 + 4CF_4 + 2CHClF_2 + 3C_2Cl_3F_3$) in the nonurban terrestrial troposphere is ~ 1.3 ppb (Fegley 1995). The corresponding total fluorine column density of $\sim 3 \times 10^{16}$ F atoms cm^{-2} is about 0.4 to 3% of the HF column density on Venus. Again, total atmospheric fluorine on Earth is dominantly due to man-made compounds, and the natural fluorine column density is significantly lower.

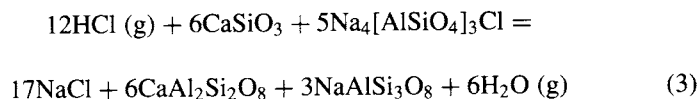
The much higher abundances of HCl and HF on Venus are directly due to the high surface temperature. The corrosive nature of HCl and HF implies that these acids are not inert components of the Venusian atmosphere, but are instead chemically reacting with minerals and rocks on the surface of the planet.

Lewis (1968,1970) and Mueller (1968,1969) proposed that HCl and HF in Venus' atmosphere are buffered by gas-solid reactions. The essentially identical HCl and HF abundances observed above the clouds (Connes et al. 1967) and below the clouds (Pollack et al. 1993) support this concept. Both HCl and HF are found in volcanic exhalations on the Earth (e.g., at Kilauea in Hawaii) and are also likely to be found in volcanic gases on Venus. Although HCl and HF in the atmosphere of Venus plausibly originated from volcanoes, their constant abundances during the 30 years since their discovery in 1967 imply that HCl and HF are probably being buffered by chemical reactions with minerals on the surface of Venus.

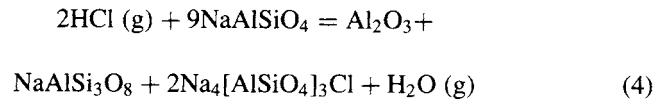
Thermochemical models of nebular condensation chemistry predict that Venus and Earth have similar Cl and F inventories (Fegley and Lewis 1980). The Cl/C and F/C ratios at the surface of the Earth (atmosphere + oceans + sediments + crust) are ~ 0.12 and 0.09 , respectively (Smith 1981; Ronov and Yaroshevsky 1976), and the Cl/F ratio is approximately unity. In contrast, the atmospheric Cl/C and F/C ratios on Venus (essentially the HCl and HF mixing ratios) are orders of magnitude smaller, and the Cl/F ratio is ~ 100 to 500 . Thus, Cl- and F-bearing phases are plausibly present in the interior and on the surface of Venus today.

Fegley and Treiman (1992) reconsidered the HCl and HF buffers suggested previously (Lewis 1968,1970; Mueller 1968,1969) using more recent thermodynamic data. They found that many of the reactions originally suggested by Lewis and Mueller as HCl and HF buffers actually did not provide a good match to the observed abundances. The discrepancies are due to changes in thermodynamic data for some minerals (e.g., for sodalite) and to increased knowledge of conditions, in particular the temperature and water vapor abundance, at the surface of Venus. Furthermore, as originally noted by Orville (1974), the buffers that did seem to match the observed hydrogen halide abundances involved mineral assemblages that were petrologically unreasonable. For example, jadeite, which is unstable below ~ 10 kilobar pressure, or the assemblage nepheline + quartz, which reacts to form albite, were used in buffer reactions.

Fegley and Treiman (1992) proposed new buffers for HCl and HF on Venus. They did so using terrestrial petrology and experimental phase equilibria as guides. Their preferred buffers, that most closely match the HCl abundance in the atmosphere of Venus, are the wollastonite-sodalite-halite buffer

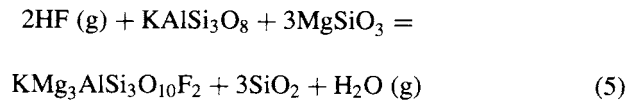


and the nepheline-albite-sodalite buffer

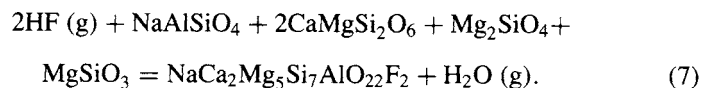
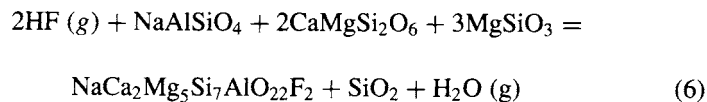


Both buffers provide the observed amount of HCl within the uncertainties of the thermodynamic data and spectroscopic observations. Reaction (4), involving nepheline+albite+sodalite, does not match the observed HCl abundance as closely as reaction (3), but the sodalite+nepheline+albite assemblage is common in terrestrial nepheline-syenites and by analogy would also be expected to be common in alkaline rocks on Venus. Reaction (3) involves the assemblage of wollastonite+sodalite which, as discussed earlier in Sec. II.B, is also found in alkaline igneous rocks.

The preferred HF buffers of Fegley and Treiman (1992) include the fluorphlogopite buffer first proposed by Lewis (1970):



and two buffers involving fluoredenite



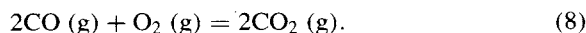
The HF buffers, like the HCl buffers and the calcite-quartz-wollastonite CO₂ buffer are generally compatible with the mineralogy of terrestrial alkaline igneous rocks and carbonatites (Kargel et al. 1994). However, pure enstatite is not found, or at least is not at all common, in terrestrial carbonatites (Hogarth 1989), but augites in alkaline igneous rocks do contain an enstatite component which can take part in buffering reactions. Kargel et al. (1994) also noted that fluoramphiboles are involved in HF buffers and that amphiboles containing up to 3 weight percent F are found in terrestrial carbonatites (Hogarth 1989).

III. OXIDATION STATE OF THE LOWER ATMOSPHERE AND SURFACE OF VENUS

A. CO Abundance and Oxygen Fugacity of the Near-Surface Atmosphere

Carbon monoxide is a minor gas in the atmosphere of Venus (Table I) and it is generally believed (Lewis 1970; Lewis and Kreimendahl 1980; Prinn 1985; Volkov et al. 1986; Fegley and Treiman 1992; Zolotov 1994) that the

oxidation state of the lower atmosphere of Venus is controlled by the net thermochemical reaction:



The oxygen fugacity as a function of temperature for reaction (8) is

$$\log_{10} f_{\text{O}_2} = 2\log_{10}\left(\frac{X_{\text{CO}}}{X_{\text{CO}_2}}\right) + 9.17 - \left(\frac{29607}{T}\right) \quad (9)$$

A combination of Earth-based and *in-situ* measurements of CO in the lower atmosphere of Venus indicates that the CO concentration decreases with decreasing altitude toward the surface of Venus (Table I). This trend was discussed by von Zahn et al. (1983), and the data in Florensky et al. (1983*a,c*), Marov et al. (1989), and Pollack et al. (1993) provide more evidence for a decreasing CO mixing ratio toward the surface of Venus. However, at present there are no direct measurements of the CO concentration at altitudes below 12 km on Venus, so the CO mixing ratio, and by inference, the oxygen fugacity and redox state at the surface are open questions.

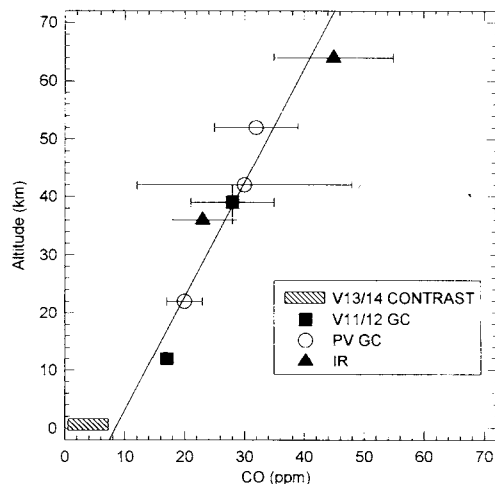


Figure 2. Observations of the CO abundance in the atmosphere of Venus (~0–70 km altitude) from the Venera 11/12 gas chromatograph (black squares), the Pioneer Venus (PV) gas chromatograph (open circles), the Venera 13/14 CONTRAST experiment (striped box), and from Earth-based infrared spectroscopy (black triangles). Table I lists the data sources. The CONTRAST experiment gave lower limits on the CO abundance (see text). Due to uncertainties in the thermodynamic data for reactions (14) and (15), these lower limits vary from 0.6 to 7 ppm CO.

The Venera 11 and 12 gas chromatograph experiment observed 17 ppm CO at 12 km altitude. Assuming no further decrease in the CO concentration with decreasing altitude and using a temperature of 740 K, Eq. (9) yields an oxygen fugacity of $10^{-21.3}$ bar at 0 km altitude. Zolotov (1996) independently calculated an oxygen fugacity of $10^{-21.3\pm 0.2}$ bar at the same temperature from his thermochemical models. Alternatively, we can assume that the CO concentration continues to decrease toward the surface of Venus at altitudes below 12 km. A linear least squares fit to the CO mixing ratios at 12, 22, 36, 39, 42, 52, and 64 km determined by the Pioneer Venus and Venera 11 and 12 gas chromatographs and Earth-based infrared spectra of Venus (Connes et al. 1968; Oyama et al. 1980; Gel'man et al. 1979; Marov et al. 1989; Pollack et al. 1993) is shown in Fig. 2 and gives the equation

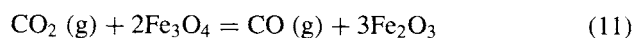
$$\text{CO}(\text{ppm}) = 8.4(\pm 3.0) + 0.51(\pm 0.07)Z(\text{km}) \quad (10)$$

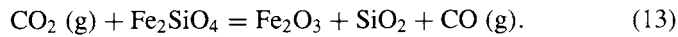
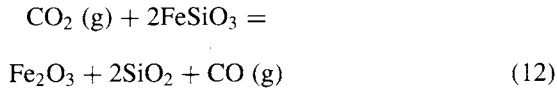
where the uncertainties are $\pm 1\sigma$ errors. The extrapolated CO mixing ratio at 0 km on Venus is then 8.4 ± 3.0 ppm and the corresponding oxygen fugacity is $10^{-20.7\pm 0.4}$ bar. For comparison, Pollack et al. (1993) deduced a CO gradient of 1.20 ± 0.45 ppm km^{-1} around 36 km altitude from their analysis of Earth-based infrared spectra. This gradient is ~ 2.4 times larger than that in Eq. (10) above. However, the CO concentration gradient derived by Pollack et al. (1993) cannot be constant from 0 to 36 km because the derived CO mixing ratio at 0 km on Venus is then less than zero, even when the stated uncertainty is considered.

The calculations discussed above indicate that the CO mixing ratio at the surface of Venus is in the range of ~ 5 to 17 ppm depending on whether or not the trend observed from 12 to 64 km continues downward to the surface. The corresponding oxygen fugacities at 740 K range from $10^{-20.3}$ bar (5 ppm CO) to $10^{-21.3}$ bar (17 ppm CO). As discussed in the next sections, the CO mixing ratio and oxygen fugacity in the near-surface atmosphere of Venus are very important factors that influence the oxidation state of the surface and the relative abundance of reduced (e.g., OCS, H₂S) and oxidized (e.g., SO₂) sulfur gases. Thus *in-situ* measurements of the CO mixing ratio and of the oxygen fugacity below 12 km altitude on Venus are highly desirable.

B. Thermochemical Equilibrium Models of the Oxidation State of the Surface of Venus

Going back to Mueller (1963,1964), theoreticians (Lewis 1970; Lewis and Kreimendahl 1980; Prinn 1985; Volkov et al. 1986; Fegley and Treiman 1992; Zolotov 1987,1994) assumed that the CO/CO₂ ratio in the hot, near-surface atmosphere of Venus controls the oxidation state of the surface of Venus via net thermochemical reactions such as





The equilibrium CO/CO₂ ratios, and the equilibrium oxygen fugacities for reactions (11–13), are independent of the total pressure because reactions (11–13) have the same number of gas molecules on each side of the equations. The fugacity and partial pressure of CO₂ are identical to ~1% under Venus surface temperatures and pressures, so deviations from ideal gas behavior are negligible. Thus, total pressure cancels out of the equilibrium constant expressions.

Thermochemical models can be used to calculate the stable Fe-bearing minerals on the surface of Venus for a given temperature, pressure, and assumed CO/CO₂ ratio in the near-surface atmosphere. This was done by several authors who concluded that the CO/CO₂ ratio in the near-surface atmosphere of Venus, while too oxidizing for either metallic Fe or wüstite (Fe_{0.947}O), is sufficiently reducing to fall within the magnetite stability field (see, e.g., Mueller 1964; Lewis 1970; Lewis and Kreimendahl 1980; Prinn 1985; Fegley and Treiman 1992). In contrast, Zolotov (1987) predicted that hematite is thermodynamically stable at high elevations on the surface of Venus. Furthermore, the recent work of O'Neill (1988) and Hemingway (1990) indicates that hematite is more stable than indicated by thermodynamic data in compilations used by the theorists cited above. Thus, we recalculated stabilities of magnetite and hematite on the surface of Venus.

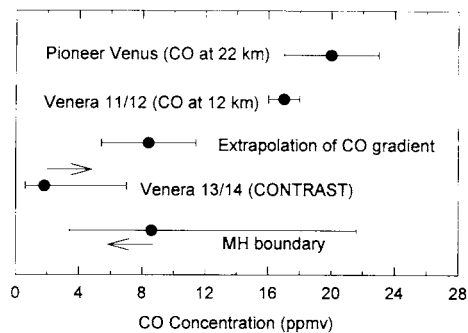


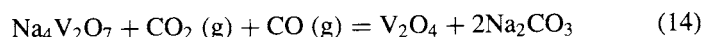
Figure 3. A comparison of observed (Table I) and predicted CO concentrations in the lower atmosphere of Venus. The extrapolated point is from Eq. (10). The uncertainty in the CO concentration at the magnetite-hematite (MH) phase boundary (Eq. 11) is from the 2 sigma uncertainties in the thermodynamic data (Robie and Hemingway 1995). The lower limit from the Venera 13 and 14 CONTRAST experiment is described in the text. The calculated CO concentrations are for 735 K.

In Fig. 3, we compare observations of CO in the lower atmosphere of Venus to the magnetite-hematite phase boundary. The figure shows that within the uncertainties of the observations and calculations, either hematite, or magnetite, or both oxides are stable at ~ 0 km altitude on Venus. Unfortunately, there are no direct measurements (e.g., by X-ray diffraction or Mössbauer spectroscopy) of the mineralogy of the surface to test these predictions.

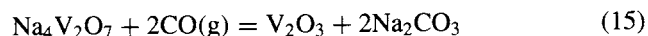
C. Venera Spacecraft Observations

Two indirect observations of the oxidation state of the surface and lower atmosphere of Venus have been made. Initially, it appeared that these two measurements contradicted one another (Florensky et al. 1983*a,c*; Pieters et al. 1986). However, it now appears that the results of the two experiments are consistent and indicate that hematite is present on the surface of Venus (Zolotov 1996; Fegley et al. 1996).

One indirect observation of the redox conditions at the surface of Venus comes from the CONTRAST experiment on the Venera 13 and 14 landers (Florensky et al. 1983*a,c*). This experiment qualitatively measured the CO content from the color change from white to dark blue for the reaction



or from white to black for the reaction



for asbestos paper impregnated with sodium pyrovanadate ($\text{Na}_4\text{V}_2\text{O}_7$). Florensky et al. (1983*a,c*) reported that the observed darkening of the asbestos paper gave a lower limit of ≥ 10 ppm for the CO mixing ratio and, assuming chemical equilibrium between CO and CO_2 , an upper limit of $\leq 10^{-21}$ bar for the oxygen fugacity. This oxygen fugacity falls inside the magnetite stability field at Venus surface temperatures.

However, Zolotov (1996) recalculated the thermodynamics of reaction (14) and derived a lower limit of ≥ 2.5 ppm CO and an upper limit of $\leq 10^{-19.7}$ bar for the oxygen fugacity (at 740 K). This oxygen fugacity implies that hematite, and not magnetite, is stable on the surface of Venus. Zolotov's (1996) results are different than those reported earlier because the thermodynamic data compilation (Naumov et al. 1971) used by Florensky et al. (1983*a,c*) did not take into account high temperature phase transitions in sodium carbonate, sodium pyrovanadate, and the vanadium oxides.

Further analysis (Fegley et al. 1996) of the thermodynamics of reactions (14) and (15) confirms Zolotov's (1996) conclusion. Fegley et al. (1996) calculate lower limits of 1.8 ppm CO for reaction (14) and 4.0 ppm CO for reaction (15) at the Venera 13 and 14 landing sites (0.7–0.8 km altitude, and 733–734 K). Because of the uncertainties in the thermodynamic data, the lower limits on the CO abundance from CONTRAST ranges from 0.6 to 0.7 ppm (Fegley et al. 1996).

As Fig. 3 shows, either hematite or magnetite may be consistent with the revised limits on CO. The uncertainties in the thermodynamic data for the magnetite-hematite boundary and for the CONTRAST experiment preclude any stronger statements. Although CONTRAST was a qualitative experiment, Fig. 2 in Florensky et al. (1983a) shows that the soil-free and soil-covered portions of the indicator could be distinguished. Recent image processing by Gektin (1996) shows that the low albedos of the soil-free areas indicates vanadium oxide formation by either reaction (14) or (15) or both. Thus, we must regard the results as suggestive, but not conclusive.

The second indirect observation of the oxidation state of the surface of Venus was made by the imaging and spectrophotometry experiments on the Venera 9, 10, 13, and 14 spacecraft (Golovin et al. 1983; Selivanov et al. 1983). Pieters et al. (1986) used a combination of the Venera 9 and 10 wide angle photometer measurements and the Venera 13 and 14 color images to derive the spectral reflectance of the Venusian surface in the 0.54 to 1.0 μm 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 infrared region apparently required Fe^{3+} -bearing phases such as hematite.

Initially, the inferred presence of hematite disagreed with the results of the CONTRAST experiment on the Venera 13 and 14 spacecraft. However, as discussed above, either magnetite or hematite may be consistent with the revised CO lower limits derived for the CONTRAST experiment. Thus, at present, the imaging and spectrophotometry data (Pieters et al. 1986) and the revised interpretation of the CONTRAST experiment (Zolotov 1996; Fegley et al. 1996) are both consistent with, but do not prove, the presence of hematite on the surface of Venus.

D. Kinetic Problems with CO-CO₂ Gas Phase Equilibration

The thermochemical models for iron oxide stability on the surface of Venus rest upon the assumption that CO and CO₂ in the near-surface atmosphere reach chemical equilibrium and thus control the oxygen fugacity. However, this assumption may not be valid at the relatively low temperatures (~ 740 K at 0 km to ~ 660 K at 10 km) over the surface of Venus. For example, Huebner (1975) measured the oxygen fugacity of CO-CO₂ gas mixtures as a function of temperature, composition, and gas flow rate. He found that chemical equilibrium was reached at high temperatures (above ~ 1373 K), but not at lower temperatures. To good first approximation, Huebner's results were independent of the CO/CO₂ ratio and gas flow rate.

More recent experiments by Fegley et al. (1995b) tested whether or not CO-CO₂ gas mixtures reached thermochemical equilibrium at temperatures of 665 to 873 K. These experiments were done at temperatures below 973 K, which is the lower temperature limit for zirconia oxygen sensors. Oxidation and reduction reactions of metal oxides were used to constrain the oxygen

fugacities of the gas mixtures.

One set of experiments was done by heating CuO powder in different CO-CO₂ gas mixtures at different temperatures. After heating, the CuO had quantitatively converted to Cu metal. The quantitative reduction of CuO to Cu metal proves that the f_{O_2} values of the CO-CO₂ gas mixtures were less than the oxygen fugacity of the CuO-Cu phase boundary because no CuO was left in the sample after heating. These experiments give upper limits to the oxygen fugacity of the CO-CO₂ gas mixtures.

Another set of experiments was done by heating weighed aliquots of magnetite in different CO-CO₂ gas mixtures at different temperatures. After heating the magnetite had partially converted to hematite. The conversion was indicated by the color change, the weight gain, the X-ray diffraction pattern, and the Mössbauer (MB) spectrum.

The latter method is especially sensitive to the amount of magnetite and hematite in the experimental samples. For example, Fig. 4 and Table VII show the MB spectra and parameters for the magnetite starting material and the almost pure hematite product from one experiment. The MB spectra “before” and “after” heating are clearly different.

TABLE VII
Mössbauer Parameters for Magnetite and Hematite
(Sample 118)

Component	Isomer Shift (mm s ⁻¹)	HF ^a (Tesla)	ΔEQ ^a (mm s ⁻¹)
Magnetite A	0.25	49.2	0.0
Magnetite B	0.64	46.2	0.0
Hematite	0.38	51.9	-0.17

^a HF = hyperfine splitting; ΔEQ = electrical quadrupole splitting.

The quantitative oxidation of magnetite to hematite shows that the oxygen fugacity of the gas mixture was above the magnetite-hematite boundary. This experiment gives a lower limit to the oxygen fugacity of the CO-CO₂ gas mixture.

In experiments done with the same CO-CO₂ gas mixture (CO₂/CO ratio = 98.0) at the same temperature (688 K, which corresponds to ~7 km altitude on Venus) CuO was quantitatively reduced to Cu metal while magnetite was partially oxidized to hematite. The combination of these two experiments shows that the oxygen fugacity of the CO-CO₂ gas mixture was somewhere between 10^{-24.9} bar (MH boundary) and 10^{-14.1} bar (Cu-CuO boundary). However, Eq. (9) predicts that this CO-CO₂ gas mixture should have an even lower oxygen fugacity of 10^{-29.9} bar at 688 K. This is ~5 orders of magnitude below the lower limit obtained from the magnetite oxidation experiment and ~15 orders of magnitude below the upper f_{O_2} limit obtained from the CuO reduction experiment. Similar results were obtained for other CO-CO₂ gas mixtures (Fegley et al. 1995b). The metal oxide redox experiments show that

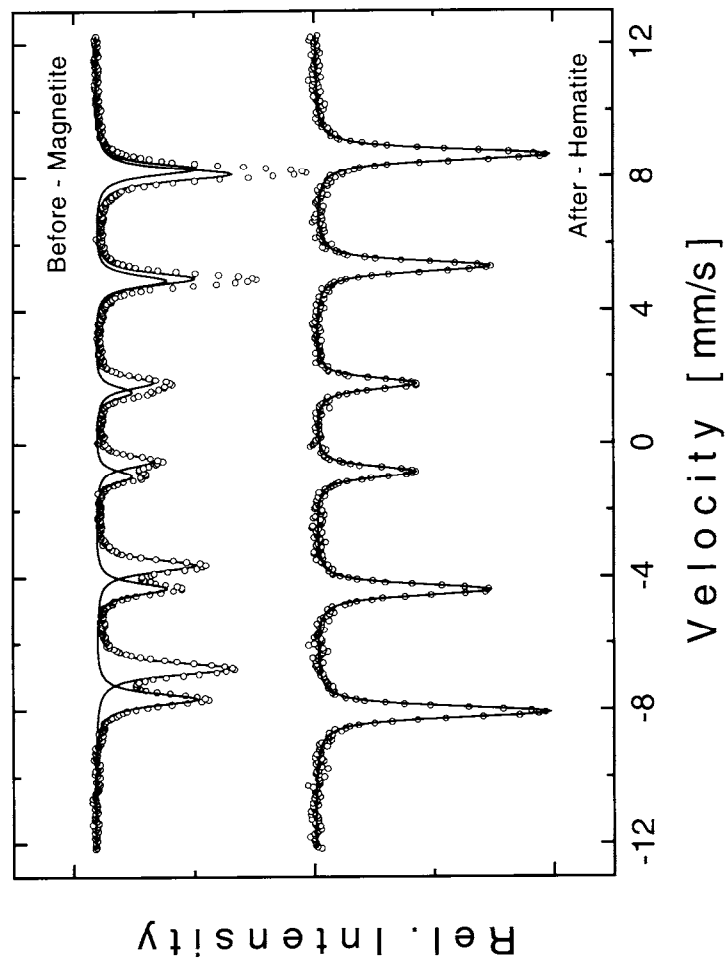


Figure 4. Mössbauer spectra "before" and "after" heating synthetic magnetite (experiment R118) for 3.8 days at 690 K in a CO-CO₂ gas mixture containing 100 ppm CO. Even though the CO/CO₂ ratio of the gas is in the magnetite stability field, almost all of the magnetite oxidized to hematite. The MB parameters are listed in Table VII.

at low temperatures CO-CO₂ gas mixtures, while extremely reducing, are still several orders of magnitude more oxidizing than predicted by thermochemical equilibrium calculations. As a result, magnetite which is heated in “reducing” CO-CO₂ gas mixtures is either partially or totally converted to hematite. A similar situation may be present on Venus.

E. Hematite Formation from Basalt in CO-CO₂ Gas Mixtures

Fegley et al. (1995*b*) also heated basalt samples in CO-CO₂ gas mixtures with CO₂/CO ratios inside the magnetite stability field. The CO molecular number density at the surface of Venus is ~0.5 (5 ppm CO) to ~2 (20 ppm CO) times that in the experiments. The mineralogy of the basalt starting material and the heated samples was determined by several analytical methods including MB spectroscopy. The results of the MB analyses are summarized in Table VIII and the MB spectra are illustrated in Fig. 5. Details of the experiments and analytical methods are described by Fegley et al. (1995*b*).

The MB spectrum of the unheated basalt powder shows that most of the Fe is present as Fe²⁺ in pyroxene, olivine, and ilmenite. The pyroxene also contains some Fe³⁺, but no hematite or magnetite were detected by MB spectroscopy, or other methods.

As shown in Table VIII and Fig. 5, hematite and magnetite are present in the MB spectra of the heated samples. In addition, the heated samples contain smaller amounts of Fe²⁺ in olivine and pyroxene, and larger amounts of Fe³⁺ in pyroxene than the starting material. The MB data for sample ZT1, heated at 505°C for 7 days, show that magnetite, which is nearly, but not exactly stoichiometric, and hematite have formed and comprise about 23.5% of the total Fe atoms in the heated basalt. The Fe³⁺ in pyroxene has also increased from ~28% of the total Fe atoms in the unheated basalt to ~34% of total Fe. Sample BBB1, heated at 803°C for 10 days, contains more hematite (~37%) and Fe³⁺ in pyroxene is 41%.

Although hematite was formed by heating the basalt in a CO-CO₂ mixture containing 1000 ppm CO, the predicted f_{O_2} of the gas mixture is inside the magnetite stability field and thus significantly lower than the actual f_{O_2} , which led to hematite formation. In the case of sample ZT1, thermochemical equilibrium calculations predict an oxygen fugacity of 10^{-22.9} bar while the presence of magnetite and hematite shows that the actual f_{O_2} was ≤10^{-19.0} bar. For sample BBB1, thermochemical equilibrium calculations predict an f_{O_2} of 10^{-12.3} bar and the presence of only hematite shows that the actual value is >10^{-9.4} bar. These results suggest that the red color observed by Pieters et al. (1986) at several Venera landing sites is hematite formed by sub-aerial oxidation of basalt on the surface of Venus.

F. Hematite Formation from Pyrite and Magnetite in CO-CO₂-SO₂ Gas Mixtures

Hematite formation was also observed in the pyrite decomposition experiments done in CO-CO₂, and CO-CO₂-SO₂ gas mixtures by Fegley et al.

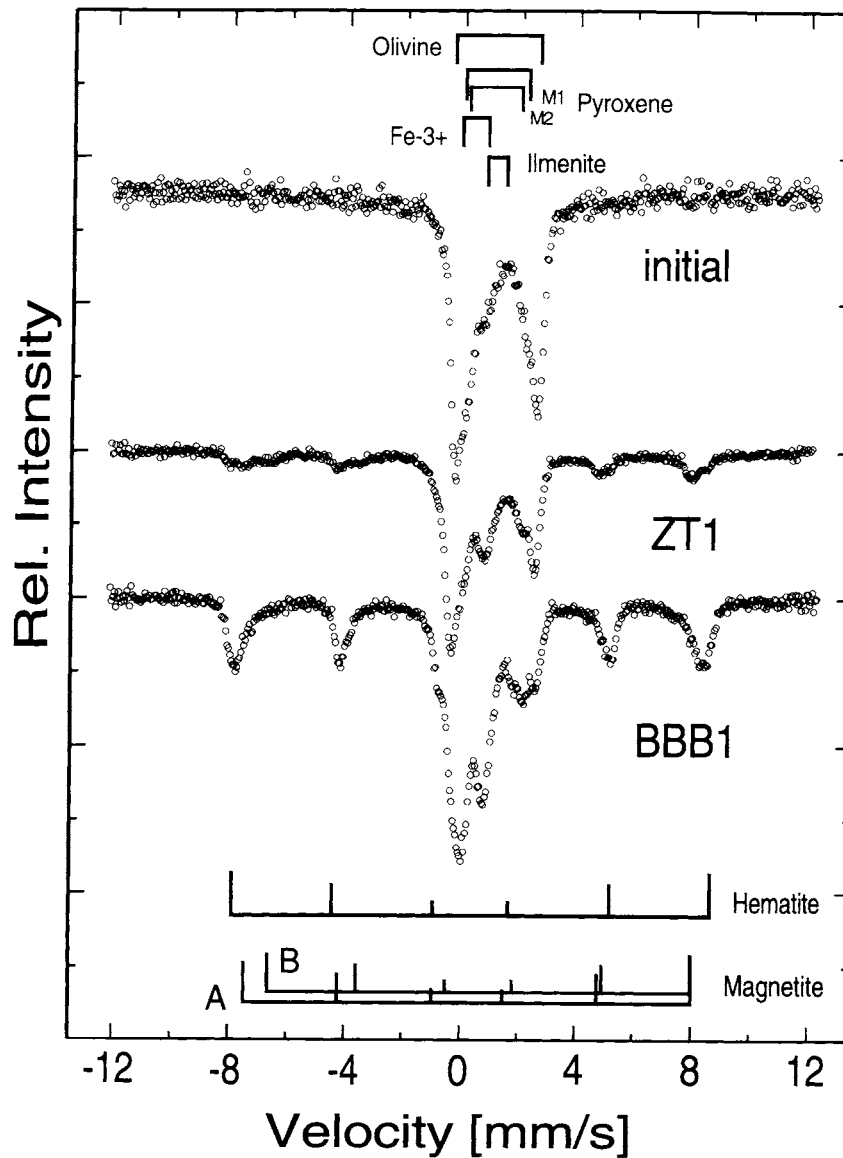


Figure 5. A comparison of the Mössbauer spectra of the unreacted basalt and two oxidized samples. The stick diagrams show the positions and relative intensities of the peaks for Fe^{2+} in olivine, Fe^{2+} in the M1 and M2 sites of clinopyroxene, Fe^{3+} in clinopyroxene, Fe^{2+} in ilmenite, Fe^{3+} in hematite, and for the A and B sites of magnetite. Sample ZT1 was heated for 7 days at 505°C and sample BBB1 was heated for 10 days at 803°C . Both samples were heated in the same CO-CO_2 gas mixture, containing 1000 ppm CO. Table VIII lists the MB parameters for the spectra, which are discussed in Fegley et al. (1995b).

TABLE VIII
Mössbauer Parameters for Unreacted and Oxidized Basalts

Component	Isomer Shift (mm s ⁻¹)	QS ^a (mm s ⁻¹) HF (Tesla)	Relative Intensity (%) ^b	Relative Mass (%)
Unreacted Basalt				
Olivine Fe ²⁺	1.15	2.94	23.5	10.5
Cpx Fe ³⁺	0.37	0.88	28.2	31.0
Cpx Fe ²⁺ (M1)	1.11	2.25	25.0	33.0
Cpx Fe ²⁺ (M2)	1.05	1.80	22.0	25.0
Ilmenite Fe ²⁺	1.11	0.71	1.3	0.5
Oxidized Basalt ZT1				
Olivine Fe ²⁺	1.12	2.94	22.0	14.0
Cpx Fe ³⁺	0.37	0.95	34.0	51.0
Cpx Fe ²⁺ (M1)	1.04	2.35	10.6	23.0
Cpx Fe ²⁺ (M2)	1.12	1.85	4.9	8.0
Ilmenite Fe ²⁺	1.11	0.68	5.0	1.1
Hematite	0.37	51.6 T	3.5	0.5
Fe ₃ O ₄ A site	0.26	48.3 T	7.0	0.8
Fe ₃ O ₄ B site	0.63	45.7 T	13.0	1.6
Oxidized Basalt BBB1				
Olivine Fe ²⁺	1.12	2.95	6.3	4.2
Cpx Fe ³⁺	0.36	0.87	41.0	63.3
Cpx Fe ²⁺ (M1)	1.14	2.16	12.4	23.3
Cpx Fe ²⁺ (M2)	1.13	1.90	3.0	5
Ilmenite Fe ²⁺	1.08	0.71	0.4	0.2
Hematite	0.36	49.76 T	10.8	1.2
	0.378	51.43 T	11.3	1.3
	0.37	43.64 T	8.5	1.0
	0.38	47.52 T	6.3	0.8

^a QS = quadrupole shift (mm s⁻¹) and HF = hyperfine splitting in Tesla (T). Hyperfine splittings are listed for hematite and magnetite and quadrupole splittings are listed for the other components.

^b The apparent variation in the ilmenite content gives an indication of the typical uncertainty in the relative intensities of strongly overlapping components. Typical uncertainties in the relative intensities of clearly resolved components, i.e., magnetite and hematite, are significantly smaller.

(1995a). As discussed below in Sec. IV.B, upon heating pyrite decomposed to pyrrhotite, which then underwent oxidation to hematite via magnetite and maghemite formation. In some cases, hematite occurred without detectable magnetite. In all cases, the CO/CO₂ ratios of the binary and ternary gas mixtures fall inside the magnetite stability field.

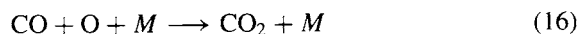
Of most interest here are the experiments done with CO-CO₂-SO₂ gas

mixtures having CO molecular number densities ~ 10 (20 ppm CO) to ~ 40 (5 ppm CO) times that at the surface of Venus, and SO₂ molecular number densities from ~ 1.2 times (150 ppm SO₂) to ~ 7.6 times (25 ppm SO₂) of that at the surface of Venus. The experiments indicate that the presence of SO₂ does not catalyze the equilibration of CO and CO₂, at least on laboratory time scales, and that the actual oxygen fugacity of the ternary mixture is still greater than that calculated assuming thermochemical equilibrium.

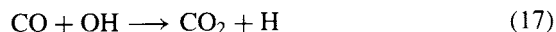
G. Mechanisms for Equilibrating CO and CO₂ at the Surface of Venus

The CO₂/CO ratios of the gas mixtures used in the experiments ranged from ~ 26 to $\sim 10,000$. In comparison, the CO₂/CO ratios at the surface of Venus range from $\sim 50,000$ (assuming 20 ppm CO) to $\sim 200,000$ (assuming 5 ppm CO). The large CO₂/CO ratios at the surface of Venus qualitatively suggest that equilibration of CO and CO₂ will also be kinetically inhibited there. Here we explore the kinetic problems involved in the equilibration of CO and CO₂ and discuss the mechanisms by which these two gases are converted.

The simplest way to convert CO to CO₂ is via the elementary reaction



where M is any third body. However, the rate constant for reaction (16) is very slow (Baulch et al. 1976) because it is spin forbidden. As a consequence reaction (16) is ineffective for converting CO back to CO₂. Instead the elementary reaction



with a rate constant of (Baulch et al. 1995)

$$k_{17} = 1.05 \times 10^{-17} T^{1.5} \exp\left(\frac{250}{T}\right) \text{cm}^3 \text{s}^{-1} \quad (18)$$

is an important component of catalytic cycles that reconvert CO to CO₂ in the atmosphere of Mars (McElroy and Donahue 1972; Nair et al. 1994). Reaction (17) also plays a major role for CO oxidation in flames and combustion processes (Warnatz 1984) but is probably less effective in the stratosphere of Venus than it is on Mars because of the extremely low abundance of hydrogen compounds above the clouds of Venus. Other catalytic cycles involving Cl and NO_x chemistry may be necessary for transforming CO back to CO₂ in the Venusian stratosphere (Yung and DeMore 1982; chapter by Esposito et al.).

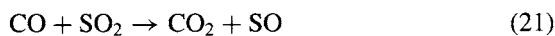
Fegley et al. (1995*b*) suggested that reaction (17) is also of limited importance at the surface of Venus because of the low water vapor abundance. Fegley and Lodders (1995) and Fegley et al. (1996) compared the chemical lifetime for CO oxidation via reaction (17)

$$t_{\text{chem}}(\text{CO}) \sim \frac{1}{(k_{17}[\text{OH}])} \quad (19)$$

to the vertical mixing time in the lower atmosphere of Venus

$$t_{\text{mix}} \sim \frac{H^2}{K_{\text{eddy}}} \quad (20)$$

The [OH] number densities were taken from thermochemical equilibrium calculations and K_{eddy} , the vertical eddy diffusion coefficient was taken as $\sim 10^4 \text{ cm}^2\text{s}^{-1}$. Higher and lower K_{eddy} values were also investigated. The pressure scale height $H (=RT/\mu g)$ is $\sim 16 \text{ km}$ at the surface of Venus. If $t_{\text{chem}} < t_{\text{mix}}$, then CO will be oxidized via reaction (17), while if $t_{\text{chem}} > t_{\text{mix}}$, then CO will not be oxidized. At 740 K, Eq. (19) yields $t_{\text{chem}}(\text{CO}) \sim 66 \text{ yr}$ vs $t_{\text{mix}} \sim 8 \text{ yr}$ from Eq. (20). For the nominal K_{eddy} value of $10^4 \text{ cm}^2\text{s}^{-1}$, reaction (17) quenched at all temperatures below $\sim 775 \text{ K}$ (i.e., at 4.5 km below the modal planetary radius). Fegley et al. (1996) also studied other reactions that may be the slow step in the conversion of CO to CO_2 at the surface of Venus. They found that the fastest reaction



quenched at $748 \pm 13 \text{ K}$ ($-1.0 \pm 1.7 \text{ km}$ below the modal radius). They concluded that CO and CO_2 only equilibrate, if at all, in the lowest levels of Venus' atmosphere below about 0.7 km altitude. A disequilibrium region, that is more oxidizing than predicted by equilibrium calculations, exists at higher elevations. Their conclusions are consistent with the inferred presence of hematite at several Venera landing sites (Pieters et al. 1986) and the experiments described above.

IV. VENUS SULFUR CYCLE

A. Background

Sulfur chemistry on Venus is a complex and controversial topic that has been discussed for the past three decades because of its importance for the global sulfuric acid cloud cover, the energy budget and greenhouse effect in the lower atmosphere, volcanism, and chemical weathering of the surface. The complexity arises because sulfur in the atmosphere is either known to, or strongly suspected to, exist as aqueous sulfuric acid cloud droplets, sulfuric acid vapor, $\text{SO}_3(\text{g})$, $\text{SO}_2(\text{g})$, $\text{SO}(\text{g})$, $(\text{SO})_2(\text{g})$, $\text{OCS}(\text{g})$, $\text{H}_2\text{S}(\text{g})$, elemental sulfur vapor S_{1-8} , and solid sulfur particles (von Zahn et al. 1983; Prinn 1985; Krasnopolsky and Pollack 1994; chapter by Esposito et al.). Sulfur has been reported on the surface of Venus (Table V), and has been suggested to exist as anhydrite (CaSO_4), pyrite (FeS_2), and pyrrhotite (Fe_7S_8) (see Lewis and Kreimendahl 1980; Pettengill et al. 1982). Controversy arises because the available measurements of sulfur gas abundances in the atmosphere do not always agree (Table I), because we do not know the composition of the lower 22 km of the atmosphere, and because we have no direct information (from MB spectroscopy or X-ray diffraction) on the mineralogy of the surface.

Over a decade ago, data from the Pioneer Venus mission, the Venera 11 and 12 missions, and Earth-based remote sensing were used to propose the Venus sulfur cycle (von Zahn et al. 1983; Prinn 1985). An expanded and revised version of the original Venus sulfur cycle is illustrated in Fig. 6. This cycle schematically shows the gas phase, gas-aerosol, and gas-rock reactions which continuously cycle sulfur between the atmosphere, the clouds, and rocks on the surface of Venus.

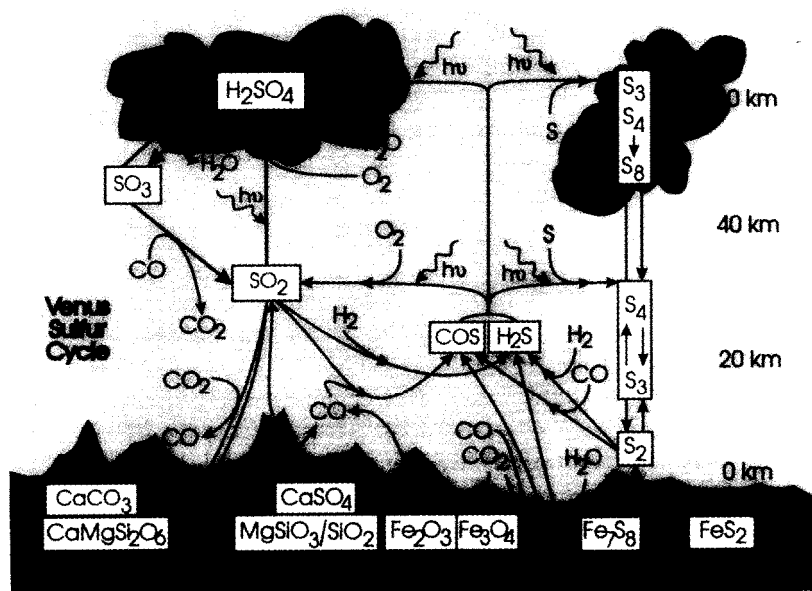


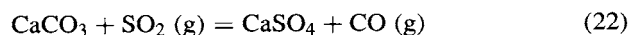
Figure 6. An expanded and revised version of the Venus sulfur cycle proposed by von Zahn et al. (1983) and Prinn (1985). Experimental results show that anhydrite (CaSO_4) formation is a sink for atmospheric SO_2 (Fegley 1988, 1990; Fegley and Prinn 1989), that pyrite decomposition is a source for atmospheric sulfur vapor (Fegley et al. 1995a), that pyrrhotite oxidation is a source for atmospheric OCS and H_2S (Treiman and Fegley 1991; Fegley et al. 1995a), and that magnetite oxidizes to hematite (Fegley et al. 1995b).

Below we consider in some detail the gas-rock reactions suggested for the Venus sulfur cycle and also briefly discuss some observations of sulfur gases in the lower atmosphere. The gas phase and gas-aerosol reactions involved in the sulfur cycle, and the observations of sulfur gases above the clouds of Venus are discussed in more detail in the chapter by Esposito et al.

B. Anhydrite Formation on Venus

Sulfur dioxide was the most abundant sulfur gas detected by the Pioneer Venus and Venera 11 and 12 spacecraft (Table I). The Venera 11 and 12 gas chromatography experiment reported 130 ± 35 ppm at 42 km altitude and below

(Gel'man et al. 1979) and the Pioneer Venus gas chromatography experiment reported 185 ± 43 ppm at 22 km (Oyama et al. 1980). These observations were surprising at the time because thermochemical equilibrium models predicted that OCS and H₂S were the dominant sulfur gases, and that SO₂ was a minor sulfur gas in the lower atmosphere of Venus (Lewis 1968,1969,1970; Lewis and Kreimendahl 1980). The thermochemical equilibrium models also predicted that the SO₂ abundance was ~ 100 times smaller than observed and was regulated by the reaction:



However, the Pioneer Venus and Venera 11 and 12 measurements indicate that the sulfur gas chemistry in the lower atmosphere of Venus is controlled by kinetic factors (von Zahn et al. 1983; Prinn 1985).

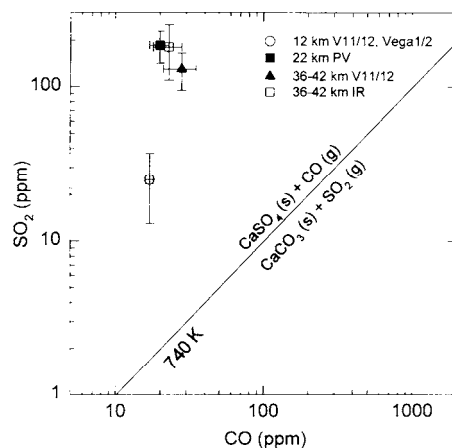


Figure 7. A comparison of the observed and calculated SO₂ abundances in the lower atmosphere of Venus. Observations of SO₂ and CO from the Pioneer Venus gas chromatograph (Oyama et al. 1980) the Venera 11 and 12 gas chromatograph (Gel'man et al. 1979; Marov et al. 1989), Earth-based infrared observations of the night side of Venus (Bézard et al. 1990,1993; Pollack et al. 1993), and from the Vega 1 and 2 ultraviolet spectroscopy experiments (Bertaux et al. 1996) are higher than the abundances of SO₂ and CO in thermochemical equilibrium with co-existing calcite and anhydrite (diagonal line). The data graphed are listed in Table I. Note that the pairs of SO₂ and CO observations refer to the same altitude or altitude range (e.g., 22 km for the Pioneer Venus gas chromatograph). Only the 12 km SO₂ data from Vega 1 and 2 are shown because the higher altitude data fall within the range of the Pioneer Venus, Venera 11 and 12, and infrared data points.

Figure 7 displays a comparison of the SO₂ abundances observed by the Pioneer Venus and Venera 11 and 12 spacecraft and the thermochemical equilibrium SO₂ abundance predicted by reaction (12) at the global mean temperature of 740 K on Venus. Also shown are subsequent measurements

of SO₂ from Earth-based infrared spectra of the lower atmosphere of Venus (Bézar et al. 1993; Pollack et al. 1993), and by ultraviolet spectroscopy on the Vega 1 and 2 probes (Bertaux et al. 1996). In each case the corresponding CO abundance measured at the same altitude is also plotted. All the data show that SO₂ in the lower atmosphere of Venus is present at abundances significantly higher than predicted by the thermochemical equilibrium models (diagonal line).

von Zahn et al. (1983) and Prinn (1985) suggested that the most plausible explanation for the overabundance of SO₂ is that the reaction of SO₂ with Ca-bearing minerals on Venus is slow and does not reach chemical equilibrium. von Zahn et al. (1983) also noted that "Laboratory experiments on the rates of various gas and gas-mineral reactions involving sulfur compounds are needed to further clarify the sulfur cycle on Venus." Experimental studies of anhydrite formation kinetics via reaction (22) (Fegley 1988,1990; Fegley and Prinn 1989; Fegley and Treiman 1992) provided the required gas-solid kinetic data.

The rate at which SO₂ reacts with calcite to form anhydrite was measured from 873 to 1123 K by isothermally heating high purity calcite crystals in flowing CO₂-SO₂ gas mixtures at ambient atmospheric pressure. Data at Venus surface temperatures were not obtained because of the extremely slow reaction rates. The gas mixtures either had about the same SO₂ number density as at the surface of Venus (if the Pioneer Venus, Venera 11 and 12, or infrared abundance data are assumed to hold at 0 km altitude), or several times higher SO₂ number densities (if the Vega 1 SO₂ abundance at 12 km altitude is taken at face value). The experimental procedures and analytical methods are described in Fegley and Prinn (1989).

The experimental rate equation (Fegley and Prinn 1989) for anhydrite formation via reaction (22) is

$$\frac{d[\text{CaSO}_4]}{dt} = 10^{19.64(\pm 0.28)} \exp\left(\frac{-15250(\pm 2970)}{T}\right) \text{mol cm}^{-2} \text{s}^{-1}. \quad (23)$$

The global mean rate of anhydrite formation of Venus was derived from Eq. (23) by convolving the surface area distribution as a function of altitude, the variation of temperature with altitude, the variation of the reaction rate with temperature, and the measured Ca content from the Venera 13,14, and Vega 2 XRF analyses (Table V).

Figure 8 shows that this global mean rate is about $4.6 \times 10^{10} \text{ mol cm}^{-2} \text{ s}^{-1}$, which corresponds to an anhydrite deposition rate of $\sim 1 \mu\text{m}$ per year. Because the growing anhydrite layer becomes less porous with time, the reaction may slow down as the anhydrite layer becomes thicker. However, aeolian weathering (Marshall et al. 1988) may plausibly remove the thin anhydrite layers fairly rapidly, so that the reaction can easily proceed. As already emphasized by several authors (Prinn 1985; Zolotov and Khodakovsky 1989; Fegley and Treiman 1992), the S/Ca ratios measured by the Venera 13,14,

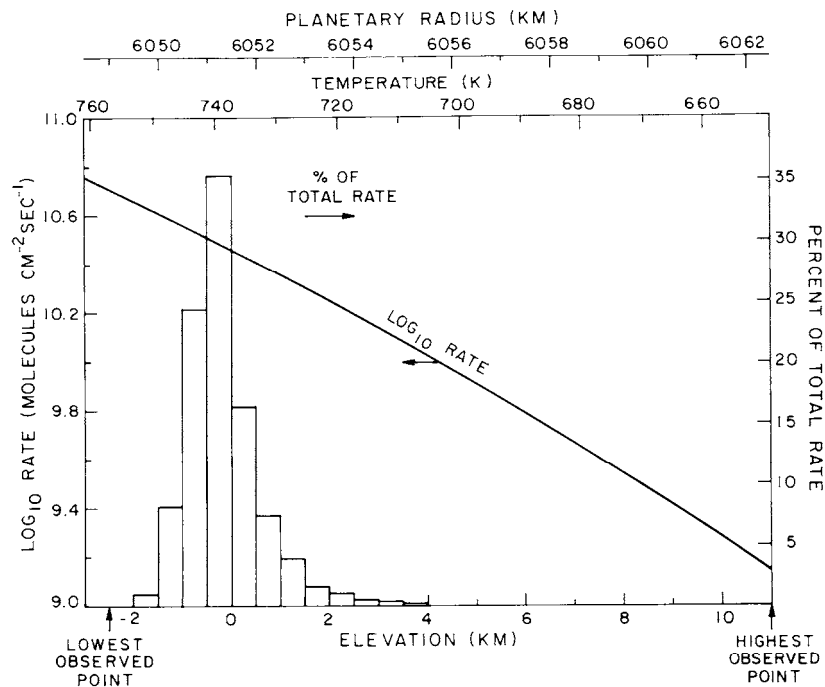


Figure 8. The rate of anhydrite formation as a function of elevation and temperature on the surface of Venus. The bar graph shows the percent of the total rate in each elevation bin. The solid line shows how the rate decreases with temperature and is an extrapolation of the rate Eq. (23). The calculations also take into account that the surface of Venus is not pure calcite. The weighted mean CaO content calculated from the Venera 13,14, and Vega 2 XRF analyses is $7.90(\pm 0.51)$ wt. %. The global mean rate of anhydrite formation is about 4.6×10^{10} mol cm⁻²s⁻¹, and corresponds to an anhydrite deposition rate of ~ 1 μ m per year (figure from Fegley 1990).

and Vega 2 spacecraft are less than that expected if all Ca were combined in CaSO₄. Therefore, at present the surface of Venus still contains reactive Ca which is a net sink for SO₂ loss via anhydrite formation.

However, the rate of SO₂ loss is very slow, and the chemical lifetime of SO₂ in the atmosphere of Venus is given by

$$t_{\text{chem}}(\text{SO}_2) \sim \frac{\sigma_{\text{SO}_2}}{d[\text{CaSO}_4]/dt} \quad (24)$$

where σ_{SO_2} is the SO₂ column density on Venus (given by the product of the pressure scale height H and the [SO₂] number density) and $d[\text{CaSO}_4]/dt$ is the global mean anhydrite formation rate from Fig. 8, which is the same as the SO₂ gas depletion rate. Fegley and Prinn (1989) calculated $t_{\text{chem}}(\text{SO}_2) \sim 1.9$ Myr based on 150 ppm SO₂ recommended by von Zahn et al. (1983). If the lower SO₂ mixing ratio of 25 ppm reported by the ultraviolet spectroscopy

experiment on Vega 1 at 12 km altitude is taken at face value, $t_{\text{chem}}(\text{SO}_2) \sim 320,000$ yr results. However, in any case, the formation of anhydrite will remove almost all ($\sim 99\%$) of the SO_2 from the atmosphere of Venus within geologic time scales unless the SO_2 is replenished in some fashion.

Fegley and Treiman (1992) calculated that reactions of SO_2 with other calcium minerals such as diopside ($\text{CaMgSi}_2\text{O}_6$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and wollastonite (CaSiO_3) are also thermodynamically favorable under Venus surface conditions. However, our unpublished laboratory experiments show that these reactions are apparently an order of magnitude or more slower than that of SO_2 with calcite. Thus, as mentioned earlier by Fegley and Treiman (1992) and Bézard et al. (1993), chemical reactions of SO_2 with diopside, anorthite, and wollastonite cannot buffer SO_2 in the lower atmosphere of Venus because of the extremely slow rate of these reactions.

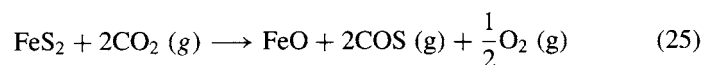
C. Rate of Volcanism on Venus

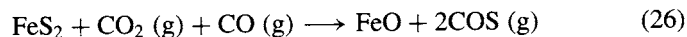
Fegley and Prinn (1989) argued that maintenance of the global sulfuric acid cloud cover, which is produced by photooxidation of SO_2 , requires a source to replenish the SO_2 currently being lost by reaction with calcite on the surface of Venus. If the SO_2 were not replenished, the global sulfuric acid clouds would eventually disappear within a geologically short time.

Fegley and Prinn (1989) argued that volcanism is the most plausible source for replacing atmospheric sulfur. The required volcanism rate is a function of the sulfur content of the erupted material (magma + gas) and of the degassing efficiency of the erupted material. The degassing efficiency is close to unity as indicated by pyrite and pyrrhotite decomposition experiments (Fegley et al. 1995a; Treiman and Fegley 1991). Different geochemical models for the sulfur content of the erupted material led to estimated volcanism rates ranging from 0.4 to $11 \text{ km}^3 \text{ yr}^{-1}$. The preferred rate of $\sim 1 \text{ km}^3 \text{ yr}^{-1}$ was calculated by assuming that material erupted onto the surface of Venus had the same composition as that determined by XRF analyses of the surface at the Venera 13,14, and Vega 2 landing sites. This geochemically estimated rate is comparable to the rate of sub-aerial volcanism on the Earth (Ivanov and Freney 1983) and is about 5% of the plate creation rate of $\sim 20 \text{ km}^3 \text{ yr}^{-1}$ on the Earth (Parsons 1981). The geochemical rate of $\sim 1 \text{ km}^3$ per year is also supported by independent geophysical estimates of volcanism rates on Venus (Grimm and Solomon 1987; Spohn 1991).

D. Pyrite Decomposition on the Surface of Venus

As illustrated in Fig. 6, an important component of the Venus sulfur cycle is pyrite decomposition, which was predicted to be a source of reduced sulfur gases at the surface of Venus (see, e.g., von Zahn et al. 1983; Prinn 1985) via the net thermochemical reactions



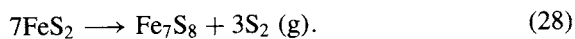


However, when the sulfur cycle was first proposed, no kinetic data were available to model the rates of these suggested pyrite decomposition reactions.

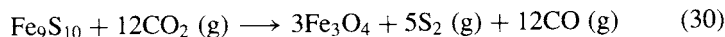
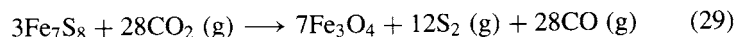
Fegley et al. (1995a) experimentally studied pyrite decomposition because of its importance for the hypothesized Venus sulfur cycle and showed that pyrite rapidly decomposes over the entire surface of Venus. They also showed that pyrite decomposition in CO_2 and CO_2 gas mixtures is a multi-stage process which is more complex than originally proposed. This work is relevant to models of atmosphere-surface interactions, for understanding the origin of the low emissivity regions seen in radar imaging, to studies of the origin and evolution of the present surface conditions on Venus, for the design of future spacecraft missions to Venus, and for the rapidly evolving Earth-based infrared observations of the lower atmosphere of Venus.

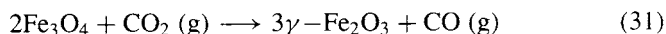
The pyrite decomposition experiments were done by isothermally heating pyrite slices for different time periods in CO_2 or CO_2 gas mixtures. This is the same general technique used earlier in the anhydrite formation experiments (Fegley and Prinn 1989), and is the same way in which many gas-solid kinetic experiments are conducted in materials science. The gas mixtures used were chosen to study the effects of the CO_2 and CO number densities on the kinetics and to study the kinetics in a ternary gas mixture with CO and SO_2 number densities similar to those at the surface of Venus. The proposed decomposition of pyrite by water vapor, reaction (27), is being studied in a subsequent series of experiments. The experiments were done along five isotherms from ~ 660 to ~ 800 K, which span the temperatures over the surface of Venus.

X-ray diffraction and MB spectroscopy of the reacted samples showed that pyrite decomposed to pyrrhotite (Fe_7S_8), which on continued heating lost more sulfur leaving behind more Fe-rich pyrrhotites. The pyrrhotite forms a layer covering the unreacted pyrite. With increasing time, more and more pyrite decomposes to pyrrhotite, until pyrrhotite is the only sulfide left in the sample. During this process, the pyrrhotites were also being oxidized to magnetite. As discussed earlier in Sec. III.F, the magnetite was oxidized to hematite via maghemite as an intermediate. These, and other data led Fegley et al. (1995a) to conclude that pyrite decomposition occurs via the net thermochemical reaction



They also suggested that pyrrhotite oxidation and magnetite oxidation to hematite occurs by net thermochemical reactions exemplified by





These proposed reactions for pyrite decomposition, pyrrhotite oxidation, and magnetite oxidation are schematically illustrated in Fig. 6. Alternative reactions for pyrrhotite oxidation, which involve the direct production of OCS, may occur in concert with or in preference to reactions suggested by Fegley et al. (1995a). The experimental data confirm the hypothesized importance of pyrite chemical weathering in the Venus sulfur cycle (von Zahn et al. 1983; Prinn 1985), although pyrite decomposition does not occur as a single step via reactions (25–26).

The experimental data show that pyrite decomposition follows zero-order kinetics and is independent of the amount of pyrite present. The data also show that within the experimental uncertainties, the rate of pyrite decomposition and the activation energy ($\sim 150 \text{ kJ mole}^{-1}$) for pyrite decomposition are independent of the gas compositions used. This suggests that the rate determining step is sulfur loss from pyrite (Fegley et al. 1995a).

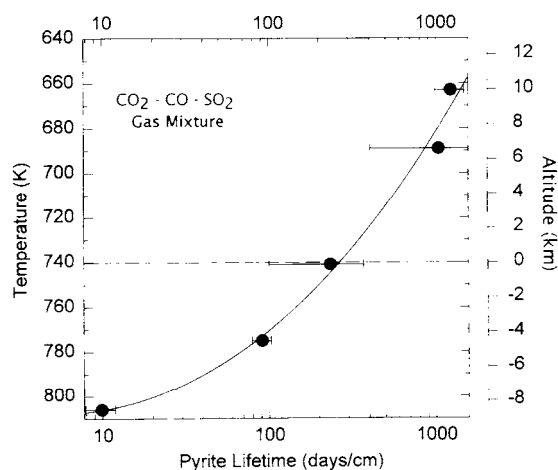


Figure 9. Pyrite decomposition lifetimes (days/cm) as a function of temperature and altitude on the surface of Venus. The error bars show the one sigma uncertainties in the pyrite lifetimes. As discussed by Fegley et al. (1995a), pyrite decomposition follows zero-order kinetics and is independent of the amount of pyrite present. Pyrite decomposition has the same rate, within experimental uncertainties, in CO_2 and in CO_2 gas mixtures. The pyrite lifetimes shown are for a $\text{CO}(1.9\%)\text{-CO}_2(96.3\%)\text{-SO}_2(1.8\%)$ gas mixture with CO and SO_2 number densities close to those at the surface of Venus. Pyrite decomposition kinetics were also independent of the CO_2 number density, within experimental uncertainties.

Figure 9 shows the rate of pyrite decomposition in a CO-CO₂-SO₂ gas mixture with CO and SO₂ number densities close to those at the surface of Venus. The decomposition rate in days/cm varies from ~10 days at ~800 K (-7 km) to ~230 days at 740 K (0 km) to ~1200 days at ~660 K (~10 km). These lifetimes are very short and show that pyrite cannot exist on Venus for any significant time.

The experiments also show that the rate of pyrrhotite oxidation is significantly slower than the rate of pyrite thermal decomposition. The fine-grained pyrrhotite produced by pyrite decomposition is oxidized to magnetite during the course of the experiments. Pyrrhotite oxidation is a diffusion-controlled process that depends on the particle size (Asaki et al. 1983; Treiman and Fegley 1991). The preliminary rate data (Treiman and Fegley 1991) predict that millimeter-sized pyrrhotite grains oxidize completely in hundreds of years, while decameter-sized masses of pyrrhotite, such as occur on Earth in magmatic sulfide deposits, have lifetimes of millions of years on the surface of Venus.

The presence of pyrrhotite, which is a source of OCS via oxidation by atmospheric CO₂ and CO (Fegley and Treiman 1992; Fegley et al. 1992), is supported by the observed increase of OCS with decreasing altitude on Venus (Pollack et al. 1993). In fact, Pollack et al. (1993) state that "these results are in remarkable agreement with calculations of buffering by surface minerals (Fegley and Treiman 1992) and thermodynamic equilibrium of gases close to Venus' surface (Krasnopolsky and Parshev 1979), both of which predict a sharply increasing OCS mixing ratio toward the surface, with a surface value of several 10s of ppm. In both cases, CO acts as one of the source gases for making OCS." Krasnopolsky and Pollack (1994) modeled sulfur chemistry in the lower atmosphere of Venus and commented that "the OCS mixing ratio near the surface, 28 ppm, is close to the value of 20 ppm and 5-30 ppm given by Krasnopolsky and Parshev (1979) and Fegley and Treiman (1992), respectively. Pyrite decomposition to pyrrhotite and pyrrhotite oxidation to iron oxides on the Venus surface (Fegley and Treiman 1992; Fegley et al. 1993) may be a source of OCS." Thus, there appears to be a convergence of experiment, observation, and theory suggesting that iron sulfide chemical weathering is a source of reduced sulfur gases in the near-surface atmosphere of Venus.

E. Sulfur Chemistry in the Near-Surface Atmosphere

Finally, we briefly consider sulfur chemistry, in particular oxidized (e.g., SO₂) and reduced (e.g., OCS, H₂S, and S₁₋₈) sulfur gases. The recent reinterpretation by Bertaux et al. (1996) of the ultraviolet spectrometer data from the Vega 1 and 2 spacecraft, suggests that the abundance of SO₂ drops to ~25 ppm at 12-km altitude. Taking these observations at face value we need to ask where the remaining ~125 ppm or so, of sulfur originally contained in SO₂ has gone?

One possibility is that SO₂ was removed by reaction with crustal minerals.

Another possibility is that sulfur has been redistributed into other gases. The reactions of SO_2 with calcium-bearing minerals discussed above, are very slow. The fastest reaction with calcite takes ~ 1.9 Myr to reduce SO_2 to its equilibrium abundance. One could imagine that SO_2 would be removed faster if fine-grained calcite were present on the surface of Venus. However, laboratory studies of anhydrite formation from SO_2 and synthetic calcium carbonate powder show that after a short period of time the fine-grained material has turned into coarse-grained lumps that are chemically cemented together. An example of this behavior is illustrated in Burke et al. (1994). Another problem is the source of the fine-grained calcite required for the rapid reaction. This is closer to beach sand than to the igneous carbonate probably present in carbonatites and alkaline rocks on the surface of Venus. Also, as discussed earlier, the XRF data show that only a few percent of the surface can be calcite. Thus, we consider this possibility unlikely.

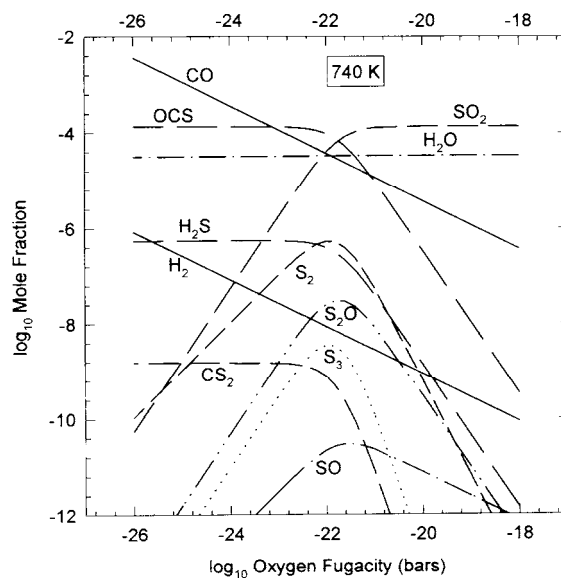


Figure 10. Thermochemical equilibrium abundances of important C-O-S-H gases as a function of the oxygen fugacity in the near-surface atmosphere of Venus (740 K, 0 km). The calculation assumes gas phase thermochemical equilibrium and neglects all gas-solid reactions. SO_2 remains the dominant sulfur-bearing gas, and OCS and H_2S are less abundant at the surface of Venus for all plausible oxygen fugacities (i.e., f_{O_2} values $> 10^{-21.3}$ bar). The thermodynamic data are taken from Fegley et al. (1996).

The second possibility, that sulfur has been redistributed into other gases, is considered in Fig. 10. This shows the results of thermochemical equilibrium calculations of gas abundances as a function of the oxygen fugacity in the near-surface atmosphere of Venus. These calculations neglect any reac-

tions with the surface. The results are in good agreement with the prior gas phase thermochemical equilibrium calculations of Krasnopolsky and Parshev (1979). Sulfur dioxide remains the dominant sulfur gas and OCS and H₂S are less abundant species for all oxygen fugacities $>10^{-21.8}$ bar. As discussed earlier, plausible CO mole fractions at the surface range from 5 to 17 ppm with the corresponding oxygen fugacities ranging from $10^{-20.3}$ bar to $10^{-21.3}$ bar. Figure 10 shows that SO₂ remains the dominant sulfur gas under these conditions.

von Zahn et al. (1983) proposed that the SO₂/H₂S, the SO₂/S₂, and by implication the SO₂/OCS and SO₂/SO₃ ratios in the lower atmosphere of Venus are maintained at approximately the gas phase equilibrium values when reactions with the surface are negligible. Thus, we do not feel that the bulk of the sulfur originally in SO₂ is redistributed into reducing sulfur gases near the surface of Venus. The recent kinetic models of Krasnopolsky and Pollack (1994) predict an OCS abundance of 28 ppm near the surface of Venus. This is similar to results in Fig. 10 at plausible oxygen fugacities. More modeling of sulfur chemistry in the near-surface atmosphere of Venus along with further analysis of the Vega 1 and 2 data for OCS, H₂S, and elemental sulfur vapor is needed to understand the Vega results.

V. GEOCHEMISTRY OF VOLATILE ELEMENTS

Interest in the volatile element geochemistry of Venus dates back to Mueller (1964) who speculated about chemical mass transport of volatile phases on Venus. Lewis (1968) also considered this concept and proposed that volatiles may be transported toward the polar regions on Venus. However, we now know that the maximum temperature range with altitude is ~ 80 K, while the maximum temperature range with latitude is probably 10 to 20 K (Seiff 1983).

The concept of volatile transport on Venus was recently revived by Brackett et al. (1995) who showed how it could explain the low radar emissivity of the highlands of Venus, the low altitude hazes observed by two Pioneer Venus entry probes (Ragent and Blamont 1980), and possibly the Pioneer Venus entry probe anomalies at 12.5 km.

Briefly, their model, which is schematically illustrated in Fig. 11, is as follows. Many volatile metals (e.g., Cu, Zn, Sn, Pb, As, Sb, Bi) form halides and chalcogenides that have high vapor pressures. Compounds of these metals are typically found around terrestrial volcanic vents and fumaroles, are enriched in volcanic aerosols, and are observed in volcanic gases. For example, CuCl(g) has been observed in volcanic gases at Kilauea in Hawaii and at Nyiragongo in Zaire (Brackett et al. 1995). Thermochemical equilibrium calculations predict that many volatile metals are transported as halides and sulfides, even in steam-rich terrestrial volcanic gases (Symonds et al. 1987). Volatile metal compounds emitted from volcanoes on Venus may form aerosol hazes in the near-surface atmosphere of Venus, or they may immediately snow out and condense out over the entire surface of the planet, and/or if sufficiently

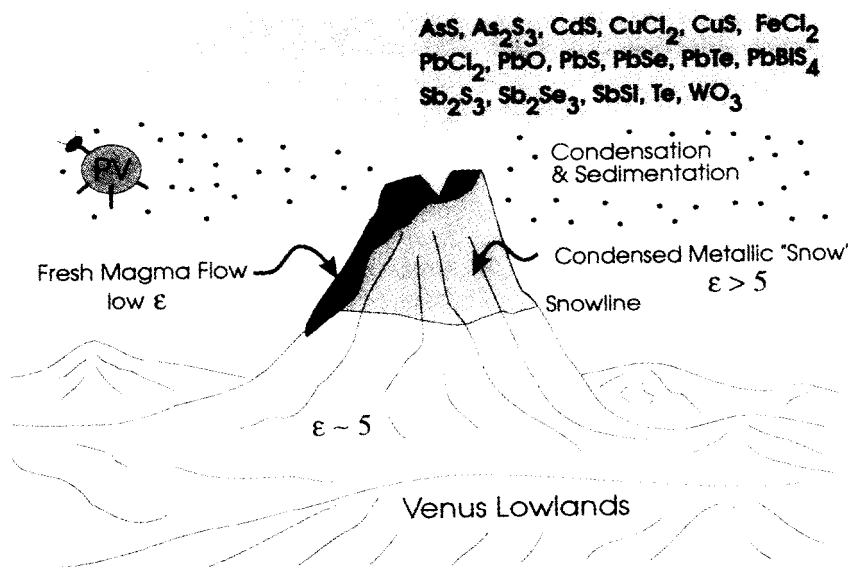


Figure 11. A cartoon schematically illustrating the metallic frost model of Brackett et al. (1995). Volatile metal halides and chalcogenides (i.e., sulfides, selenides, and tellurides), are erupted into the atmosphere of Venus. Some vapor may immediately form aerosol hazes in the near-surface atmosphere of Venus, which may be the cause of the low-altitude hazes observed by two Pioneer Venus entry probes (Ragent and Blamont 1980). Some vapor may immediately snow out and condense out over the entire surface of the planet, and other more volatile species may remain in the near-surface atmosphere. See text for details.

volatile, such as many Hg compounds (Lewis 1968,1969), they may remain in the near-surface atmosphere.

The higher vapor pressures of volatile metal condensates in the hotter plains of Venus, coupled with the altitude-dependent temperature gradient over the surface of Venus eventually leads to the vapor transport of the volatile metal compounds to the cooler highland regions of Venus. Brackett et al. (1995) modeled this transport process and concluded that, depending on the vapor pressure of the particular species, significant amounts of material could be transported in geologically short time scales. Many metal halides and chalcogenides have high dielectric constants (see, e.g., Young and Frederikse 1973) and many are ferroelectric (Lines and Glass 1977), leading to the deposition of high dielectric constant "frost" at high elevations.

Because the emission of volatile metal compounds is an ongoing process on the Earth, and because of the presence of S, Cl, and F on Venus, it is plausible that volcanic emissions on Venus contain volatile metal compounds. What is unknown, and what cannot be determined without remote sensing or *in-situ* analyses, are the exact metals and compounds present.

VI. SUMMARY

We conclude by identifying some of the key questions about the geochemistry and mineralogy of the surface of Venus and by suggesting observational studies, spacecraft experiments, laboratory experiments, and theoretical studies that can improve our knowledge of these important issues.

Perhaps the single most fundamental question facing us today is the mineralogy of the surface of Venus. von Zahn et al. (1983) emphasized this point by stating: "If we are ignorant of some of the details of atmospheric composition at the venusian surface, we are infinitely more ignorant of the nature of surface minerals." In discussing our lack of knowledge about the mineralogy of the surfaces of Venus and Mars, Fegley and Treiman (1992) emphasized that: "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." Here we can only second these recommendations and once again emphasize the overriding importance of developing spacecraft instruments, using methods such as X-ray diffraction (see, e.g., Blake et al. 1994), Mössbauer spectroscopy (see, e.g., Klingelhöfer et al. 1995), and nuclear magnetic resonance, to directly determine the mineralogy of the surface of Venus. It is important to determine whether or not the minerals which are apparently buffering CO₂, HCl, and HF are present. These techniques are also needed to determine the nature of the high dielectric phases in lower radar emissivity regions.

The second key question is the chemical composition of the lower 22 km (~80% by mass) of Venus' atmosphere. The remarkable advances during the past few years in Earth-based infrared spectroscopy (Bézard et al. 1990, 1993; Pollack et al. 1993) have provided a wealth of new information about the composition of the sub-cloud atmosphere of Venus. Additional advances will undoubtedly occur. However, even this method has its limitations. For example, the positions of the near-infrared "windows" that allow observations of the near-surface atmosphere do not match the positions of absorption bands for all gases of interest. Thus, there is still a pressing need for a deep atmospheric spacecraft to measure the chemical composition of the lower 22 km of the atmosphere. The gases of most interest are H₂O, CO, SO₂, OCS, S₁₋₈, and H₂S and the method of choice for measuring them is probably infrared spectroscopy, although other techniques such as mass spectroscopy and gas chromatography should also be considered.

The third key issue that needs to be addressed is the oxidation state of the surface of Venus. The work of Pieters et al. (1986) suggesting the presence

of hematite on the surface of Venus, the revised interpretation (Zolotov 1996; Fegley et al. 1996) of the CONTRAST experiment which now also suggests the presence of hematite, and the recent laboratory studies (Fegley et al. 1995*a,b*) showing that hematite is formed by basalt oxidation and magnetite oxidation in gases with CO/CO₂ ratios inside the magnetite stability field, suggests that the surface of Venus is more oxidized than previously believed by many workers. In order to determine the oxidation state of the surface and near-surface atmosphere it will be necessary to measure the CO abundance and oxygen fugacity below 12 km, to determine the mineralogy of iron-bearing minerals on the surface, for example by MB spectroscopy or visible/infrared reflection spectroscopy, and to determine the relative abundances of oxidized and reduced sulfur gases.

Acknowledgments. Work at Washington University was supported by a grant from NASA. The collaborative work between Washington University and the Technische Hochschule, Darmstadt was supported by a NATO Collaborative Research grant. We thank J. S. Kargel, J. S. Lewis, and M. Yu. Zolotov for their constructive reviews and comments. We also thank E. Kankeleit and P. Held for their support and assistance.

REFERENCES

- Anders, E., and Grevesse, N. 1989. Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* 53:197–214.
- Arvidson, R. E., et al. 1994. Microwave signatures and surface properties of Ovda Regio and surroundings, Venus. *Icarus* 112:171–186.
- Asaki, Z., Matsumoto, K., Tanabe, T., and Kondo, Y. 1983. Oxidation of dense iron sulfide. *Metall. Trans. B* 14:109–116.
- Banin, A., Clark, B. C., and Wänke, H. 1992. Surface chemistry and mineralogy. In *Mars*, eds. H. H. Kieffer, B. M. Jakosky, C. W. Snyder and M. S. Matthews (Tucson: Univ. of Arizona Press), pp. 594–625.
- Barath, T. T., et al. 1964. Mariner 2 radiometer experiment results. *Astron. J.* 69:49–58.
- Barsukov, V. L., Volkov, V. P., and Khodakovsky, I. L. 1980. The mineral composition of Venus surface rocks: A preliminary prediction. *Proc. Lunar Planet. Sci. Conf.* 11:765–773.
- Barsukov, V. L., Volkov, V. P., and Khodakovsky, I. L. 1982. The crust of Venus: Theoretical models of chemical and mineral composition. *Proc. Lunar Planet. Sci. Conf.* 13, *J. Geophys. Res. Suppl.* 87:3–9.
- Barsukov, V. L., Surkov, Yu. A., Dmitriyev, L. V., and Khodakovsky, I. L. 1986. Geochemical studies on Venus with the landers from the Vega 1 and Vega 2 probes. *Geochem. Intl.* 23:53–65.
- Basilevsky, A. T., Nikolaeva, O. V., and Weitz, C. M. 1992. Geology of the Venera 8 landing site region from Magellan data: Morphological and geochemical

- considerations. *J. Geophys. Res.* 97:16315–16335.
- Baulch, D. L., Drysdale, D. D., Duxbury, J., and Grant, S. J. 1976. Evaluated kinetic data for high temperature reactions. In *Homogeneous Gas Phase Reactions of the O₂-O₃ System, the CO₂-O₂-H₂ System and of Sulphur-Containing Species (London: Butterworths)*.
- Baulch, D. L., et al. 1995. Evaluated kinetic data for combustion modelling supplement I. *J. Phys. Chem. Ref. Data* 23:847–1033.
- Bertaux, J. L., et al. 1996. Vega-1 and Vega-2 entry probes: An investigation of local UV absorption (220–400 nm) in the atmosphere of Venus (SO₂, aerosols, cloud structure). *J. Geophys. Res.* 101:12709–12745.
- Bézard, B., de Bergh, C., Crisp, D., and Maillard, J. P. 1990. The deep atmosphere of Venus revealed by high-resolution nightside spectra. *Nature* 345:508–511.
- Bézard, B., et al. 1993. The abundance of sulfur dioxide below the clouds of Venus. *Geophys. Res. Lett.* 20:1587–1590.
- Blake, D. F., Vaniman, D. T., and Bish, D. L. 1994. A mineralogical instrument for planetary applications. *Lunar Planet. Sci.* XXV:121–122 (abstract).
- Brackett, R. A., Fegley, B., Jr., and Arvidson, R. E. 1995. Volatile transport on Venus and implications for surface geochemistry and geology. *J. Geophys. Res.* 100:1553–1563.
- Burke, K., Fegley, B., Jr., and Sharpton, V. L. 1994. Are steep slopes on Venus preserved as a result of chemical cementation of pore-spaces in surface rocks? *Lunar Planet. Sci. Conf.* XXV:201–202 (abstract).
- Chase, M. W., Jr., et al. 1985. *JANAF Thermochemical Tables* (New York: American Chemical Soc. and American Inst. of Physics).
- Clark, B. C., et al. 1977. The Viking X ray fluorescence experiment: Analytical methods and early results. *J. Geophys. Res.* 82:4577–4594.
- Clark, B. C., et al. 1982. Chemical composition of Martian fines. *J. Geophys. Res.* 87:10059–10067.
- Connes, P., Connes, J., Benedict, W. S., and Kaplan, L. D. 1967. Traces of HCl and HF in the atmosphere of Venus. *Astrophys. J.* 147:1230–1237.
- Connes, P., Connes, J., Kaplan, L. D., and Benedict, W. S. 1968. Carbon monoxide in the Venus atmosphere. *Astrophys. J.* 152:731–743.
- de Bergh, C., et al. 1989. Ground-based high resolution spectroscopy of Venus near 3.6 microns. *Bull. Amer. Astron. Soc.* 21:926 (abstract).
- de Bergh, C., et al. 1995. Water in the deep atmosphere of Venus from high-resolution spectra of the night side. *Adv. Space Res.* 15:79–88.
- Deer, W. A., Howie, R. A., and Zussman, J. 1963. *Rock-Forming Minerals*, vols. 1–5 (London: Longmans Green).
- Donahue, T. M., Hoffman, J. H., Hodges, R. R., Jr., and Watson, A. J. 1982. Venus was wet: A measurement of the ratio of deuterium to hydrogen. *Science* 216:630–633.
- Ekonomov, A. P., Golovin, Yu. M., and Moshkin, B. E. 1980. Visible radiation observed near the surface of Venus: Results and their interpretation. *Icarus* 41:65–75.
- Fegley, B., Jr. 1988. Thermochemical kinetics of SO₂ reactions with possible Venus crustal minerals: First data for calcite. *Lunar Planet. Sci. Conf.* XIX:315–316 (abstract).
- Fegley, B., Jr. 1990. The applications of chemical thermodynamics and chemical kinetics to planetary atmospheres research. In *First International Conference on Laboratory Research for Planetary Atmospheres*, eds. K. Fox, J. E. Allen, Jr., L. J. Stief and D. Quillen, NASA CP-3077, pp. 267–302.
- Fegley, B., Jr. 1995. Properties and composition of the terrestrial oceans and of the atmospheres of the Earth and other planets. In *Global Earth Physics A Handbook of Physical Constants*, ed. T. Ahrens (Washington, D. C.: American Geophysical

- Union), pp. 320–345.
- Fegley, B., Jr., and Lewis, J. S. 1980. Volatile element chemistry in the solar nebula: Na, K, F, Cl, Br, and P. *Icarus* 41:439–455.
- Fegley, B., Jr., and Lodders, K. 1995. Chemical models of the lower atmosphere of Venus. *Bull. Amer. Astron. Soc.* 27:1072 (abstract).
- Fegley, B., Jr., and Prinn, R. G. 1989. Estimation of the rate of volcanism on Venus from reaction rate measurements. *Nature* 337:55–58.
- Fegley, B., Jr., and Treiman, A. H. 1992. Chemistry of atmosphere-surface interactions on Venus and Mars. In *Venus and Mars: Atmospheres, Ionospheres, and Solar Wind Interactions*, eds. J. G. Luhmann, M. Tatrallyay and R. O. Pepin (Washington, D. C.: American Geophysical Union), pp. 7–71.
- Fegley, B., Jr., Treiman, A. H., and Sharpton, V. L. 1992. Venus surface mineralogy: Observational and theoretical constraints. *Proc. Lunar Planet. Sci. Conf.* 22:3–20.
- Fegley, B., Jr., Lodders, K., and Klingelhöfer, G. 1993. Kinetics and mechanism of pyrite decomposition on the surface of Venus. *Bull. Amer. Astron. Soc.* 25:1094 (abstract).
- Fegley, B., Jr., Lodders, K., Treiman, A. H., and Klingelhöfer, G. 1995a. The rate of pyrite decomposition on the surface of Venus. *Icarus* 115:159–180.
- Fegley, B., Jr., Klingelhöfer, G., Brackett, R. A., Izenberg, N., Kremser, D. T., and Lodders, K. 1995b. Basalt oxidation and hematite formation on the surface of Venus. *Icarus* 118:373–383.
- Fegley, B., Jr., Zolotov, M. Yu., and Lodders, K. 1996. The oxidation state of the lower atmosphere and surface of Venus. *Icarus*, in press.
- Florensky, C. P., et al. 1977a. First panoramas of the venusian surface. *Proc. Lunar Sci. Conf.* 8:2655–2664.
- Florensky, C. P., et al. 1977b. The surface of Venus as revealed by Soviet Venera 9 and 10. *Geol. Soc. Amer. Bull.* 88:1537–1545.
- Florensky, C. P., et al. 1983a. Redox indicator “CONTRAST” on the surface of Venus. *Lunar Planet. Sci. Conf.* XIV:203–204 (abstract).
- Florensky, C. P., et al. 1983b. Venera 13 and Venera 14: Sedimentary rocks on Venus? *Science* 221:57–59.
- Florensky, C. P., et al. 1983c. The oxidizing-reducing conditions on the surface of Venus according to the data of the “KONTRAST” geochemical indicator on the Venera 13 and Venera 14 spacecraft. *Cosmic Res.* 21:278–281.
- Ford, P. G., and Pettengill, G. H. 1992. Venus topography and kilometer-scale slopes. *J. Geophys. Res.* 97:13103–13114.
- Garvin, J. B., and Head, J. W. 1985. High dielectric surfaces on the terrestrial planets. *Lunar Planet. Sci. Conf.* XVI:264–265 (abstract).
- Gektin, Yu. M. 1996. Personal communications to M. Yu. Zolotov.
- Gel'man, B. G., et al. 1979. Analysis of chemical composition of Venus atmosphere by gas chromatography on Venera 12. *Cosmic Res.* 17:585–589.
- Golovin, Yu. M., Moshkin, B. Ye., and Ekonomov, A. P. 1983. Some optical properties of the Venus surface. In *Venus*, eds. D. M. Hunten, L. Colin, T. M. Donahue and V. I. Moroz (Tucson: Univ. of Arizona Press), pp. 131–136.
- Grimm, R. E., and Solomon, S. C. 1987. Limits on modes of lithospheric heat transport on Venus from impact crater density. *Geophys. Res. Lett.* 14:538–541.
- Hemingway, B. S. 1990. Thermodynamic properties for bunsenite, NiO, magnetite, Fe₃O₄, and hematite, Fe₂O₃, with comments on selected oxygen buffer reactions. *Amer. Mineral.* 75:781–790.
- Hoffman, J. H., Hodges, R. R., Donahue, T. M., and McElroy, M. B. 1980a. Composition of the Venus lower atmosphere from the Pioneer Venus mass spectrometer. *J. Geophys. Res.* 85:7882–7890.

- Hoffman, J. H., Oyama, V. I., and von Zahn, U. 1980b. Measurements of the Venus lower atmosphere composition: A comparison of results. *J. Geophys. Res.* 85:7871–7881.
- Hogarth, D. D. 1989. Pyrochlore, apatite, and amphibole: Distinctive minerals in carbonatite. In *Carbonatites: Genesis and Evolution*, ed. K. Bell (London: Unwin Hyman), pp. 105–148.
- Huebner, J. S. 1975. Oxygen fugacity values of furnace gas mixtures. *Amer. Mineral.* 60:815–823.
- Ivanov, M. V., and Freney, J. R., eds. 1983. *The Global Biogeochemical Sulphur Cycle* (New York: J. Wiley and Sons), pp. 25–127.
- Johannsen, A. 1937. *A Descriptive Petrography of the Igneous Rocks*, vol. IV, (Chicago: Univ. of Chicago Press).
- Kargel, J. S., et al. 1991. Compositional constraints on outflow channel-forming lavas on Venus. *Lunar Planet. Sci. Conf.* XXII:685–686 (abstract).
- Kargel, J. S., Komatsu, G., Baker, V. R., and Strom, R. G. 1993. The volcanology of Venera and VEGA landing sites and the geochemistry of Venus. *Icarus* 103:253–275.
- Kargel, J. S., Kirk, R. L., Fegley, B., Jr., and Treiman, A. H. 1994. Carbonate-sulfate volcanism on Venus? *Icarus* 112:219–252.
- Klingelhöfer, G., et al. 1995. Mössbauer spectroscopy in space. *Hyp. Int.* 95:305–339.
- Klose, K. B., Wood, J. A., and Hashimoto, A. 1992. Mineral equilibria and the high radar reflectivity of Venus mountaintops. *J. Geophys. Res.* 97:16353–16369.
- Krasnopolsky, V. A., and Parshev, V. A. 1979. Chemical composition of Venus' troposphere and cloud layer based on Venera 11 and 12 and Pioneer Venus measurements. *Cosmic. Res.* 17:630–637.
- Krasnopolsky, V. A., and Pollack, J. B. 1994. H₂O-H₂SO₄ system in Venus' clouds and OCS, CO, and H₂SO₄ profiles in Venus' troposphere. *Icarus* 109:58–78.
- Kridelbaugh, S. J. 1973. The kinetics of the reaction calcite + quartz = wollastonite + carbon dioxide at elevated temperatures and pressures. *Amer. J. Sci.* 273:757–777.
- Lewis, J. S. 1968. An estimate of the surface conditions of Venus. *Icarus* 8:434–456.
- Lewis, J. S. 1969. Geochemistry of the volatile elements on Venus. *Icarus* 11:367–385.
- Lewis, J. S. 1970. Venus: Atmospheric and lithospheric composition. *Earth Planet. Sci. Lett.* 10:73–80.
- Lewis, J. S. 1971. Venus: Surface temperature variations. *J. Atmos. Sci.* 28:1084–1086.
- Lewis, J. S., and Kreimendahl, F. A. 1980. Oxidation state of the atmosphere and crust of Venus from Pioneer Venus results. *Icarus* 42:330–337.
- Lines, M. E., and Glass, A. M. 1977. *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Clarendon Press).
- Marov, M. Ya., et al. 1989. Lower atmosphere. In *The Planet Venus: Atmosphere, Surface, Interior Structure*, eds. V. L. Barsukov and V. P. Volkov (Moscow: Nauka Press), pp. 25–67.
- Marshall, J. R., Greeley, R., and Tucker, D. W. 1988. Aeolian weathering of Venus surface materials: Preliminary results from laboratory simulations. *Icarus* 74:495–515.
- Mayer, C. H., McCullough, T. P., and Sloanaker, R. M. 1958. Observations of Venus at 3.15 cm wavelength. *Astrophys. J.* 127:1–10.
- McElroy, M. B., and Donahue, T. M. 1972. Stability of the martian atmosphere. *Science* 177:986–988.
- Mitchell, R. H. 1986. *Kimberlites: Mineralogy, Geochemistry, and Petrology* (New York: Plenum Press).

- Moroz, V. I., Parfent'ev, N. A., and San'ko, N. F. 1979. Spectrophotometric experiment on the Venera 11 and 12 descent modules. 2. Analysis of Venera 11 spectra by layer-addition method. *Cosmic. Res.* 17:601–614.
- Mueller, R. F. 1963. Chemistry and petrology of Venus: Preliminary deductions. *Science* 141:1046–1047.
- Mueller, R. F. 1964. A chemical model for the lower atmosphere of Venus. *Icarus* 3:285–298.
- Mueller, R. F. 1968. Sources of HCl and HF in the atmosphere of Venus. *Nature* 220:55–57.
- Mueller, R. F. 1969. Planetary probe: Origin of atmosphere of Venus. *Science* 163:1322–1324.
- Mukhin, L. M., et al. 1983. Gas chromatograph analysis of the chemical composition of the atmosphere of Venus by the landers of the Venera 13 and Venera 14 spacecraft. *Cosmic. Res.* 21:168–172.
- Na, C. Y., Esposito, L. W., and Skinner, T. E. 1990. International ultraviolet explorer observations of Venus SO₂ and SO. *J. Geophys. Res.* 95:7485–7491.
- Nair, H., Allen, M., Anbar, A. D., and Yung, Y. L. 1994. A photochemical model of the Martian atmosphere. *Icarus* 111:124–150.
- Naumov, G. B., Ryzhenko, B. N., and Khodakovsky, I. L. 1971. *Handbook of Thermodynamic Data* (Moscow: Atomizdat).
- Nozette, S., and Lewis, J. S. 1982. Venus: Chemical weathering of igneous rocks and buffering of atmospheric composition. *Science* 216:181–183.
- O'Neill, H. St. C. 1988. Systems Fe-O and Cu-O: Thermodynamic data for the equilibria Fe-“FeO”, Fe-Fe₃O₄, “FeO”-Fe₃O₄, Fe₃O₄-Fe₂O₃, Cu-Cu₂O and Cu₂O-CuO from emf measurements. *Amer. Mineral.* 73:470–486.
- Orville, P. 1974. Crust-atmosphere interactions. In *The Atmosphere of Venus*, ed. J. E. Hansen (New York: Goddard Institute for Space Studies), pp. 190–195.
- Oyama, V. I., et al. 1980. Pioneer Venus gas chromatograph of the lower atmosphere of Venus. *J. Geophys. Res.* 85:7891–7902.
- Parsons, B. 1981. The rate of plate consumption and creation. *Geophys. J. Roy. Astron. Soc.* 67:437–448.
- Pettengill, G. H., Ford, P. G., and Nozette, S. 1982. Venus: Global surface radar reflectivity. *Science* 217:640–642.
- Pettengill, G. H., Ford, P. G., and Chapman, B. D. 1988. Venus: Surface electromagnetic properties. *J. Geophys. Res.* 93:14881–14892.
- Philpotts, A. R. 1990. *Principles of Igneous and Metamorphic Petrology* (Englewood Cliffs, N. J.: Prentice-Hall).
- Pieters, C. M., et al. 1986. The color of the surface of Venus. *Science* 234:1379–1383.
- Pollack, J. B., et al. 1993. Near infrared light from Venus' nightside: A spectroscopic analysis. *Icarus* 103:1–42.
- Prinn, R. G. 1985. The photochemistry of the atmosphere of Venus. In *The Photochemistry of Atmospheres*, ed. J. S. Levine (New York: Academic Press), pp. 281–336.
- Ragent, B., and Blamont, J. 1980. The structure of the clouds of Venus: Results of the Pioneer Venus Nephelometer Experiment. *J. Geophys. Res.* 85:8089–8105.
- Robie, R. A., and Hemingway, B. S. 1995. *Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 Bar (10⁵ Pascals) Pressure and at Higher Temperatures*, U.S.G.S Bull. No. 2131.
- Ronov, A. B., and Yaroshevsky, A. A. 1976. A new model for the chemical structure of the Earth's crust. *Geochem. Intl.* 13:89–121.
- Seiff, A. 1983. Thermal structure of the atmosphere of Venus. In *Venus*, eds. D. M. Hunten, L. Colin, T. M. Donahue and V. I. Moroz (Tucson: Univ. Arizona Press), pp. 215–279.

- Selivanov, A. S., et al. 1983. The first color panoramas of the surface of Venus, sent by Venera 13 and 14. *Cosmic Res.* 21:129-136.
- Semenov, E. I. 1974. Economic mineralogy of alkaline rocks. In *The Alkaline Rocks*, ed. H. Sorensen (London: Wiley), pp. 543-552.
- Shepard, M. K., Arvidson, R. E., Brackett, R. A., and Fegley, B., Jr. 1994. A ferroelectric model for the low emissivity highlands on Venus. *Geophys. Res. Lett.* 21:469-472.
- Smith, J. V. 1981. Halogen and phosphorus storage in the Earth. *Nature* 289:762-765.
- Sorensen, H. 1974. Alkali syenites, feldspathoidal syenites and related lavas. In *The Alkaline Rocks*, ed. H. Sorensen (London: Wiley), pp. 22-52.
- Spohn T. 1991. Mantle differentiation and thermal evolution of Mars, Mercury, and Venus. *Icarus* 90:222-236.
- Surkov, Yu. A. 1977. Geochemical studies of Venus by Venera 9 and 10 automatic interplanetary stations. *Proc. Lunar Sci. Conf.* 8:2665-2689.
- Surkov, Yu. A., et al. 1983. Determination of the elemental composition of rocks on Venus by Venera 13 and Venera 14 (preliminary results). *Proc. Lunar Planet. Sci. Conf.* 13, *J. Geophys. Res. Suppl.* 88:481-493.
- Surkov, Yu. A., et al. 1984. New data on the composition, structure, and properties of Venus rock obtained by Venera 13 and Venera 14. *Proc. Lunar Planet. Sci. Conf.* 14, *J. Geophys. Res. Suppl.* 89:393-402.
- Surkov, Yu. A., et al. 1985. Method, instruments, and results of the determination of elements contained in Venusian rock by the Vega-2 interplanetary probe. *Astron. Vestn.* 19:177-186.
- Surkov, Yu. A., et al. 1986. Venus rock composition at the Vega 2 landing site. *Proc. Lunar Planet. Sci. Conf.* 17, *J. Geophys. Res. Suppl.* 91:215-218.
- Surkov, Yu. A., et al. 1987a. Uranium, thorium, and potassium in the venusian rocks at the landing sites of Vega 1 and 2. *Proc. Lunar Planet. Sci. Conf.* 17, (*J. Geophys. Res. Suppl.* 92:537-540).
- Surkov, Yu. A., et al. 1987b. Abundances of natural radioactive elements in the rocks of Venus from data from the Vega-1 and Vega-2 stations. *Cosmic Res.* 25:590-594.
- Surkov, Yu. A., et al. 1987c. Element makeup of the rocks of Venus in the northeastern part of Aphrodite Terra (from Vega-2 lander data). *Cosmic Res.* 25:751-761.
- Symonds, R. B., et al. 1987. Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia. *Geochim. Cosmochim. Acta* 51:2083-2101.
- Timco, G. W. 1977. High-Pressure Dielectric Properties of Perovskite Ferroelectrics. Ph.D. Thesis, Univ. of Western Ontario.
- Toulmin, P., III, et al. 1977. Geochemical and mineralogical identification of the Viking inorganic chemical results. *J. Geophys. Res.* 82:4625-4634.
- Treiman, A. H., and Fegley, B., Jr. 1991. Venus: The chemical weathering of pyrrhotite, $Fe_{1-x}S$. *Lunar Planet. Sci. Conf.* XXII:1409-1410 (abstract).
- Urey, H. C. 1952. *The Planets* (New Haven: Yale Univ. Press).
- Vaniman, D. T., Bish, D. L., and Chipera, S. J. 1991. In-situ planetary surface analyses: The potential of X-ray diffraction with simultaneous X-ray fluorescence. *Lunar Planet. Sci.* XXII:1429-1430 (abstract).
- Vinogradov, A. P., and Volkov, V. P. 1971. On the wollastonite equilibrium as a mechanism determining Venus' atmospheric composition. *Geochem. Intl.* 8:463-467.
- Vinogradov, A. P., Surkov, Yu. A., and Kirnozov, F. F. 1973. The contents of uranium, thorium, and potassium in the rocks of Venus as measured by Venera 8. *Icarus* 20:253-259.
- Volkov, V. P., Zolotov, M. Yu., and Khodakovskiy, I. L. 1986. Lithospheric-atmospheric

- interactions on Venus. In *Chemistry and Physics of Terrestrial Planets*, ed. S. K. Saxena (New York: Springer-Verlag), pp. 136–187.
- Von Hippel, A. 1954. *Dielectric Materials and Applications* (Cambridge: MIT Press).
- von Zahn, U., Kumar, S., Niemann, H., and Prinn, R. 1983. Composition of the Venus atmosphere. In *Venus*, eds. D. M. Hunten, L. Colin, T. M. Donahue and V. I. Moroz (Tucson: Univ. Arizona Press), pp. 299–430.
- Warnatz, J. 1984. Rate coefficients in the C/H/O system. In *Combustion Chemistry*, ed. W. C. Gardiner, Jr. (New York: Springer-Verlag), pp. 197–360.
- Wilson, M. 1989. *Igneous Petrogenesis* (Boston: Unwin Hyman).
- Woolley, A. R., and Kempe, D. R. C. 1989. Carbonatites: Nomenclature, average chemical compositions, and element distribution. In *Carbonatites Genesis and Evolution*, ed. K. Bell (London: Unwin Hyman), pp. 1–14.
- Young, K. F., and Frederikse, H. P. R. 1973. Compilation of the static dielectric constants of inorganic solids. *J. Phys. Chem. Ref. Data* 2:313–409.
- Young, L. D. G. 1972. High resolution spectra of Venus—A review. *Icarus* 17:632–658.
- Young, L. D. G., Young, A. T., and Zasova, L. V. 1984. A new interpretation of the Venera 11 spectra of Venus. *Icarus* 60:138–151.
- Yung, Y. L., and DeMore, W. B. 1982. Photochemistry of the stratosphere of Venus: Implications for atmospheric evolution. *Icarus* 51:199–247.
- Zolotov, M. Yu. 1987. Redox conditions on Venus surface. *Lunar Planet. Sci. XVIII*:1134–1135 (abstract).
- Zolotov, M. Yu. 1994. Near-surface atmosphere of Venus: New estimations of redox conditions based on new data. *Lunar Planet. Sci. Conf. XXV*:1569–1570 (abstract).
- Zolotov, M. Yu. 1996. A model of thermochemical equilibrium in the near-surface atmosphere of Venus. *Geochem. Intl.* 33:80–100.
- Zolotov, M. Yu., and Khodakovsky, I. L. 1989. Exogenic processes. In *The Planet Venus: Atmosphere, Surface, Interior Structure*, eds. V. L. Barsukov and V. P. Volkov (Moscow: Nauka Press), pp. 262–290.