Hydrous Silicates and Water on Venus

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We used thermochemical equilibrium calculations to predict stabilities of pure rock-forming hydrous silicates on Venus' surface as a function of elevation, atmospheric H_2O and SO_2 concentrations, and oxygen fugacity (f_{O_2}). About 50 different hydrous silicates were included in our calculations. We find that many of these are unstable on Venus's surface because of the low atmospheric H_2O content of 30–45 parts per million by volume (ppmv) and the high surface temperatures (660 K on Maxwell Montes to 740 K in the plains). Hydrous Fe^{2+}-bearing silicates are unstable due to oxidation to magnetite and/or hematite at the f_{O_2} of the near-surface atmosphere. Ca-bearing hydrous silicates are unstable because of sulfatization to anhydrite. Some Fe-free micas (e.g., eastonite, eastonite–phlogopite micas), and some alkali amphiboles might be stable on Venus' surface, especially in the lower temperature highlands. We discuss hydrous mineral formation in the interior and on the surface of Venus. We review the literature on mica and amphibole thermal decomposition and find that dehydration of phlogopitic micas and fibrous amphiboles produces (metastable) dehydroxylated anhydrides that decompose to more stable minerals at temperatures hundreds of degrees higher than the onset of dehydroxylation. These observations raise the possibility that anhydrides formed from hydrous silicates, which may have been present during a wetter period in Venus' history, may persist somewhere on Venus' present surface. We discuss experiments that could be used on future spacecraft missions to detect hydroxyl in rocks and hydrous silicates on Venus. Finally, we review estimates of the amount of water and OH (hydroxyl) in the Earth's mantle. Based on this review, we suggest that even if no hydrous silicates are stable on Venus, significant amounts of water are plausibly present in surface rocks as OH in nominally anhydrous minerals. © 1997 Academic Press

Key Words: Venus; surface; mantle; mineralogy; hydrous silicates; water; micas; amphiboles; tremolite; phlogopite; anhydrite; magnetite; hematite.

INTRODUCTION

Water vapor, present at 30–45 parts per million by volume (ppmv) in Venus' subcloud atmosphere (Drossart *et al.* 1993; Pollack *et al.* 1993; DeBergh *et al.* 1995; Meadows and Crisp 1996; Ignatiev *et al.* 1997), is one of the three most important greenhouse gases (CO_2, H_2O, SO_2) in the present-day atmosphere of Venus. Water vapor is also the major reservoir of hydrogen in the lower atmosphere, and is an important reactant in chemical weathering reactions that probably control the atmospheric abundances of HCl and HF on Venus. At present and during the past, loss of water from Venus, via oxidation of the surface and hydrogen escape to space, has been important in influencing the oxidation state of the atmosphere and surface. At sufficiently high abundances, water vapor also participates in chemical weathering reactions leading to the formation of hydrous minerals on Venus's surface.

Information about the presence (or absence) of hydrous minerals and OH-bearing nominally anhydrous minerals on Venus's surface is important to understanding the present and past atmospheric–lithospheric water cycle and water inventory on Venus, the petrology of convergent margins of lithospheric blocks, the generation and physical properties of magmas, the atmospheric D/H ratio, the stability of Venus's current climate and its evolution, the rate of water outgassing from volcanism, the supply of water from cometary and asteroidal impacts, and the physical properties (e.g., visible and infrared (IR) reflectance, electrical and thermal conductivity, dielectric properties, mechanical strength) of Venus's lithosphere, surface rocks, and soil.

Although during the present epoch interactions of atmospheric water with surface rocks have been severely limited

because of high surface temperatures and the low atmospheric water vapor pressure, hydration of surface rocks was plausibly much more important in the past during a wetter era of Venus's history. The observed HDO/H$_2$O ratio corresponds to D/H $\sim$1.9–2.5% and to an enhancement of $\sim$120–160 times the terrestrial value of 1.6×10^{-4}, the ratio in Standard Mean Ocean Water (SMOW) (DeBergh *et al.* 1991; Bjoraker *et al.* 1992). This enhancement suggests that earlier in its history, Venus had at least 0.1% as much water as found in Earth's oceans, and plausibly much more (Donahue *et al.* 1982; Donahue 1995). Whether or not all of this water was lost to space or some of it was transported into Venus's interior is still unknown.

However, a first order mass balance calculation shows it is unlikely that atmospheric water vapor represents Venus's total water inventory today. Taking 30 ppmv H$_2$O in Venus's atmosphere gives a total water abundance of $\sim$6 $\times$ 10^{15} kg, while only 1 nanogram/gram water in the silicate fraction of Venus (taken here as 70% of the total mass) gives $\sim$3 $\times$ 10^{15} kg water, equal to 50% of the atmospheric inventory. In comparison, geophysical and geochemical estimates for the water content of Venus's mantle and magmas are a few to a few tens of micrograms H$_2$O per gram rock (Namiki 1995; Grinspoon 1993), giving 500–5,000 times more water inside Venus than is observed in the atmosphere. Therefore, the atmosphere contains only a small fraction of Venus' total water inventory.

What do we know about the presence (or absence) of hydrous silicates and OH-bearing nominally anhydrous minerals on the surface of Venus? Despite the wealth of information returned by US (Mariner, Pioneer Venus (PV), Galileo, Magellan) and Russian (Venera, Vega) space missions to Venus over the past 35 yr, we still possess no direct information about the mineralogy of Venus's surface. The elemental analyses obtained by X-ray fluorescence (XRF) experiments at the Venera 13 and 14 and Vega 2 landing sites, like the Viking XRF experiments, do not give results for elements lighter than Mg and hence provide no data on the hydrogen content of Venus's surface. Some petrologic interpretations of the mineralogies calculated from the XRF analyses suggest derivation of magmas by partial melting in a water-bearing mantle (Barsukov 1992). However, Kargel *et al.* (1993) attribute the mafic alkaline character of Venus's crust to magma formation in a generally anhydrous, carbonated mantle.

Spectral reflectance data at the Venera 9 and 10 landing sites (Golovin *et al.* 1983) cover the 0.4–1.06 μm range and do not reach the longer wavelength IR region where mineral OH and H$_2$O absorption bands occur. Earth-based IR observations of Venus's lower atmosphere reach the surface, but only around 1 μm where no hydrous mineral bands occur. However, the Earth-based observations give data on the atmospheric water vapor abundance (Meadows and Crisp 1996).

The microwave emissivity data and derived dielectric constants from the Pioneer Venus, Venera 15/16, and Magellan orbiters likewise provide no data about the possible presence of hydrous silicates on the surface. The radar imaging from these spacecraft indirectly suggests a currently "dry" lithosphere because of the lack of water related geologic landforms, the paucity of Earth-like convergent margins, and the lack of evidence for ongoing plate tectonics. Magellan radar images show little evidence for pyroclastic volcanic activity (Head *et al.* 1992) that might suggest water-bearing volcanic gases. On the other hand, the layered morphology and low density of rock at the Venera 9, 10, 13, and 14 landing sites have been interpreted in terms of volcanic ash deposits (Florensky *et al.* 1983; Nikolayeva 1989). Water is the most plausible candidate to provide pyroclastic eruptions on Venus (Head and Wilson 1986; Thornhill 1993). If so, then some fraction of the water outgassed volcanically could originate from dehydration of hydrous minerals recycled through the lithosphere (as on Earth where most outgassed water is recycled). But overall it is fair to say that the available geological and geochemical data sets neither strongly support nor rule out the presence of hydrous silicates in Venus's interior or on its surface.

However, observations of water vapor in Venus's atmosphere, coupled with the concept that atmosphere–surface reactions occur at the temperatures (660–740 K) and pressures (96–48 bars) at Venus's surface allow us to address the question of hydrous silicate stability using thermochemical equilibrium calculations. This approach has been used by a number of workers and it is instructive to review the prior results before proceeding with our discussion.

The presence of hydrous silicates on Venus's surface was probably first suggested by Rupert Wildt. Based on the estimated CO$_2$ abundance on Venus, Wildt (1940) concluded that Venus's surface temperature "appears to be higher than the terrestrial boiling point of water." Shortly thereafter, Wildt (1942) proposed that the major reservoir of water on Venus must be hydrous silicates because of Venus's high surface temperature and the apparent absence of atmospheric water vapor. However, Wildt's suggestion was not pursued until two decades later, after the Mariner 2 flyby showed Venus's high surface temperature and Bottema *et al.* (1964) discovered water vapor in Venus's atmosphere. Mueller (1964) assumed that the water vapor content above the clouds was representative of that at the surface and used Bottema *et al.*'s data to set an upper limit of 10–100 ppmv water vapor at Venus's surface. Mueller (1964) realized, like Wildt (1942), that only hydrous silicates with high thermal stability could possibly be stable under such conditions and suggested amphiboles or micas, in particular phlogopite, as likely candidates.

A few years later, Lewis developed the concept that Venus's atmospheric composition was buffered by gas–

TABLE I
Prior Studies about Hydrous Silicates on Venus

Reference	Comments
Wildt 1942	suggested any water present on Venus must be in hydrous silicates, no calculations made
Mueller 1964	suggested micas (phlogopite) & amphiboles on Venus, but no calculations made
Lewis 1968	predicts two micas, muscovite & phlogopite are stable
Lewis 1970	tremolite is stable, but muscovite & phlogopite are unstable
Lewis & Kreimendahl 1980	tremolite is stable, but muscovite & phlogopite are unstable
Nozette & Lewis 1982	tremolite is stable, but muscovite & phlogopite are unstable
Khodakovsky et al. 1979a	epidote, glaucophane, tremolite, phlogopite, and annite are stable
Khodakovsky 1982	no hydrous minerals are stable
Barsukov et al. 1982	no hydrous minerals are stable
Volkov et al. 1986	no hydrous minerals are stable
Fegley & Treiman 1992	no pure hydrous minerals, including tremolite & phlogopite are stable, suggest that F-OH micas & some amphiboles (F-OH amphiboles, edenite, richterites & alkali amphiboles) may be stable, but thermodynamic data are needed to do calculations
This Work	some micas (eastonite, eastonite-phlogopite solutions), some alkali amphiboles may be stable, F-OH micas & amphiboles may be stable, assess methods for detecting hydrous minerals

solid reactions and used it in a series of papers to predict the mineralogy of Venus's surface (Lewis 1968, 1970; Lewis and Kreimendahl 1980; Nozette and Lewis 1982). A similar approach was taken by a group at the Vernadsky Institute in Russia in order to interpret results from the Venera and Vega missions to Venus (Khodakovsky et al. 1979a,b; Barsukov et al. 1980, 1982; Khodakovsky 1982; Volkov et al. 1986). However, problems with unavailable or unreliable thermodynamic data for hydrous minerals, uncertainty about the actual water vapor content of Venus' subcloud atmosphere, and uncertainty about an apparent decrease in water vapor toward the surface led to a series of sometimes contradictory predictions about which (if any) hydrous minerals were stable on Venus's surface, and the roles played by hydrous minerals in buffering atmospheric water vapor or in acting as a water vapor sink (see Table 1).

Several recent developments led us to reexamine the question of whether or not any hydrous silicates are present on Venus's surface. First, the Earth-based and Galileo spacecraft IR observations of Venus's subcloud atmo-

sphere provide data on the water vapor abundance from ~0 to 40 km altitude (Drossart et al. 1993; Pollack et al. 1993; DeBergh et al. 1995; Meadows and Crisp 1996). The PV mass spectrometer data (Donahue and Hodges 1993) and the recently reevaluated Venera 11, 13, and 14 spectrophotometer data (Ignatiev et al. 1997) give water vapor abundances in good agreement with these spectroscopic data. Also, recently published results from the Vega 1/2 missions give information on the SO_2 abundance down to 12 km altitude (Bertaux et al. 1996), which is important for calculating the stability of Ca-bearing hydrous silicates, which can react to form anhydrite ($CaSO_4$). Another motivation is the availability of new thermodynamic data for hydrous silicates and their dehydration products (e.g., Robie and Hemingway 1995). Finally, the ongoing development of visible–IR spectroscopy, X-ray diffraction, and Mössbauer spectroscopy experiments for new lander, penetrator, and automated balloon missions to Venus requires firm predictions of surface mineralogy for optimizing these experiments.

In the rest of this paper we first present our results for hydrous silicate stability and then compare them with prior work by other groups. Next we discuss formation and decomposition of hydrous silicates on Venus's surface and interior. After that we review the literature on dehydration kinetics and mechanisms for micas and amphiboles. We then discuss the implications of our results for the design and optimization of geochemical experiments for detecting hydrous minerals and OH in minerals on future spacecraft missions to Venus. Finally, we briefly review data on water in the Earth's mantle and discuss the amount of water in the silicate portion of Venus.

ATMOSPHERIC STRUCTURE AND COMPOSITION MODEL

The Venus International Reference Atmosphere (VIRA) model (Seiff et al. 1986) for the variation of temperature and pressure with altitude in the lower atmosphere of Venus was used in our calculations. The zero level in the VIRA model corresponds to a planetary radius of 6052.0 km (735.3 K, 92.1 bars), which is 0.6 km above the modal planetary radius of 6051.4 km (Ford and Pettengill 1992). Our results are presented for the modal radius (740 K, 95.6 bars) and for the upper part of Maxwell Montes (660 K, 48 bars), part of the highest mountain range on Venus, which has a maximum elevation about 10.4 km above the modal radius.

Water vapor, SO_2, and O_2 are the three most important gases in our calculations because they are involved in hydration/dehydration, sulfatization, and oxidation of hydrous silicates. We take 30 ppmv as the nominal water vapor mixing ratio, with an uncertainty range of 15–70 ppmv, based on the Earth-based and Galileo IR observa-

tions of Venus's lower atmosphere (Drossart *et al.* 1993; Pollack *et al.* 1993; DeBergh *et al.* 1995; Meadows and Crisp 1996), on the PV mass spectrometer data (Donahue and Hodges 1993), and on the Venera 11, 13, 14 spectrophotometer data (Ignatiev *et al.* 1997). We adopt a constant water vapor profile with altitude. We take 130 ppmv for the nominal SO_2 mixing ratio with an uncertainty range of 20–185 ppmv based on the Pioneer Venus and Venera 11/12 gas chromatography measurements (Oyama *et al.* 1980; Gel'man *et al.* 1979), on the Vega 1/2 UV spectroscopy measurements (Bertaux *et al.* 1996), and on the Earth-based IR observations in the 2.3 μm window (Pollack *et al.* 1993). At 740 K we take a nominal oxygen fugacity (f_{O_2}) of $10^{-20.8}$ bars with uncertainties ranging from $10^{-21.7}$ to 10^{-20} bar, from our study of the oxidation state of Venus's surface and atmosphere (Fegley *et al.* 1997).

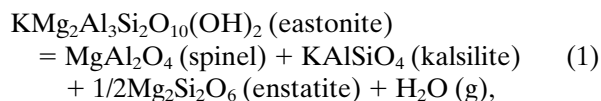## THERMODYNAMIC DATA SOURCES AND CALCULATIONS

Thermodynamic data for minerals and gases. Table II lists the hydrous minerals included in our calculations, the standard Gibbs free energies of formation ($\Delta_f G°$) at 740 K, and the thermodynamic data sources used. We considered all hydrous silicates, in particular amphiboles and micas, for which we found thermodynamic data. Highly hydrous minerals, such as clays and hydroxides were not included because they are known to be unstable at Venus surface temperatures and water vapor pressures. The other minerals and gases included in the calculations and their standard Gibbs free energies of formation ($\Delta_f G°$) at 740 K are listed in Table III.

Hydrous silicate thermodynamic calculations. Hydrous silicates on Venus's surface may lose water (and/or OH) and decompose to other minerals plus water vapor because of the high temperature and low water vapor partial pressure. We call this overall process dehydration. In contrast, dehydroxylation is the loss of structural water and/or hydroxyl groups with the formation of the anhydrous mineral (its anhydride) *without* decomposition to the thermodynamically stable products. Dehydroxylation is one step during dehydration and cannot be predicted using thermodynamic calculations because thermodynamic data are unavailable for the (metastable) anhydrides produced. We discuss dehydroxylation reactions later.

In addition, at Venus surface conditions, Fe^{2+}-bearing hydrous silicates can be oxidized to Fe^{3+}-bearing minerals, and Ca-bearing hydrous silicates can react with SO_2 to form anhydrite ($CaSO_4$). We refer to the reaction of a mineral with SO_2 (to form anhydrite) as sulfatization. One example is the formation of anhydrite when calcite ($CaCO_3$) or diopside ($CaMgSi_2O_6$) is heated in SO_2–CO_2 gas mixtures (Fegley and Prinn 1989). Only Ca-bearing minerals are predicted to react with SO_2 at Venus surface
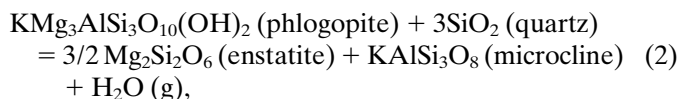
conditions (e.g., Fegley and Treiman 1992). Thus, we considered four types of reactions in our thermodynamic calculations:

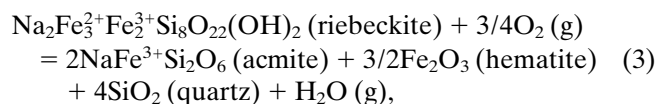(A) Simple dehydration reactions exemplified by the dehydration of eastonite,

$$\begin{aligned} &KMg_2Al_3Si_2O_{10}(OH)_2 \text{ (eastonite)} \\ &= MgAl_2O_4 \text{ (spinel)} + KAlSiO_4 \text{ (kalsilite)} \quad (1) \\ &+ 1/2Mg_2Si_2O_6 \text{ (enstatite)} + H_2O \text{ (g)}, \end{aligned}$$

were considered for all hydrous silicates (Table IV).

(B) Complex dehydration reactions, exemplified by the dehydration of phlogopite,

$$\begin{aligned} &KMg_3AlSi_3O_{10}(OH)_2 \text{ (phlogopite)} + 3SiO_2 \text{ (quartz)} \\ &= 3/2\,Mg_2Si_2O_6 \text{ (enstatite)} + KAlSi_3O_8 \text{ (microcline)} \quad (2) \\ &+ H_2O \text{ (g)}, \end{aligned}$$
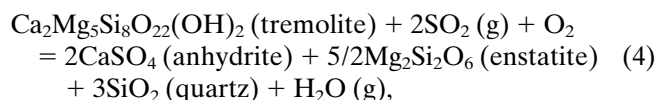
were considered only for some key hydrous silicates because these reactions require cation exchange between two minerals. This cation exchange is probably slow (at Venus surface temperatures) in the absence of a fluid phase and complex dehydration reactions may not be important on Venus's surface. (However, the effects of supercritical CO_2 on the rates of complex dehydration reactions need to be studied experimentally.)

(C) Coupled oxidation and dehydration reactions, exemplified by riebeckite decomposition,

$$\begin{aligned} &Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2 \text{ (riebeckite)} + 3/4O_2 \text{ (g)} \\ &= 2NaFe^{3+}Si_2O_6 \text{ (acmite)} + 3/2Fe_2O_3 \text{ (hematite)} \quad (3) \\ &+ 4SiO_2 \text{ (quartz)} + H_2O \text{ (g)}, \end{aligned}$$

were also considered, in addition to simple dehydration, for Fe^{2+}-bearing hydrous silicates (Table V). This was done because fayalite (Fe_2SiO_4), a possible breakdown product of Fe^{2+}-bearing hydrous silicates, is unstable on Venus's surface, which is at the f_{O_2} of the magnetite–hematite phase boundary (Zolotov 1996; Fegley *et al.* 1997).

(D) Coupled sulfatization and dehydration, exemplified by tremolite decomposition,

$$\begin{aligned} &Ca_2Mg_5Si_8O_{22}(OH)_2 \text{ (tremolite)} + 2SO_2 \text{ (g)} + O_2 \\ &= 2CaSO_4 \text{ (anhydrite)} + 5/2Mg_2Si_2O_6 \text{ (enstatite)} \quad (4) \\ &+ 3SiO_2 \text{ (quartz)} + H_2O \text{ (g)}, \end{aligned}$$

were also considered, in addition to simple dehydration, for Ca-bearing hydrous silicates (Table VI). This was done because SO_2 is predicted to react with Ca-bearing minerals on Venus's surface (Von Zahn *et al.* 1983; Volkov *et al.* 1986; Fegley and Prinn 1989; Fegley and Treiman 1992).

TABLE II
Thermodynamic Data for Hydrous Silicates

Mineral Name and Abbreviation		Ideal Formula	$\Delta_f G°$ (740 K) (kJ/mol)[c]	Data Sources		
				$\Delta_f H°$	$S°$	$C_p(T)$
am	amesite	$Mg_4Al_4Si_2O_{10}(OH)_8$	-7378.9 ± 5.0	HP	HP	HP
ann	annite	$KFe_3AlSi_3O_{10}(OH)_2$	-4284.7 ± 5.0	RH	RH	RH
ant	anthophyllite	$Mg_7Si_8O_{22}(OH)_2$	-10278.3 ± 8.5	G	G	RH
bcc	bicchulite	$Ca_2Al_2SiO_6(OH)_2$	-3675.5 ± 5.2	RH	RH	RH
cel	celadonite	$KMgAlSi_4O_{10}(OH)_2$	-4896.7 ± 3.2	HP	HP	HP
clnc	clinochlore	$Mg_5Al_2Si_3O_{10}(OH)_8$	-7272 ± 21	RH	RH	RH
cum	cummingtonite	$Mg_7Si_8O_{22}(OH)_2$	-10273.1 ± 9.3	G	G	HP
czo	clinozoisite	$Ca_2Al_3Si_3O_{12}(OH)$	-5911.7 ± 4.1	HP	HP	HP
de	deerite	$Fe_{12}^{2+}Fe_6^{3+}Si_{12}O_{40}(OH)_{10}$	-14698 ± 16	HP	HP	HP
east	eastonite	$KMg_2Al_3Si_2O_{10}(OH)_2$	-5400.2 ± 6.0	CN	CN	HP
ed	edenite	$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$	-10767.0 ± 7.0	HP	HP	HP
ep	epidote	$Ca_2Fe^{3+}Al_2Si_3O_{12}(OH)$	-5506.8 ± 3.3	HP	RH	HP
fame	ferroamesite	$Fe_4Al_4Si_2O_{10}(OH)_8$	-6066.6 ± 4.6	HP	HP	HP
fant	ferroanthophyllite	$Fe_7Si_8O_{22}(OH)_2$	-8007.6 ± 8.4	HP	HP	HP
fcar	ferrocarpholite	$FeAl_2Si_2O_6(OH)_4$	-3563.8 ± 2.4	HP	HP	HP
fcel	ferroceladonite	$KFeAlSi_4O_{10}(OH)_2$	-4575.4 ± 3.2	HP	HP	HP
fchl	ferrochloritoid	$FeAl_2SiO_5(OH)_2$	-2628.8 ± 6.4	HP	HP	HP
fgl	ferroglaucophane	$Na_2Fe_3Al_2Si_8O_{22}(OH)_2$	-9152.2 ± 8.4	HP	HP	HP
fhb	ferrohornblende	$Ca_2Fe_4Al_2Si_7O_{22}(OH)_2$	-9317.6 ± 7.5	HP	HP	HP
ftr	ferrotremolite	$Ca_2Fe_5Si_8O_{22}(OH)_2$	-8865.9 ± 7.8	HP	HP	HP
ftst	ferrotschermak's talc	$Fe_2Al_2Si_3O_{10}(OH)_2$	-4387.6 ± 3.6	HP	HP	HP
gl	glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$	-10138 ± 10	RH	RH	RH
gr	grunerite	$Fe_7Si_8O_{22}(OH)_2$	-8000 ± 10	G	G	RH
hb	hornblende	$Ca_2Mg_4Al_2Si_7O_{22}(OH)_2$	-10614.2 ± 6.9	HP	HP	HP
htpz	hydrotopaz	$Al_2SiO_4(OH)_2$	-2378 ± 12	B	B	B
ilv	ilvaite	$CaFe_2^{2+}Fe^{3+}Si_2O_8(OH)$	-3058.9 ± 5.0	RH	RH	RH
mcar	magnesiocarpholite	$MgAl_2Si_2O_6(OH)_4$	-3893.0 ± 2.2	HP	HP	HP
mchl	magnesiochloritoid	$MgAl_2SiO_5(OH)_2$	-2947.9 ± 1.9	HP	HP	HP
mi	minnesotaite	$Fe_3Si_4O_{10}(OH)_2$	-3962.6 ± 4.2	HP	HP	HP
mrbc	magnesioriebeckite	$Na_2Mg_3Fe_2^{3+}Si_8O_{22}(OH)_2$	-9313.4 ± 9.2	HP	HP	HP
mrg	margarite	$CaAl_4Si_2O_{10}(OH)_2$	-5288.7 ± 2.6	RH	RH	HP
mst	magnesiostaurolite	$Mg_2Al_9Si_{3.75}O_{22}(OH)_2$	-10680.1 ± 6.6	HP	HP	HP
mu	muscovite[a]	$KAl_3Si_3O_{10}(OH)_2$	-5039.5 ± 4.9	RH	RH	RH
phl	phlogopite[b]	$KMg_3AlSi_3O_{10}(OH)_2$	-5267.3 ± 3.5	CN	CN	RH
prgn	paragonite[a]	$NaAl_3AlSi_3O_{10}(OH)_2$	-4998.9 ± 3.9	RH	RH	RH
prgs	pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$	-10889 ± 22	RH	RH	RH
prh	prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$	-5266.4 ± 2.0	RH	RH	RH
prph	pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	-4712.3 ± 1.5	RH	RH	RH
rbc	riebeckite	$Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$	-8341 ± 10	TW	RH	RH
rsnh	rosenhahnite	$Ca_3Si_3O_8(OH)_2$	-4415.1 ± 3.1	RH	RH	RH
sdph	siderophyllite	$KFe_2Al_3Si_2O_{10}(OH)_2$	-4718.5 ± 4.5	HP	HP	HP
sphl	sodiumphlogopite	$NaMg_3AlSi_3O_{10}(OH)_2$	-5224.4 ± 4.5	HP	HP	HP
st	staurolite	$Fe_4Al_{18}Si_8O_{46}(OH)_2$	-20331 ± 21	H	H	H
ta	talc	$Mg_3Si_4O_{10}(OH)_2$	-4959.0 ± 5.0	RH	RH	RH
tr	tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	-10500 ± 7.0	RH	RH	RH
tsta	Tschermak's talc	$Mg_2Al_2Si_3O_{10}(OH)_2$	-5048.7 ± 3.1	HP	HP	HP
zo	zoisite	$Ca_2Al_3Si_3O_{12}(OH)$	-5917.8 ± 3.3	RH	RH	RH

Note. RH: Robie and Hemingway (1995). B: Barton (1982). HP: Holland and Powell (1990). H: Holdaway *et al.* (1995). G: Ghiorso *et al.* (1995). CN: Circone and Navrotsky (1992). TW: based on scheme of Miyano and Klein (1983) and data for acmite from Robie and Hemingway (1995).

[a] Disordered.

[b] Partially ordered.

[c] Uncertainty range on $\Delta_f G°$ is $\pm 2\sigma$; uncertainties at 740 K are the same as at 298.15 K.

TABLE III
Thermodynamic Data for Additional Substances Included in the Calculations[a]

Mineral Name and Abbreviation		Ideal Formula	$\Delta_f G°$ (740 K) (kJ/mol)
ab	albite	$NaAlSi_3O_8$	-3377.5 ± 2.6
acm	acmite	$NaFe^{3+}Si_2O_6$	-2168.2 ± 4.0
alm	almandine	$Fe_3Al_2Si_3O_{12}$	-4468.0 ± 3.0
an	anorthite	$CaAl_2Si_2O_8$	-3673.8 ± 2.0
and	andalusite	Al_2SiO_5	-2222.4 ± 2.0
andr	andradite	$Ca_3Fe_2^{3+}Si_3O_{12}$	-4922.7 ± 5.9
anh	anhydrite	$CaSO_4$	-1152.3 ± 4.2
caol	calcium olivine	Ca_2SiO_4	-2025.7 ± 2.5
cor	corundum	Al_2O_3	-1443.7 ± 1.3
di	diopside	$CaMgSi_2O_6$	-2769.6 ± 2.0
en	enstatite	$Mg_2Si_2O_6$	-2659.5 ± 3.0
fa	fayalite	Fe_2SiO_4	-1235.9 ± 1.3
fo	forsterite	Mg_2SiO_4	-1877.3 ± 2.0
fs	ferrosilite	$Fe_2Si_2O_6$	-2013.7 ± 6.0
grs	grossular	$Ca_3Al_2Si_3O_{12}$	-5744.7 ± 3.2
hed	hedenbergite	$CaFeSi_2O_6$	-2436.8 ± 3.0
hm	hematite	Fe_2O_3	-628.2 ± 1.3
kls	kalsilite	$KAlSiO_4$	-1834.0 ± 3.1
lc	leucite	$KAlSi_2O_6$	-2630.9 ± 2.8
mc	microcline	$KAlSi_3O_8$	-4311.1 ± 3.9
mt	magnetite	Fe_3O_4	-868.7 ± 2.1
nph	nepheline	$NaAlSiO_4$	-1803.8 ± 3.9
qz	quartz	SiO_2	-776.0 ± 1.0
sp	spinel	$MgAl_2O_4$	-1994.9 ± 2.4
woll	wollastonite	$CaSiO_3$	-1422.9 ± 1.4
-	water vapor	H_2O	-206.64 ± 0.04
-	sulfur dioxide, gas	SO_2	-298.7 ± 0.2

[a] Thermodynamic data are from Robie and Hemingway (1995).

We generally used laboratory phase equilibrium studies of hydrous silicate dehydration and field observations of partially reacted mineral assemblages to choose the simple and complex dehydration reactions that we included in our reaction list. Where no laboratory studies or field observations were available, we wrote down and calculated several possible dehydration reactions and picked the ones with the more stable reaction products. To save space, the reactions in Tables IV–VI are written using the mineral name abbreviations listed in Tables II and III.

The thermodynamic calculations were done as follows. The Gibbs free energy change ($\Delta_r G$) for each dehydration reaction was calculated from

$$\Delta_r G = \Sigma(\Delta_f G°)_{products} - \Sigma(\Delta_f G°)_{reactants} \qquad (5)$$

and the equilibrium constant (K_{eq}) for each dehydration reaction was then calculated from

$$K_{eq} = \exp[-\Delta_r G/(RT)], \qquad (6)$$

where R is the ideal gas constant and T is temperature in kelvin. The equilibrium water vapor fugacity (f_{H_2O}) was then calculated from K_{eq} for each reaction. Because we are considering reactions of pure, crystalline minerals, the thermodynamic activities of all solids are unity and the equilibrium constant expressions involve only gases. In the case of simple dehydration (type A) and complex dehydration reactions (type B) the equilibrium constant expressions involve only water vapor. Taking reaction (1), eastonite dehydration, as an example,

$$f_{H_2O} = K_1, \qquad (7)$$

where K_1 is the equilibrium constant for reaction (1). The equilibrium constant expressions for coupled oxidation-dehydration reactions (type C) involve both O_2 and water. The f_{H_2O} for riebeckite oxidation is thus given by

$$f_{H_2O} = K_3 f_{O_2}^{3/4}, \qquad (8)$$

where f_{O_2} is the oxygen fugacity. The equilibrium constant expressions for coupled sulfatization–dehydration reactions (type D) involve both SO_2 and water, and in the case of reaction (4), tremolite sulfatization–dehydration,

$$f_{H_2O} = K_4 f_{SO_2}^2 f_{O_2}, \qquad (9)$$

where f_{SO_2} is the SO_2 fugacity. Analogous equations were used to calculate the f_{H_2O} values for all of the reactions in Tables IV–VI.

The uncertainties in the f_{H_2O} values were calculated next. The dispersion ($\delta\Delta_r G$) in the $\Delta_r G$ at 298.15 K for each dehydration reaction is

$$\delta\Delta_r G = (\Sigma(d_i E_i)^2)^{1/2} \qquad (10)$$

where d_i is the number of moles of i (reactant and product) involved in the reaction and E_i is the tabulated 2σ error in the $\Delta_f G°$ for each reactant and product at 298.15 K. We used Eq. (6) to compute the corresponding error in K_{eq} at 700 K, the middle of the 660–740 K range, by assuming that $\delta\Delta_r G$ is the same as at 298.15 K. (This assumption is made because the errors in $\Delta_f G°$ values are generally available only at 298.15 K, and not at higher temperatures.) The uncertainty in f_{H_2O} was then calculated from the equilibrium constant expression for each reaction.

TABLE IV

Equilibrium Water Vapor Fugacities for Dehydration Breakdown Reactions at Venus's Surface

Reaction #	Reaction	$\log_{10} f_{H2O}$ (bars)		$\pm\sigma$
		Plains (Modal Radius)[a]	Summit of Maxwell Montes[b]	
(1)	east = sp + kls + 0.5 en + H_2O	−2.46	−3.74	0.52
(2)	prgs = 1.5 di + fo + nph + 0.5 an + 0.5 sp + H_2O	−0.87	−2.06	1.73
(3)	phl = 1.5 fo + 0.5 lc + 0.5 kls + H_2O	−0.86	−1.96	0.36
(4)	ed = 0.25 ab + 1.5 fo + 2 di + 0.75 nph + H_2O	−0.57	−1.57	0.64
(5)	sphl = fo + 0.5 en + nph + H_2O	−0.49	−1.50	0.50
(6)	mrbc = 1.5 en + 2 acm + qz + H_2O	−0.36	−1.46	1.03
(7)	rbc = 2 acm + 1.5 fs + qz + H_2O	−0.06	−1.24	1.67
(8)	bcc = caol + cor + H_2O	0.04	−0.86	0.47
(9)	sdph = cor + fa + kls + H_2O	0.13	−0.78	0.49
(10)	ann = 1.5 fa + 0.5 kls + 0.5 lc + H_2O	0.58	−0.24	0.46
(11)	ftr = 2 hed + 1.5 fs + qz + H_2O	0.77	−0.22	0.94
(12)	tr = 2 di + 1.5 en + qz + H_2O	0.80	−0.13	0.73
(13)	ant = 3.5 en + qz + H_2O	0.88	0.07	0.99
(14)	ta = 1.5 en + qz + H_2O	0.91	−0.02	0.53
(15)	hb = and + 2 di + en + H_2O	0.95	0.16	0.72
(16)	3 st = 4 alm + 14 and + 11 cor + 3 H_2O	1.11	−0.60	2.09
(17)	cum = 3.5 en + qz + H_2O	1.25	0.44	1.09
(18)	clnc = en + fo + sp + 4 H_2O	1.52	0.73	0.16
(19)	mu = cor + mc + H_2O	1.55	0.92	0.48
(20)	fant = 3.5 fs + qz + H_2O	1.62	0.57	1.73
(21)	am = en + 2 sp + 4 H_2O	1.71	0.92	0.60
(22)	prgn = ab + cor + H_2O	2.04	1.40	0.36
(23)	6 zo = 6 an + 2 grs + cor + 3 H_2O	2.09	1.20	0.57
(24)	3 fchl = alm + 2 cor + 3 H_2O	2.10	1.31	0.47
(25)	fame = 2 cor + 2 fa + 4 H_2O	2.11	1.38	0.50
(26)	gr = 3.5 fs + qz + H_2O	2.12	1.08	1.78
(27)	gl = 2 ab + fo + 0.5 en + H_2O	2.14	1.03	0.79
(28)	6 ep = 2 andr + 6 an + hm + 3 H_2O	2.25	1.49	0.61
(29)	mchl = cor + 0.5 en + H_2O	2.27	1.50	0.31
(30)	ilv = 0.5 hm + woll + fa + 0.5 H_2O	2.44	1.06	0.40
(31)	mrg = an + cor + H_2O	2.51	1.76	0.26
(32)	prh = an + woll + H_2O	2.61	1.87	0.29
(33)	fcar = 0.5 fs + and + 2 H_2O	2.78	2.08	0.38
(34)	tsta = and + en + H_2O	2.81	2.21	0.36
(35)	mi = 1.5 fs + qz + H_2O	2.86	2.15	0.78
(36)	6 czo = 6 an + 2 grs + cor + 3 H_2O	2.97	1.99	0.66
(37)	prph = and + 3 qz + H_2O	3.16	2.52	0.29
(38)	mst = 1.75 and + en + 2.75 cor + H_2O	3.20	2.46	0.72
(39)	cel = lc + 0.5 en + qz + H_2O	3.29	2.50	0.40
(40)	de = 4.5 fs + 3 mt + 3 qz + 5 H_2O	3.34	2.78	0.45
(41)	fcel = 0.5 fs + mc + H_2O	3.47	2.90	0.48
(42)	htpz = and + H_2O	3.62	3.00	0.92
(43)	fgl = 2 ab + fa + 0.5 fs + H_2O	3.68	2.68	0.80
(44)	ftst = fs + and + H_2O	3.89	3.40	0.57
(45)	rsnh = 3 woll + H_2O	4.26	3.82	0.53

Note. σ: dispersion of $\log_{10} f_{H_2O}$; see text.

[a] 740 K, 95.6 bars, 0.6 km below 6052 km (0 km level in VIRA model, Seiff *et al.* 1986).

[b] 660 K, 48.0 bars, 9.8 km above 6052 km.

TABLE V
Equilibrium Water Fugacities for Oxidation of Hydrous Fe-Bearing Minerals on the Surface of Venus

Reaction #	Reaction	$\log_{10} f_{H2O}$ (bars)	$\pm \sigma$
(46)	sdph + 0.5 O_2 = hm + kls + and + H_2O	1.79	0.46
(47)	rbc + 0.75 O_2 = 2 acm + 1.5 hm + 4 qz + H_2O	1.97	0.97
(48)	fchl + 0.25 O_2 = 0.5 hm + and + H_2O	2.87	0.61
(49)	fame + O_2 = 2 hm + 2 and + 4 H_2O	2.94	0.13
(50)	fcar + 0.25 O_2 = 0.5 hm + and + qz + 2 H_2O	3.12	0.10
(51)	ann + 0.75 O_2 = 1.5 hm + mc + H_2O	3.83	0.50
(52)	fcel + 0.25 O_2 = 0.5 hm + mc + qz + H_2O	4.15	0.50
(53)	st + O_2 = 2 hm + 8 and + cor + H_2O	4.21	1.88
(54)	de + 3 O_2 = 9 hm + 12 qz + 5 H_2O	4.56	0.33
(55)	mi + 0.75 O_2 = 1.5 hm + 4 qz + H_2O	4.90	0.46
(56)	ftst + 0.5 O_2 = hm + and + 2 qz + H_2O	5.25	0.36
(57)	fgl + 0.75 O_2 = 1.5 hm + 2 ab + 2 qz + H_2O	5.84	0.75
(58)	fant + 1.75 O_2 = 3.5 hm + 8 qz + H_2O	6.37	0.92
(59)	gr + 1.75 O_2 = 3.5 hm + 8 qz + H_2O	6.87	1.04

Note. At 740 K and 95.6 bars. Oxygen fugacity corresponds to the hematite–magnetite equilibrium at 740 K ($\log_{10} f_{O_2} = -20.8$).

The next step was to compare the calculated equilibrium water fugacity for each dehydration reaction to the corresponding atmospheric water vapor partial pressure on Venus. We assume that partial pressures of gases in Venus's atmosphere are equal to fugacities, that is ideal gas behavior. This has been done by other workers and is justified because deviations from ideality are ~1% (Fegley and Treiman 1992). The atmospheric water vapor partial pressure on Venus is about 3 millibar ($\log P_{H_2O} = -2.54$) at 740 K (modal radius) and about 1 millibar ($\log P_{H_2O} = -2.84$) at 660 K (on Maxwell Montes) for the nominal water vapor concentration of 30 ppmv. A hydrous silicate is stable if the equilibrium water fugacity is less than or equal to the atmospheric water vapor partial pressure and is unstable if the reverse is true.

RESULTS

Tables IV–VI list the calculated equilibrium water vapor fugacities in order of decreasing stability (i.e., most stable minerals listed first). The coupled oxidation–dehydration reactions and the coupled sulfatization–dehydration reactions were only calculated for the modal radius (740 K) because the oxygen fugacity in the highland regions is uncertain due to quenching of gas phase equilibria at higher temperatures in the lowlands (Fegley *et al.* 1997).

Simple dehydration reactions. All calculated f_{H_2O} values are listed in Table IV. The calculated f_{H_2O} values for

the most stable hydrous silicates are compared to the atmospheric P_{H_2O} values on Venus (15–70 ppmv water) in Figs. 1a and 1b. The equilibrium water vapor fugacities for most hydrous silicates are greater than the atmospheric water vapor partial pressures at the modal radius and at the top of Maxwell. Thus, most pure hydrous silicates are unstable and can decompose on Venus's surface. Later we discuss the kinetics and mechanisms for dehydration and dehydroxylation of micas and amphiboles.

Eastonite, with the ideal formula $KMg_2Al_3Si_2O_{10}(OH)_2$, is a trioctahedral mica that seems to be stable over Venus's entire surface. However, this result is tentative because of the uncertainty in the thermodynamic data for eastonite. Formation of eastonite by chemical weathering on Venus's surface requires reaction of atmospheric water vapor with three minerals (e.g., spinel, kalsilite, and enstatite) and is probably slow (or even impossible) in geologically reasonable times because of slow cation diffusion at 660–740 K. Thus, any eastonite present on Venus probably formed in the interior and was then brought to the surface. On the Earth, eastonite formation requires a high Al chemical

TABLE VI
Equilibrium Water Fugacities for Sulfatization of Hydrous Ca-Bearing Minerals on the Surface of Venus

Reaction #	Reaction	$\log_{10} f_{H2O}$ (bars)	$\pm \sigma$
(60)	prgs + 2 SO_2 + O_2 = 2 anh + and + 2 fo + ab + H_2O	2.16	1.72
(61)	mgr + SO_2 + 0.5 O_2 = anh + 2 and + H_2O	2.95	0.45
(62)	tr + 2 SO_2 + O_2 = 2 anh + 2.5 en + 3 qz + H_2O	2.97	1.00
(63)	ed + 2 SO_2 + O_2 = 2 anh + fo + 1.5 en + ab + H_2O	2.96	0.93
(64)	hb + 2 SO_2 + O_2 = 2 anh + 2 en + and + 2 qz + H_2O	3.12	0.94
(65)	prh + 2 SO_2 + O_2 = 2 anh + and + 2 qz + H_2O	5.15	0.68
(66)	zo + 2 SO_2 + O_2 = 2 anh + 1.5 and + 1.5 qz + 0.5 H_2O	5.84	1.42
(67)	ep + 2 SO_2 + O_2 = 2 anh + 0.5 hm + and + 2 qz + 0.5 H_2O	6.12	1.42
(68)	fhb + 2 SO_2 + 2 O_2 = 2 anh + 2 hm + and + 6 qz + H_2O	6.19	0.96
(69)	czo + 2 SO_2 + O_2 = 2 anh + 1.5 and + 1.5 qz + 0.5 H_2O	6.72	1.48
(70)	ftr + 2 SO_2 + 2.25 O_2 = 2 anh + 2.5 hm + 8 qz + H_2O	7.73	1.05
(71)	bcc + 2 SO_2 + O_2 = 2 anh + and + H_2O	7.90	0.74
(72)	ilv + SO_2 + O_2 = anh + 1.5 hm + 2 qz + 0.5 H_2O	9.97	1.06
(73)	rsnh + 3 SO_2 + 1.5 O_2 = 3 anh + 3 qz + H_2O	11.09	0.98

Note. At 740 K and 95.6 bars. The SO_2 is taken as 130 ppm and oxygen fugacity corresponds to the hematite-magnetite equilibrium at 740 K ($\log_{10} f_{O_2} = -20.8$).
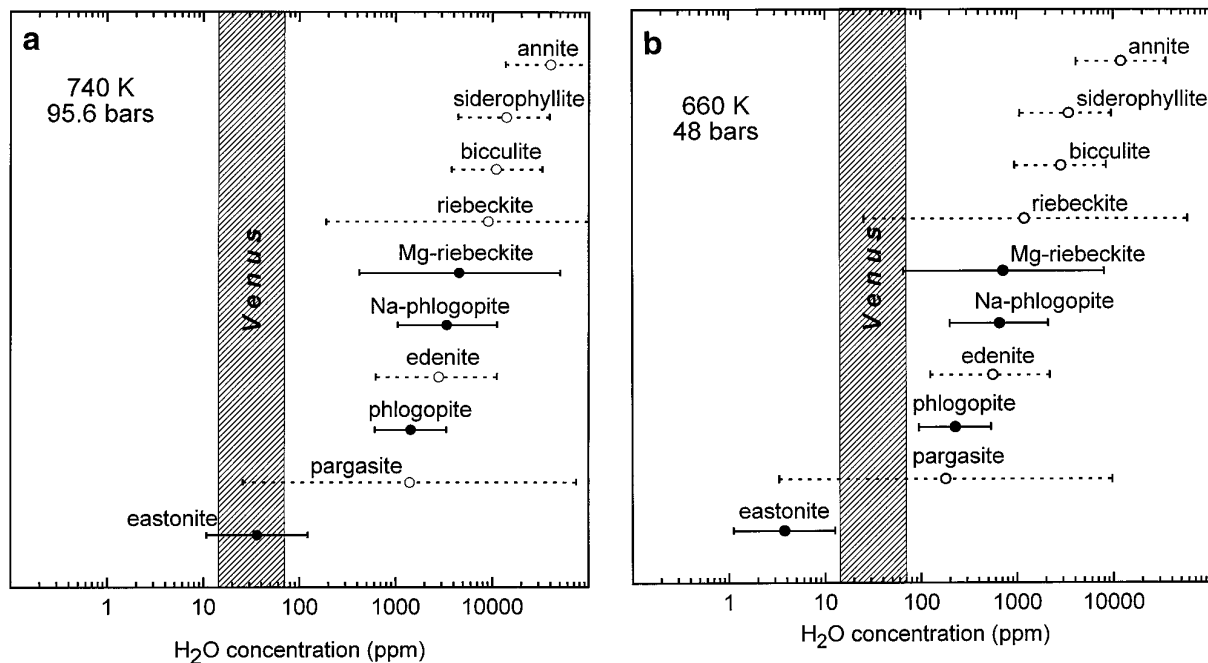
FIG. 1. Equilibrium water vapor concentrations in parts per million by volume for simple dehydration reactions of the most stable hydrous silicates we studied. The reactions plotted are equations 1–10 in Table IV. The nominal values and two sigma ranges in the equilibrium water vapor contents are compared to the observed water vapor content (15–70 ppmv) in Venus' deep atmosphere. The dashed lines and hollow dots are for hydrous Fe^{2+}- and/or Ca-bearing minerals that may be oxidized or sulfatized. The solid lines and black dots are for hydrous minerals unaffected by either oxidation or sulfatization. (a) Hydrous mineral stability at Venus's modal radius (6051.4 km) where $T = 740$ K and $P = 95.6$ bar. The modal radius is 0.6 km below the zero level (6052 km) in the VIRA model (Seiff *et al.* 1986). (b) Hydrous mineral stability on Maxwell Montes (6061.8 km) where $T = 660$ K and $P = 48$ bars.

potential and it is much less abundant than other micas, even though the terrestrial continental crust is Al-enriched. However, our results also show that micas along the eastonite–phlogopite join (micas formed by Al substitution into phlogopite) are also predicted to be stable on Venus (Zolotov *et al.* 1997). Thus, eastonite–phlogopite micas are potential hydrous phases on Venus's surface.

Pargasite, ideal formula $NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$, and riebeckite, ideal formula $Na_2Fe_3^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2$, are alkali amphiboles. The calculated range, although not the nominal value, for pargasite's equilibrium f_{H_2O} overlaps the observed P_{H_2O} range at Venus's modal radius and on top of Maxwell. The calculated range for riebeckite, but not the nominal value for the equilibrium f_{H_2O}, overlaps the observed P_{H_2O} range, but only at 660 K. However, pargasite can react with SO_2 in Venus's atmosphere and riebeckite can be oxidized to hematite on Venus's surface. Thus, both minerals are stable if only dehydration is considered, but sulfatization will convert pargasite to anhydrite, other anhydrous minerals, and water vapor, while oxidation will convert riebeckite to hematite, other anhydrous minerals, and water vapor.
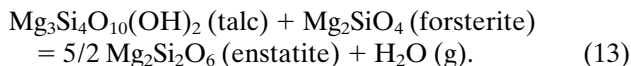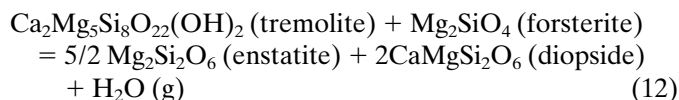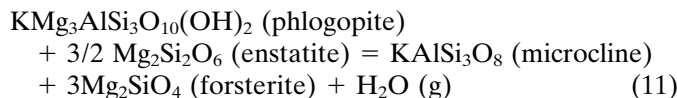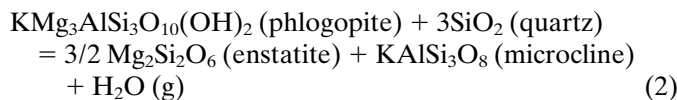
Three other minerals, although calculated to be unstable on Venus' surface, deserve mention. Phlogopite has the

ideal formula $KMg_3AlSi_3O_{10}(OH)_2$ and is one end-member of a solid solution series involving F–OH, Fe–Mg, and Al–(Mg,Si) substitution. Phlogopite nominally requires ~230 ppmv water (660 K) or ~1440 ppmv water (740 K) to be stable on Venus. However, within the formal uncertainties of the thermodynamic data, the equilibrium water values range from ~100 to 520 ppmv (660 K) and ~630 to 3310 ppmv (740 K). Conceivably, phlogopite could be stable in the highlands if atmospheric water vapor were ~3 to ~15 times higher than observed at present. As discussed by Zolotov *et al.* (1997), phlogopite can also be stabilized by partial substitution of OH by F and by Al substitution for Mg and Si.

Edenite, with ideal formula $NaCa_2Mg_5AlSi_7O_{22}(OH)_2$, is a Ca-bearing alkali amphibole and needs ~560 (130–2450) ppmv water at 660 K or ~2820 (645–12,300) ppmv water at 740 K to be stable on Venus. However, edenite can be attacked by SO_2. Magnesioriebeckite, with ideal formula $Na_2Mg_3Fe_2^{3+}Si_8O_{22}(OH)_2$, is an Fe^{3+}-bearing alkali amphibole. It needs ~720 (70–7740) ppmv water at 660 K or ~4170 (390–44,700) ppmv water at 740 K to be stable on Venus. Magnesioriebeckite is not subject to oxidation or attack by SO_2 and phase equilibrium data (Ernst 1960) show that it is stable over broad temperature, f_{H_2O}, and

f_{O_2} ranges. Only magnesiohastingsite and richterite have higher thermal stabilities (Gilbert *et al.* 1982), but no thermodynamic data are available for these two amphiboles.

Complex dehydration reactions. These equilibria are important in terrestrial metamorphic reactions (Deer *et al.* 1963). Four reactions were considered for phlogopite, tremolite, and talc:

$$KMg_3AlSi_3O_{10}(OH)_2 \text{ (phlogopite)} + 3SiO_2 \text{ (quartz)}$$
$$= 3/2 \, Mg_2Si_2O_6 \text{ (enstatite)} + KAlSi_3O_8 \text{ (microcline)}$$
$$+ H_2O \text{ (g)} \qquad (2)$$

$$KMg_3AlSi_3O_{10}(OH)_2 \text{ (phlogopite)}$$
$$+ 3/2 \, Mg_2Si_2O_6 \text{ (enstatite)} = KAlSi_3O_8 \text{ (microcline)}$$
$$+ 3Mg_2SiO_4 \text{ (forsterite)} + H_2O \text{ (g)} \qquad (11)$$

$$Ca_2Mg_5Si_8O_{22}(OH)_2 \text{ (tremolite)} + Mg_2SiO_4 \text{ (forsterite)}$$
$$= 5/2 \, Mg_2Si_2O_6 \text{ (enstatite)} + 2CaMgSi_2O_6 \text{ (diopside)}$$
$$+ H_2O \text{ (g)} \qquad (12)$$

$$Mg_3Si_4O_{10}(OH)_2 \text{ (talc)} + Mg_2SiO_4 \text{ (forsterite)}$$
$$= 5/2 \, Mg_2Si_2O_6 \text{ (enstatite)} + H_2O \text{ (g)}. \qquad (13)$$

The equilibrium water vapor fugacities are 6.6, 0.33, 17.0, and 22.4 bar, respectively, for reactions (2), (11), (12) and (13). These values are higher than those in Table IV, showing that hydrous silicate stability is decreased if reactions with other minerals are considered. We did not consider other complex dehydration reactions because cation diffusion is probably so slow at Venus surface temperatures that hydrous minerals will decompose faster by water loss, oxidation, or sulfatization by atmospheric SO_2 than by complex dehydration reactions involving other minerals on the surface. However, the lower temperatures in the venusian highlands make these regions more favorable overall for hydrous minerals because the minerals are thermodynamically more stable at the lower temperatures and their decomposition rates (by dehydration, oxidation, or sulfatization) will be slower than in the hotter lowlands.

Coupled oxidation–dehydration reactions. All Fe^{2+}-bearing hydrous silicates on Venus' surface are also subject to oxidation because the f_{O_2} at Venus's surface, while still quite low, is sufficiently oxidizing for hematite to exist (Pieters *et al.* 1986; Zolotov 1996; Fegley *et al.* 1997). The results of our calculations for simple dehydration reactions (Table IV) and coupled oxidation–dehydration reactions (Table V) show that stabilities of all Fe^{2+}-bearing hydrous silicates are decreased when oxidation reactions are considered: the present atmosphere is too oxidizing for these minerals to be stable. This situation is illustrated in Fig. 2 for the modal radius (740 K). All the Fe^{2+}-bearing hydrous silicate stability fields lie in the bottom region of the graph at oxygen fugacities several orders of magnitude below the range for Venus. Calculations of coupled oxidation–
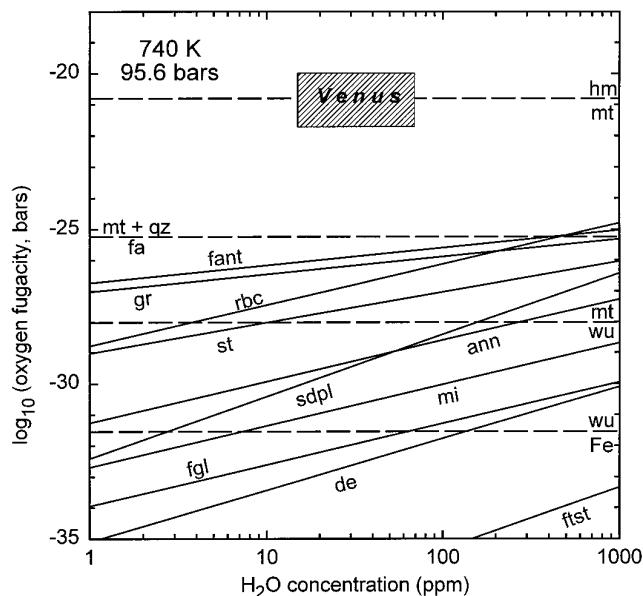

FIG. 2. The stability of Fe^{2+}-bearing hydrous silicates at the conditions of Venus' modal radius as a function of oxygen fugacity and water abundance. The different minerals are stable below the labeled lines. The shaded box shows the range of oxygen fugacity and water abundance at the surface of Venus. The horizontal dashed line shows the oxygen fugacity at the magnetite-hematite phase boundary calculated from the data of Robie and Hemingway (1995). The reactions plotted are equations 46–59 in Table V. The mineral abbreviations are given in Tables II and III. No Fe^{2+}-bearing hydrous silicates are stable on Venus.

dehydration equilibria in the highlands are hindered by uncertainties in the atmospheric oxygen fugacity in this region. Because gas phase equilibria are apparently quenched at or close to 730 K (Fegley *et al.* 1997), the f_{O_2} in the cooler highlands cannot be calculated easily. The lower limit to the atmospheric f_{O_2} at 660 K in the highlands is $10^{-24.7}$ bar (Zolotov 1996; Fegley *et al.* 1997), but Fe^{2+}-bearing hydrous silicates are unstable even at this f_{O_2} and need lower oxygen fugacities to be stable.

Coupled sulfatization–dehydration reactions. Table VI lists the equilibrium water vapor fugacities for coupled sulfatization-dehydration reactions of Ca-bearing hydrous silicates. The results are presented graphically in Figs. 3a–3c. We find that the stability fields of all of these minerals are far from present conditions on Venus's surface, even when the uncertainties in the thermodynamic data, and gas abundances are taken into account. At the modal radius (740 K), Ca-bearing hydrous silicates require either <1 ppmv SO_2 at the oxygen fugacity of $10^{-20.8}$ bar or $f_{O_2} < 10^{-25}$ bars at an SO_2 abundance of 130 ppmv. The Ca-bearing hydrous silicates are also unstable in the highlands. Thermodynamically, SO_2 decreases significantly the stability of Ca-bearing hydrous silicates because of the greater stability of anhydrite. However, the reaction rates involved need to be measured in the laboratory.
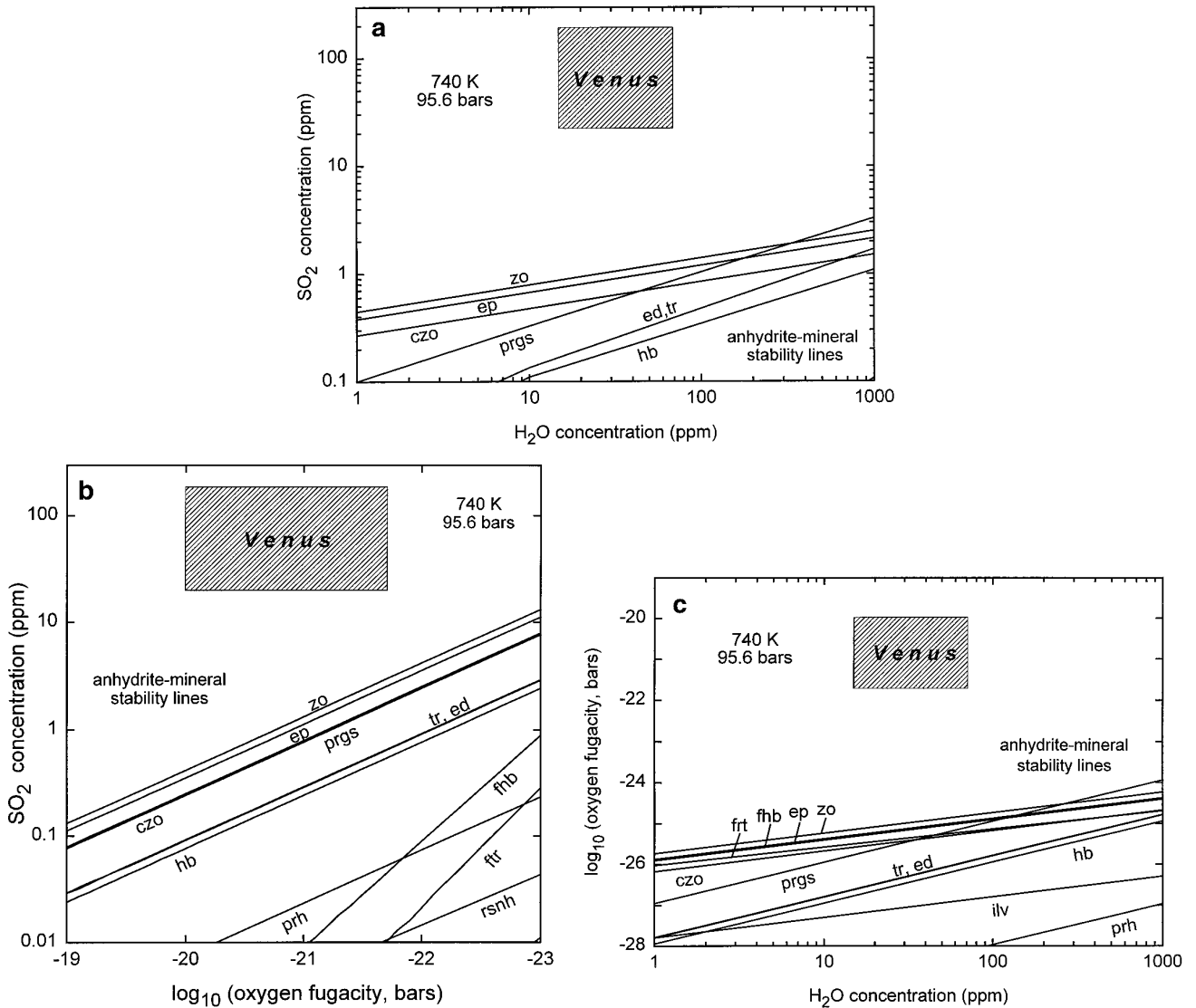
FIG. 3. The stability of Ca-bearing hydrous silicates at the conditions of Venus' modal radius. The different minerals (see Table II for abbreviations) are stable below the labeled lines. The reactions plotted are Equations 60–73 in Table VI. No Ca-bearing hydrous silicates are stable on Venus. (a) Mineral stability as a function of SO_2 and H_2O concentration for $f_{O_2} = 10^{-20.8}$ bar, the f_{O_2} at the hematite–magnetite phase boundary at 740 K. The shaded box shows the range of SO_2 (25–130 ppmv) and H_2O (15–70 ppmv) concentrations in Venus's deep atmosphere. (b) Mineral stability as a function of SO_2 concentration and f_{O_2} at 30 ppmv H_2O. (c) Mineral stability as a function of f_{O_2} and H_2O concentration at 130 ppmv SO_2.

DISCUSSION

We find that most hydrous silicates are unstable on Venus and that only a few micas and amphiboles are possibly stable, probably in the cooler highlands. Our conclusions broadly agree with earlier suggestions that mica and amphibole solid solutions were the only hydrous silicates that could be stable, and that these minerals were probably found only in the highlands (Fegley and Treiman 1992; Zolotov and Volkov 1992). However, tremolite and phlogopite, although unstable, are worthy of discussion because they are frequently suggested as being present on Venus

(Mueller 1964; Lewis 1970; Khodakovsky *et al.* 1979a,b; Lewis and Kreimendahl 1980; Nozette and Lewis 1982).

Phlogopite on Venus? We find that pure phlogopite is unstable on Venus, although the thermodynamic data are sufficiently uncertain that 100 ppmv water vapor may be enough to stabilize phlogopite at 660 K on Maxwell. This is about twice as large as the 45 ppmv water vapor derived by Meadows and Crisp (1996) for Venus's near-surface atmosphere, and about three times higher than the nominal value of 30 ppmv used here. Earlier, Fegley and Treiman (1992) also concluded that pure phlogopite was unstable,

requiring 1060 ppmv water at 740 K and 125 ppmv water at 663 K. However, the uncertainties in thermodynamic data from different compilations showed surprisingly large differences, corresponding to ranges of 500–2200 ppmv water at 740 K and 55–280 ppmv water at 663 K for phlogopite stability (Fegley and Treiman 1992). Reactions of phlogopite with quartz (reaction 2) and enstatite (reaction 11) make it even more unstable. However, even though quartz and enstatite may be present on Venus's surface, reactions (2) and (11), and similar dehydration equilibria are probably unimportant because of slow cationic diffusion rates at Venus surface temperatures.

At present, phlogopite thermodynamic data are still fairly uncertain, especially as a function of the Al–Si ordering state. We used the data of Circone and Navrotsky (1992) which suggest a zero enthalpy of ordering, but Robie and Hemingway (1984, 1995) use 20 kJ mol^{-1} for the ordering enthalpy. The Robie and Hemingway (1995) data make phlogopite (ordered and disordered) more stable than calculated here.

We also studied the effects of Fe–Mg, F–OH, and Al–(Mg,Si) substitutions on phlogopite and eastonite stability because these micas are end-members in solid solutions involving these substitutions (Zolotov et $al.$ 1997). Substitution of Fe^{2+} for Mg^{2+} along the phlogopite–annite join and along the eastonite–siderophyllite join decreases mica stability. Neither phlogopite–annite nor annite–siderophyllite solid solutions are stable, but it is reasonable to expect some amount of siderophyllite (i.e., Fe^{2+}) solubility in eastonite, if the latter is found on Venus. Substitution of F$^-$ for OH$^-$ along the phlogopite–fluorphlogopite join and substitution of Al^{3+} for Mg^{2+} and Si^{4+} along the phlogopite–eastonite join increases mica stability. So, some phlogopitic micas could be stable on Venus, mainly in the cooler highlands regions.

Tremolite on Venus?   Tremolite is unstable on Venus for two reasons. First, the atmospheric water vapor pressure on Venus is lower than the equilibrium water fugacity for tremolite. To be stable, tremolite needs 6.6% water vapor at 740 K and 1.5% at 660 K (Table V), much larger than the 30 ppmv water vapor in the atmosphere. Using thermodynamic data from Robie et $al.$ (1979), Fegley and Treiman (1992) calculated that tremolite needed 915 ppmv at 740 K and 150 ppmv at 663 K. These values are larger than the 20 ppmv atmospheric water vapor used in their paper. However, within the uncertainties of the Robie et $al.$ (1979) data, Fegley and Treiman (1992) calculated that 15 ppmv to 5.8% water vapor was needed at 740 K and 0.9 ppmv to 1.2% at 663 K. After their calculations were completed, work by Jenkins et $al.$ (1991) on the thermodynamics of synthetic tremolite led Fegley and Treiman (1992) to conclude that "it is unlikely that tremolite is thermodynamically stable anywhere on the Venusian surface." Our results confirm their conclusion that tremolite is unstable on Venus.

We also calculate that atmospheric SO$_2$ on Venus will attack tremolite and convert it to anhydrite, other anhydrous minerals, and water vapor. Sulfatization of Ca-bearing hydrous silicates should occur on Venus because it is thermodynamically favorable and SO$_2$–CO$_2$ gas mixtures react with calcite and diopside in the laboratory (Fegley and Prinn 1989). However, the rate of tremolite sulfatization has not been measured, so we do not know if dehydration is faster than sulfatization or if the two reactions proceed concurrently.

Other amphiboles.   Earlier we discussed our results for three alkali amphiboles: pargasite, edenite, and magnesioriebeckite. All three may be stable against dehydration within the uncertainties of the thermodynamic data. However, the venusian atmosphere is too oxidizing for riebeckite to be stable. We obtain the same result for crocidolite, the fibrous form of riebeckite, using the data of Bennington et $al.$ (1978). In general, our calculated dehydration reactions, petrologic phase equilibria (Gilbert et $al.$ 1982), and natural assemblages (Deer et $al.$ 1963) indicate that alkali amphiboles are very stable against dehydration and hence are the most likely hydrous minerals to be stable on Venus's surface. However, predictions of amphibole stability on Venus are difficult for several reasons.

First, the existing thermodynamic data for pure amphiboles are sufficiently uncertain that the equilibrium water vapor fugacities vary over wide ranges. Gibbs free energy data obtained from hydrothermal bomb experiments done at higher temperatures and high water pressures need to be extrapolated downward to Venus temperatures and pressures. Calorimetric measurements of enthalpies and heat capacities for reactants and products span Venus temperatures, but the calculated Gibbs free energies of reaction have high formal uncertainties. For example, thermodynamic data taken from Holland and Powell (1990) for several amphiboles (e.g., edenite, ferrohornblende, and magnesioriebeckite) and some other hydrous minerals are characterized by them as preliminary. No experimental data on amphibole dehydration are available for Venus surface temperatures, pressures, and water vapor concentrations. There is a wide gap between the petrologic phase equilibria in hydrothermal bombs and Venus surface conditions that needs to be filled by other types of experiments.

Second, thermodynamic data are still unavailable for several amphiboles that could be even more stable than those considered here. For example, substitution of Fe^{3+} for Al^{3+} generally increases amphibole stability. Magnesiohastingsite (NaCa$_2$Mg$_4$Fe^{3+}Si$_6$Al$_2$O$_{22}$(OH)$_2$), formed as a result of Fe^{3+} substitution for one Al^{3+} in pargasite, seems to be one of the most stable amphiboles known (Gilbert et $al.$ 1982), but Gibbs free energy data for it are unavail-

able. Petrologic phase equilibrium experiments (Charles 1977) and natural assemblages (Deer *et al.* 1963) indicate that richterite ($Na_2CaMg_5Si_8O_{22}(OH)_2$) also has high thermal stability, but only incomplete thermodynamic data are available. Kaersutite ($Ca_2(Na, K)(Mg, Fe^{2+}, Fe^{3+})_4Ti [Si_6Al_2O_{22}](O, OH, F)_2$) is a common amphibole in mantle xenoliths on Earth and has high thermal stability. However, no thermodynamic data are available to calculate kaersutite stability against dehydration, oxidation, and sulfatization on Venus. The Ca-free amphibole "magnesiorichterite" ($Na_2Mg_6Si_8O_{22}(OH)_2$) should be even more stable because it will not be attacked by SO_2. Fluorine substitution for OH increases amphibole stability (see the discussion in Fegley and Treiman 1992), but thermodynamic data are unavailable for F–OH amphibole solid solutions of interest to Venus (or for most F–OH amphiboles for that matter).

Third, the effect of SO_2 on amphibole stability can be calculated but is really unknown in terms of reaction kinetics and mechanisms. Our calculations predict that Ca-bearing amphiboles (e.g., pargasite and edenite) can be attacked by SO_2 to form anhydrite, water, and anhydrous minerals. Whether or not this really happens remains to be seen once experiments are done.

Formation of hydrous silicates. We now address the question of whether hydrous silicates on Venus's surface formed there by chemical weathering or were brought there after their formation in Venus's interior. The formation of hydrous minerals requires reaction of water vapor with anhydrous minerals. For example, in the case of pargasite, water vapor must react with diopside, forsterite, nepheline, anorthite, and spinel, and at the same time the oxygen anions and the cations in these five minerals must rearrange to form pargasite. In the absence of liquid water or another fluid to speed up mass transport, the ionic migration proceeds via solid state diffusion. No kinetic data exist for hydration of anhydrous minerals by water vapor at Venus conditions. However, ionic diffusion and hence hydrous silicate formation via gas–solid and solid–solid reactions is probably very slow at these temperatures.

Formation of micas and amphiboles in Venus's interior is probably hindered by the availability of water. We calculated earlier that the atmospheric water inventory on Venus is equivalent to only 2 ng water/gram rock, and hence the interior of Venus almost certainly contains many orders of magnitude more water than the atmosphere. Current tentative estimates are in the range of 1–10 μg water/gram Venus rock, less than the (poorly constrained) amount of water ($\sim$100–1000 μg water/g rock) in the bulk silicate Earth or the $\sim$300 μg water/g rock in the degassed terrestrial mantle (Table VII), and immediately raises the question of whether the venusian interior is wet enough to form hydrous minerals.

TABLE VII
Water in Venus and Earth
(Micrograms Water/Grams Rock)

Venus	
Magmas (Grinspoon 1993)	50
Present mantle (Namiki 1995)	<15
Atmospheric water distributed throughout bulk silicate Venus[a]	0.001
Earth	
Water in MORB glasses (Jambon 1995)[b]	1,000–6,000
MORB source region (Jambon 1995)[c]	100–600
MORB source region (Wood 1995)[c]	200
MORB source region (Namiki 1995)[d]	70–550
Residual peridotite (Bell & Rossman 1992; Dixon *et al.* 1988)	5–35
Bulk silicate Earth (Prinn & Fegley 1987)[e]	590
Bulk silicate Earth (Kargel & Lewis 1993)[e]	490
Bulk silicate Earth (Jambon 1995)[e]	1,100
Degassed mantle (Jambon 1995)[f]	300

[a] For 30 ppmv atmospheric water vapor and 70% (by mass) bulk silicate Venus (Basaltic Volcanism Study Project 1981).

[b] MORB is an abbreviation for mid ocean ridge basalts.

[c] Assuming MORB is the product of 10% partial melting (Wood 1995).

[d] Taken by Namiki (1995) from estimates by Byers *et al.* (1986); Dixon *et al.* (1988); Michael (1988); Jambon and Zimmerman (1990); Bell and Rossman (1992).

[e] Bulk silicate Earth = mantle, crust, oceans, and atmosphere with a mass of 4×10^{24} kg (about 67% by mass of the Earth), which is essentially the mass of the mantle.

[f] On the basis of the terrestrial ^{40}Ar budget, Jambon (1995) defines the degassed mantle as 50% of the entire mantle.

This question is difficult to answer. On the one hand, hydrous silicate formation in Venus's interior is probably more favorable than on the surface. Chemical reactions will proceed faster at the higher temperatures and pressures inside Venus than on the surface. On the other hand, hydrous silicate formation inside Venus is probably less favorable than hydrous silicate formation inside Earth. Table VII shows that the water content of Venus's interior is plausibly two orders of magnitude lower than that of the silicate Earth (defined here as the oceans + crust + mantle). In addition, on Earth subduction of oceanic lithosphere brings water-bearing sediments and hydrated oceanic slabs into the upper mantle. Also, on Earth, meteoric and oceanic water can participate in hydrous silicate formation in hydrothermal settings.

The plausible lack of liquid water in the venusian lithosphere and undersaturation of water in venusian magmas may exclude formation of magmatic hydrous minerals and may also suppress local hydrothermal formation of hydrous minerals. On the other hand, the Venera 13 XRF analysis

suggesting subalkaline igneous rocks (Barsukov 1992), the proposed deficiency of quartz-bearing rocks (Hess and Head 1990), and the suggested oxidized character of the crust and surface (Zolotov 1996; Fegley *et al.* 1997) are factors that favor the formation of alkali amphiboles and eastonite–phlogopite micas during regional and/or contact metamorphism. We conclude that formation of hydrous silicates in Venus's interior is more favorable than by chemical weathering on Venus's surface, but much less favorable than in the terrestrial crust and mantle.

Dehydration kinetics and mechanisms. Dehydration kinetics of hydrous silicates on Venus's surface are important because sufficiently slow dehydration kinetics may lead to preservation of fossil hydrous minerals from Venus's interior and/or from chemical weathering on the surface during a cooler, wetter period in Venus's past. The dehydration kinetics of hydrous silicates are also important for climate modeling because the water evolved is released to the atmosphere. Finally, the dehydration mechanisms are also important because metastable intermediates, which persist for some period of time and perhaps are characteristic of the original hydrous phases, may also be produced.

Although there are some discrepancies between results from different groups, studies by thermogravimetric and differential thermal analysis, X-ray diffraction, infrared, and Mössbauer spectroscopy of phlogopite and biotite dehydration in air, inert gas (N_2, Ar), vacuum, and reducing atmospheres show that the overall reaction proceeds via four or five stages with increasing temperature (Vedder and Wilkins 1969; Rouxhet 1970; Hogg and Meads 1975; Metsik *et al.* 1982; Chandra and Lokanathan 1982, 1988; Litsarev *et al.* 1992):

(1) Escape of nonstructural water at low temperatures (generally below about 150–200°C, although some nonstructural water can be retained until higher temperatures)

(2) Oxidation of Fe^{2+} to Fe^{3+} in different crystallographic sites, loss of H_2 (deprotonation), and formation of oxymicas above ~200°C. This stage occurs for biotite and Fe-bearing phlogopite heated in air, but does not occur when these minerals are heated in inert gas (N_2, Ar), vacuum, or a reducing atmosphere (in a graphite crucible).

(3) Loss of structural hydroxyl (dehydroxylation) at temperatures above about 500°C. This stage may overlap stage (2) to some extent. A dehydroxylated phlogopite, which preserves the original phlogopite structure to some extent (e.g., a similar XRD pattern but with smaller interlayer distance) is produced, and can be rehydroxylated to phlogopite.

(4) Structural breakdown of the dehydroxylated phlogopite at high temperatures: 1060–1160°C (Chandra and Lokanathan 1988); 1080°C (Vedder and Wilkins 1969); 1030–1265°C (Litsarev *et al.* 1992). The XRD pattern of

dehydroxylated phlogopite disappears and amorphous material is produced during the structural breakdown.

(5) Growth of new crystalline phases. This occurs in the same temperature range as structural breakdown. Phlogopite decomposition in hydrothermal bombs at 900–1010°C and 100–400 bars yields kalsilite, forsterite, leucite, and water (Yoder and Eugster 1954; Wones 1967). Chandra and Lokanathan (1982, 1988) used Mössbauer spectroscopy to study biotite and Fe-bearing phlogopite decomposition. They reported that micas decomposed to hematite and/or Fe-bearing spinels. Litsarev *et al.* (1992) reported leucite and forsterite from decomposition of OH–phlogopite.

Less work has been done on amphibole dehydration kinetics and mechanisms, with the focus on crocidolite (fibrous riebeckite) and amosite (fibrous grunerite) because of their economic importance (Hodgson *et al.* 1965; Freeman 1966; Clark and Freeman 1967; Ghose 1981).

Crocidolite breakdown occurs via four stages with increasing temperature, analogous to mica decomposition: (1) escape of nonstructural water at 50–400°C, (2) exothermic evolution of H_2 and oxidation of most Fe^{2+} to Fe^{3+}, probably via proton and electron migration, and formation of an oxyamphibole at 300–450°C, (3) endothermic dehydroxylation to an anhydrous amphibole with a crystal structure similar to the starting material at 500–700°C, and (4) structural breakdown of the dehydroxylated crocidolite to acmite, cristobalite, a spinel, and liquid at about 800°C (heating in N_2, Ar) or to acmite, hematite, cristobalite, and a spinel at about 600–950°C (heating in O_2, air). The second step, H_2 evolution and Fe^{2+} oxidation, occurs during heating in O_2 and air, but not during heating in N_2 or Ar. Also, the dehydroxylation step overlaps Fe^{2+} oxidation during heating in O_2 or air. *In vacuo*, crocidolite dehydroxylation occurs at 550–700°C with an activation energy of about 205 kJ mol^{-1} and is diffusion controlled by radial diffusion (of water through the product layer?) out of a cylinder (Clark and Freeman 1967). However, the kinetics and activation energy of the decomposition of the anhydrous amphibole have not been studied.

In contrast, the work of Hodgson *et al.* (1965) shows that amosite dehydroxylation and decomposition occur concurrently instead of consecutively. Nonstructural water is lost below 500°C and endothermic dehydroxylation starts at 500°C during static heating in N_2 or Ar. Decomposition to pyroxene and other phases occurs in the same temperature range. At about 1000°C the anhydrous amphibole decomposes to olivine and cristobalite and then melts (1100°C). During static heating in O_2 or air, nonstructural water is again lost below 500°C and at 350–1200°C overlapping oxidation–dehydrogenation, dehydroxylation, and decomposition reactions occur. An oxyamphibole is the main product formed in the 350–800°C range. A spinel, hema-

tite, a pyroxene, and amorphous material are the main decomposition products at 800–1100°C. Tremolite decomposition is apparently similar to amosite decomposition, but less work has been done on this (Freeman and Taylor 1960; Freeman 1966). Some work has been done on decomposition of anthophyllite and alkali amphiboles, but more studies are needed for amphiboles of interest on Venus.

The mica and amphibole dehydration studies have several important implications for Venus. First, high Mg/Fe and high F/OH ratios in phlogopites (Chandra and Lokanathan 1988; Litsarev *et al.* 1992) and high Mg/Fe ratios in amphiboles (Freeman 1966) lead to greater thermal stability. This is in agreement with petrologic phase equilibria summarized by Hewitt and Wones (1984) and Gilbert *et al.* (1982), with our thermodynamic calculations, and with calculations by Fegley and Treiman (1992). Second, the data show that phlogopite has a higher thermal stability than muscovite (Vedder and Wilkins 1969). These results also agree with our thermodynamic calculations. Third, the experiments suggest that dehydroxylated micas and amphiboles and for Fe-bearing minerals, oxymicas and oxyamphiboles, could be formed on Venus's surface (as metastable phases) instead of the thermodynamically predicted decomposition products. The (metastable) dehydroxylated minerals and oxy minerals may persist for some period of time. However, experimental work needs to be done on mica and amphibole decomposition in CO_2 and CO_2 gas mixtures relevant to Venus. Last, the experiments show that dehydroxylated micas can easily be rehydroxylated to yield the original micas (Vedder and Wilkins 1969; Rouxhet 1970).

Work needs to be done on rehydroxylation of dehydroxylated amphiboles such as hornblendes, alkali amphiboles, and tremolite to assess the importance of these fossil weathering products. Dehydroxylated micas (and possibly dehydroxylated amphiboles) on Venus's surface may be transformed back into OH-bearing phases during cooler, wetter periods on Venus or possibly after large injections of water vapor from volcanism or impacts. Alternatively, as suggested by a referee, massive injections of water vapor may lead to higher temperatures, due to the greenhouse effect of water vapor, and decrease hydrous mineral stability. Detailed theoretical modeling is necessary to clarify the effect of large water vapor injections from volcanism or impacts on hydrous mineral stability.

Detection of hydrous silicates on Venus. The detection of hydrous minerals, or the metastable dehydroxylated and oxy intermediates, or OH-bearing nominally anhydrous minerals on Venus would be very important. Thus we briefly assess spacecraft experiments that could be used on lander, penetrator, probe, or automated balloon missions for the detection of hydrous silicates on Venus. These experiments fall into two categories: (1) detection and mea-

surement of hydrogen, hydroxyl, and water, and (2) mineralogical analyses. We consider them in turn below.

In situ neutron spectroscopy for detecting hydrogen on Mars has been extensively discussed and neutron spectrometers were included in the aborted Phobos and Mars 96 missions. However, the hydrogen content of the venusian surface is almost certainly below detection limits for this method. Thermogravimetric and/or differential thermal analysis (TGA/DTA) could be used for detection of bound volatiles such as H_2O and OH, CO_2 (as carbonate), SO_2 (as sulfate), and S_2 (as sulfide) in surface materials on Venus. However, the samples should be heated at least to 1200°C for detecting water from the micas and alkaline amphiboles proposed to be present on Venus. The evolved gases could be analyzed by gas chromatography or mass spectroscopy, since one of these instruments would probably be included on the spacecraft for chemical analyses of atmospheric gases. A TGA/DTA evolved gas analyzer would be useful for detecting hydrous minerals, carbonates, sulfates, and sulfides. On the other hand, this type of experiment is not optimal for identifying volatile-free minerals or for constraining the oxidation state of rocks.

Instead, experiments in the second category, mineralogical analyses, are preferable. X-ray diffraction (XRD) could be used to identify both volatile-free and volatile-bearing minerals. Development of a spacecraft X-ray diffractometer involves significant (but not insurmountable) challenges including sample acquisition and preparation, and development of low mass, low power X-ray sources (e.g., Blake *et al.* 1997). In addition, it is difficult to distinguish between the hydroxylated, dehydroxylated, and oxy forms of phlogopitic micas and fibrous alkali amphiboles because the X-ray patterns are similar. However, an internal calibration should remove this problem. In the laboratory this is done by adding Si powder to samples, although a different method possibly could be used in the spacecraft experiment. We refer the reader to descriptions of a prototype XRD/XRF spacecraft instrument (Blake *et al.* 1994, 1997).

Mineral spectroscopy in the gamma ray (Mössbauer spectroscopy), UV, visible, and IR regions is also very useful. Mössbauer (MB) spectroscopy can identify Fe-bearing minerals and provide much information on Fe^{2+}/Fe^{3+} ratios and site occupancies (Klingelhöfer *et al.* 1995). UV and visible spectroscopy give information on the oxidation state and crystal sites of metal ions (e.g., Fe^{2+}, Fe^{3+}) in minerals and can identify Fe-bearing minerals (anhydrous and hydrous) (Rossman 1988a). But neither MB nor UV-visible spectroscopy directly measure OH or water in minerals, although both spectroscopic methods are very useful in several respects.

Infrared reflectance spectroscopy seems to be the best method for *in situ* detection of OH-bearing minerals. Infrared reflectance spectroscopy can be used to distinguish between physically absorbed water, water in fluid inclu-

sions, and chemically bound water in minerals, to identify micas and amphiboles, estimate their chemical composition, and determine the ordering state of the minerals (Rossman 1984, 1988b). In addition, transmission infrared spectroscopy can be used to measure the OH and water content of minerals (e.g., Bell and Rossman 1992). Fundamental OH absorption bands occur in the 2.6–3.0 μm region and measurements with high spectral resolution in this region are probably the best way to detect hydrous minerals on Venus' surface. Amphiboles and micas have characteristic OH bands at 2.7–2.8 μm (Rossman 1984, 1988b; Hawthorne 1981; Salisbury *et al.* 1991), with slightly different band positions and shapes giving information on the mineral and the cations bound to the OH groups. Much work, including systematic studies of IR absorptions of the predicted micas and amphiboles as a function of particle size, Mg/Fe, and F/OH content needs to be done to develop imaging IR spectroscopy experiments for future space missions. The interference from thermal radiation on Venus also needs to be minimized or subtracted from the data.

Although each technique has its own advantages, a combination of infrared reflectance spectroscopy, imaging, and XRD–XRF analyses is really needed to distinguish between soil and rocks, provide geological context, identify the minerals present, and measure the bulk elemental abundances at one or more sites. With the inclusion of a Mössbauer spectrometer, the Fe-bearing mineralogy and the oxidation state of Venus's surface could also be measured.

Water and hydroxyl in Venus.   Finally we consider how much water may be in bulk silicate Venus (the silicate portion of the planet, denoted BSV), even in the absence of any hydrous minerals. Water and hydroxyl are present in several forms (as dissolved species, as vapor in gas inclusions, in defects, etc.) in minerals and glass in terrestrial rocks and not only as hydrous minerals (Ihinger *et al.* 1995; McMillan 1995).

For example, Bell and Rossman (1992) discuss OH (hydroxyl) in nominally anhydrous minerals in the Earth's mantle. Water or hydroxyl has been detected in many silicate and oxide minerals (e.g., the Al_2SiO_5 polymorphs (kyanite, andalusite, and sillimanite), feldspars, garnets, olivine, ortho- and clinopyroxenes, quartz, rutile, scapolite, titanite, and zircon). Hydroxyl contents determined by IR spectroscopy of nominally anhydrous minerals in mantle xenoliths range from a few to ~140 μg H_2O/g rock in olivine, about 50–200 μg H_2O/g rock in orthopyroxene (with one sample at 460 μg/g), about 150–1080 μg H_2O/g rock in clinopyroxene, and <5 to about 51 μg H_2O/g rock in garnet (Bell and Rossman 1992). The ubiquitous presence of OH and water in "anhydrous" minerals from terrestrial mantle xenoliths leads us to expect water and hy-

droxyl in bulk silicate Venus, even without any hydrous minerals being present.

Even though BSV plausibly contains only 1% of the amount of water in the bulk silicate Earth (Table VII), this amount of water is still substantial when compared to the atmospheric water inventory. For example, Namiki (1995) estimated <15 μg H_2O/g rock in Venus's mantle and noted that this upper limit falls within the 5–35 μg H_2O/g rock left in residual peridotite after basalt extraction. Namiki's upper limit (15 μg/g) corresponds to about 7,500 times more water than in Venus's atmosphere, while the lower value (5 μg/g) for water in residual peridotite is still 2,500 times larger than the atmospheric water inventory.

Venus's interior is probably the largest reservoir of water on the planet and has probably played an important role in the outgassing of water on Venus over geologic time and in the climatic evolution of Venus. However, it is unlikely that all of the water currently in Venus's interior can exchange with the atmosphere on a short timescale (or at all). It is more plausible that only a smaller fraction of the total water inside Venus can degas or can exchange with the atmosphere. For example, on Earth, the degassed mantle may be 50% by mass of the entire mantle (Jambon 1995). However it is very difficult to constrain the fraction of Venus' interior that may have degassed (e.g., Namiki 1995). Instead of doing this we have calculated the amount of water-bearing rock needed to balance the atmospheric water inventory. Figure 4 shows our results as a function of the water content and density of the rock. If the surface and "crust" of Venus are relatively water-rich, containing as much water as in terrestrial mid-ocean ridge basalt (MORB) glasses, then a few meters to few tens of meters of rock contain as much water as Venus's atmosphere. If the surface and "crust" of Venus are relatively water-poor, containing only as much water as in residual peridotite, then several hundred meters to a kilometer of rock is needed to match the atmospheric water inventory. Based on the observed abundances of water and hydroxyl in "anhydrous" minerals in Earth's mantle (Bell and Rossman 1992), we conclude that the latter case is certainly reasonable. The former case also cannot be ruled out, depending on whether or not any hydrous minerals are stable on Venus's surface.

SUMMARY

Table VIII summarizes our thermodynamic evaluations of pure hydrous mineral stability on Venus. Because of the high surface temperature and low water vapor content of the atmosphere, most of the hydrous silicates we considered are thermodynamically unstable and can dehydrate to water vapor and anhydrous minerals. In addition, Fe^{2+}-bearing hydrous silicates are susceptible to oxidation to
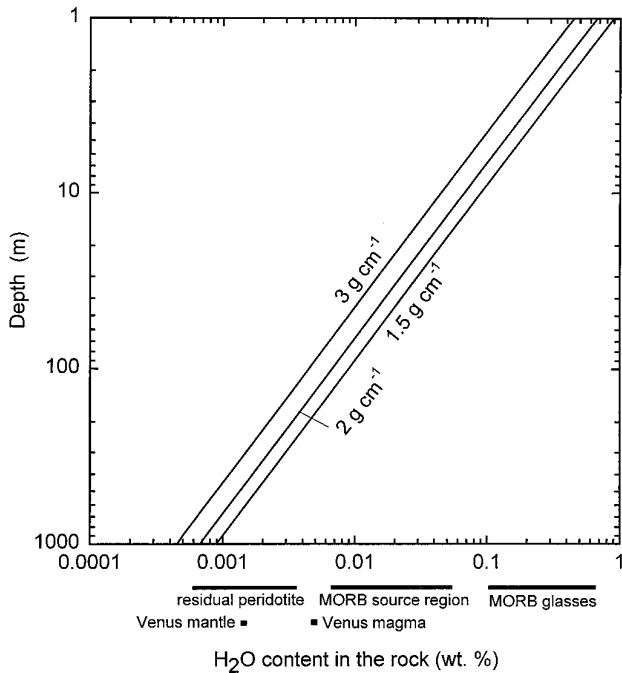
FIG. 4. The amount of rock (in meters depth) needed to balance the amount of water in Venus' atmosphere (6×10^{15} kg) as a function of rock density and water content. The water contents of terrestrial MORB glasses, the MORB source region, residual peridotite, and the estimated water contents of Venusian magmas (Grinspoon 1993) and the Venusian mantle (Namiki 1995) are also shown. For reference, the Venera 13 and 14 landers measured rock densities of 1.15–1.5 g cm^{-3} (Zolotov and Volkov 1992).

hematite and/or magnetite because Venus's atmosphere, while extremely reducing ($f_{O_2} \sim 10^{-21}$ bars at 740 K), is still too oxidizing for Fe^{2+}-hydrous silicates to be stable. Likewise, Ca-bearing hydrous silicates are unstable due to sulfatization to form anhydrite. On the other hand, several Ca- and Fe^{2+}-free alkali amphiboles and micas may be stable, particularly in the cooler highlands. However, magnesioriebeckite and eastonite cannot be stable in the same locality because magnesioriebeckite requires a low Al chemical potential while eastonite requires a high Al chemical potential. The two minerals may be stable in different locations with different Al contents.

Experimental phase equilibria, geologic occurrences, our calculations, and calculations by Zolotov *et al.* (1997) show that substitution of Mg^{2+} for Fe^{2+}, of Al^{3+} for (Mg^{2+}, Si^{4+}), Fe^{3+} for Al^{3+}, and of F^- for OH^- in micas and amphiboles generally increases the thermal stabilities of these types of minerals. Therefore, it is reasonable to expect that Mg^{2+}-, Al^{3+}-, Fe^{3+}-, and F-enriched solid solutions of phlogopitic micas and alkali amphiboles may exist on Venus. However, detailed predictions are difficult to make because in most cases some of the necessary thermodynamic data are lacking.

At present, formation of hydrous minerals on Venus's surface is probably kinetically hindered because of slow cation solid state diffusion rates. Formation of hydrous minerals in the interior of Venus appears more favorable than formation on the surface, but is probably much less favorable than hydrous mineral formation in Earth's crust and mantle because of the deficiency of water on Venus. If, as suggested by some authors, there is a deficiency of silica, an oxidized crust, and an enrichment of alkali elements in Venus' lithosphere, the formation and preservation of alkali amphiboles and eastonite–phlogopite micas would be more favorable than formation of other hydrous minerals. On Earth, phlogopitic micas and alkali amphiboles are important hydrous minerals in the mantle.

Laboratory studies of the dehydration of phlogopite, biotite, and muscovite micas and fibrous amphiboles show that dehydration proceeds in several stages. After the loss of nonstructural (e.g., adsorbed) water, metastable dehydroxylated anhydrides are produced. The anhydrides then decompose to more stable minerals at temperatures hundreds of degrees above the onset of dehydroxylation (e.g., above about 1000°C for phlogopite). Iron-bearing micas and amphiboles heated in oxidizing atmospheres also lose

TABLE VIII
Summary of Thermodynamic Stability of Hydrous Silicates on the Surface of Venus

Mineral group	Definitely Unstable			Can be stable
	simple breakdown dehydration	oxidation	sulfatization	
Micas	mu	mi	mrg	east
	cel	fcel		phl (?)
	prgn	sdph		phlogopite
	sphl	ann		solid solutions
Amphiboles	ant	fhb	fhb	mrbc
	cum	ftr	ftr	
	gl	fgl	hb	alkali
		rbc	tr	amphibole
		fant	prgs	solid
		gr	ed	solutions
Others	prph	fchl	ilv	
	htpz	fcar	bcc	
	mchl	ftst	prh	
	mcar	fame	zo	
	tsta	st	czo	
	ta	de	ep	
	mst		rsnh	
	am			
	clnc			

H_2 and form oxymicas and oxyamphiboles. The laboratory studies suggest that metastable anhydrides and oxy-phases may be formed during dehydration of hydrous silicates on Venus. These anhydrous phases may exist for some time on the surface and may be rehydroxylated when the atmospheric water vapor content increases (e.g., as a result of intense volcanism or after impacts of cometary or CI chondritic material). Later, the rehydroxylated phases may transform back to the anhydrides as atmospheric water vapor decreases. The anhydrides, hydrous phases, and oxy-phases may also react with atmospheric HF to form F-enriched micas and amphiboles. Experimental studies are needed to investigate these possible reactions, the thermodynamic properties of the anhydrides and oxy-phases, the reaction rates, and the best methods for distinguishing anhydrides and oxy-phases from their parent hydroxylated micas and amphiboles.

Finally, IR spectroscopy shows that many "anhydrous" minerals contain OH and water and that concentrations of hundreds of micrograms H_2O/gram rock are found in pyroxenes and some other minerals (Bell and Rossman 1992) that are also expected to be present on Venus's surface and in its lithosphere (Fegley and Treiman 1992; Zolotov and Volkov 1992). Thus, it is important to include experiments designed to detect hydrous minerals, as well as hydroxyl and water in "anhydrous" minerals on future spacecraft missions to Venus.

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