Stability of micas on the surface of Venus

M. Yu. Zolotov[a,b], B. Fegley Jr.[a,*], K. Lodders[a]

[a] *Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Washington University, One Brookings Drive, St Louis, Missouri 63130-4899, U.S.A.*
[b] *Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin Str. 19, Moscow 1178975, Russia*

Abstract

Recent thermodynamic modeling shows that some micas might be stable on Venus' surface. However, prior studies considered only pure micas and did not consider mica solid solutions, which are commonly observed on Earth. Here we use chemical equilibrium calculations to evaluate the stability of mica solid solutions on Venus' surface as a function of atmospheric chemistry (H_2O and HF abundances, and redox state), and surface elevation. Our prior calculations show that the end-member micas eastonite ($KMg_2Al_3Si_2O_{10}(OH)_2$) and fluorphlogopite ($KMg_3AlSi_3O_{10}F_2$) are stable on Venus' surface, while the end-member micas phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$), annite ($KFe_3AlSi_3O_{10}(OH)_2$), and siderophyllite ($KFe_2^{2+}Al_3Si_2O_{10}(OH)_2$) are unstable. Based on these results and known petrologic phase relationships, we consider binary solutions of eastonite with either phlogopite or siderophyllite, and fluorphlogopite with phlogopite. We calculate that micas along all three binaries are stable on Venus. Micas containing ~ 20 mole% eastonite and $\sim 80\%$ phlogopite are stable in the lower temperature highlands, and very eastonite-rich micas are stable over Venus' entire surface. Fluorphlogopite-rich micas are also stable over Venus' surface, while fluorphlogopite-poor micas are stable at higher elevations. Iron-poor micas along the eastonite-siderophyllite join, containing > 80 mole% eastonite, are stable in both the highlands and lowlands. Finally, we use the thermodynamic calculations, terrestrial geology, and petrologic phase equilibria to discuss plausible geological settings where micas may be present on Venus. These suggestions are important for the design of geochemical experiments on future lander and automated balloon missions to Venus. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

At present, liquid water is unstable on Venus' surface because of the high surface temperature (740 K at the modal radius), and the sub-cloud atmosphere is extremely dry, containing only 30–45 parts per million by volume (ppmv) water vapor (Donahue, 1995; Donahue and Hodges, 1993; Drossart et al., 1993; Pollack et al., 1993; DeBergh et al., 1995; Meadows and Crisp, 1996; Ignatiev et al., 1997). Under these severe environmental conditions, the only possible reservoirs of water on Venus are thermally stable hydrous minerals, such as some micas and amphiboles and hydroxyl (OH) in nominally anhydrous minerals (e.g., see Zolotov et al., 1997).

The realization that only a restricted suite of hydrous minerals could possibly exist on Venus' surface dates back to Wildt (1942), although thermodynamic modeling of hydrous mineral stability was only possible after the first spectroscopic measurements of the water vapor abundance in Venus' atmosphere were made in the early

1960s (Bottema et al., 1964). Assuming that the measured water contents were representative of those at Venus' surface, Mueller (1964) suggested that micas and amphiboles, in particular phlogopite ($KMg_3AlSi_3O_{10}(OH)_2$), had the requisite thermal stability to be present on Venus.

However, detailed calculations of hydrous mineral stability were not done until Lewis' seminal work in the late 1960s and early 1970s (Lewis, 1968; 1970). Lewis considered buffering of the atmospheric water partial pressure by reactions involving micas and amphiboles such as tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and phlogopite. He originally concluded that phlogopite and muscovite ($KAl_3Si_3O_{10}(OH)_2$) were stable on Venus (Lewis, 1968), but later concluded (from revised thermodynamic data, and new compositional measurements and thermal profiles of Venus' atmosphere) that these two micas were unstable, and that only tremolite was stable on Venus (Lewis, 1970; Lewis and Kreimendahl, 1980; Nozette and Lewis, 1982).

In the last 1970s, similar thermodynamic modeling of Venusian atmospheric chemistry (e.g., Florensky et al., 1978) and geochemistry (e.g., Khodakovsky et al., 1979a,b) was undertaken by a group at the Vernadsky

* Corresponding author. Tel.: 001 314 935 4852; fax: 001 314 935 4853; e-mail: bfegley@levee.wustl.edu

Institute in Russia to interpret results from the Venera missions to Venus. Khodakovsky et al. (1979a) calculated that a number of hydrous minerals including tremolite, phlogopite, and annite ($KFe_3AlSi_3O_{10}(OH)_2$), an Fe^{2+}-bearing mica, would be stable on Venus' surface. However, later theoretical modeling by this group predicted that no hydrous minerals were stable on Venus (Barsukov et al., 1980; 1982; Khodakovsky et al., 1979b; Volkov et al., 1986). The apparently contradictory predictions about hydrous mineral stability reported by Lewis and colleagues and by the Russian group reflect problems with unreliable and/or unavailable thermodynamic data, and uncertainty about the water vapor content of and vertical profile in Venus' sub-cloud atmosphere (e.g., see Von Zahn et al. (1983) for a discussion of the latter two problems).

More recently Fegley and Treiman (1992) and Zolotov et al. (1997) re-examined the stability of many pure hydrous minerals on Venus' surface. Their calculations were motivated by improved thermodynamic data for hydrous minerals and their decomposition products, recent advances in Earth-based observations of water vapor in Venus' sub-cloud atmosphere, and updated analyses of water vapor measurements from the Pioneer Venus mass spectrometer (Donahue and Hodges, 1993), and the Venera 11, 13, and 14 spectrophotometers (Ignatiev et al., 1997).

Fegley and Treiman (1992) considered 15 pure hydrous minerals and found that none of them were stable on Venus because of the high temperatures and low atmospheric water vapor content. They also suggested that some amphiboles, which have high thermal stability, and fluorine-bearing solid solutions of some amphiboles and micas may be present on Venus. However, the lack of thermodynamic data prevented them from doing calculations. In addition, the surprisingly large differences in thermodynamic properties based on either calorimetric measurements (e.g., $\Delta_f G^o$ values listed by Robie et al. (1979)) or on petrologic phase equilibria (e.g., $\Delta_f G^o$ values given by Helgeson et al. (1978)) allowed both tremolite and phlogopite to be stable within the (large) formal uncertainties in the thermodynamic data.

Subsequently, Zolotov et al. (1997) calculated the stability of about 50 different pure hydrous minerals on Venus. They also considered the effects of oxygen fugacity (fO_2, which can be regarded as the O_2 partial pressure) and the SO_2 partial pressure on the stabilities of Fe^{2+}-bearing and Ca-bearing hydrous minerals, respectively, because these hydrous minerals can be oxidized to Fe oxides or converted to anhydrite ($CaSO_4$) on Venus' surface. Zolotov et al. (1997) found that eastonite ($KMg_2Al_3Si_2O_{10}(OH)_2$), which is a rare mica on Earth, and some alkali amphiboles might be stable on Venus, especially in the lower temperature highlands. The improved thermodynamic data for tremolite and phlogopite (see their Table II) led them to also conclude that

both of these pure minerals are unstable on Venus. Finally, Zolotov et al. (1997) also proposed that some mica and amphibole solid solutions may be stable on Venus.

Here we explore these suggestions and consider the stability of mica solid solutions on Venus. Our choice of micas is guided by the prior calculations of pure mica stability on Venus and by terrestrial geology and petrologic phase equilibria. We first review some basic facts about mica mineralogy and then describe our thermodynamic modeling and its results. Then we consider plausible geologic settings where micas may be present on Venus.

2. Mineralogy of micas

Micas are hydrous sheet silicates, and are common rock-forming minerals in terrestrial metamorphic and igneous rocks (Deer et al., 1992). Micas are important reservoirs of bound water (in the form of OH) in the terrestrial lithosphere and upper mantle. Their general formula is $XY_{2-3}Z_4O_{10}(OH,F)_2$ where X is usually K or Na; Y is generally Mg, Fe^{2+} or Al; and Z is usually Si or Al. The linked $(Si,Al)O_4$ tetrahedra form two-layer sheets. Magnesium, Fe^{2+}, and Al^{3+} cations are sandwiched between the layers in octahedral sites. The most common micas are muscovite, biotite, and phlogopite. Here we consider only trioctahedral micas (i.e., biotites and phlogopites), because the other micas (e.g., muscovite, paragonite, margarite) are unstable on the surface of Venus (Fegley and Treiman, 1992; Zolotov et al., 1997.

The compositions of biotite (Fe-rich) and phlogopite (Fe-poor) micas are schematically shown in Fig. 1, where the shaded region and heavy lines indicate the range of commonly observed mica compositions on Earth. The substitution of Fe^{2+} for Mg^{2+} along the phlogopite-annite binary is limited at the high iron end. In the phlogopite-eastonite and annite-siderophyllite binaries, Al^{3+} substitution for Mg^{2+} and Fe^{2+} in octahedral sites is balanced by the corresponding substitution of Al^{3+} for Si^{4+} in tetrahedral sites. Phase equilibrium experiments indicate limited Al substitution along the phlogopite-eastonite join, and Hewitt and Wones (1975), Robert (1976), and Circone et al. (1991) report that the maximum eastonite content in phlogopite-eastonite micas are 62 mole%, 50%, or 38%, respectively. Natural phlogopites usually contain less than 30–50 mole% eastonite (Guidotti, 1984; Livi and Veblen, 1987). The limited substitution might be caused by subsolidus immiscibility of phlogopite-eastonite micas (Circone and Navrotsky, 1992). Micas along the eastonite-siderophyllite join are rarely observed on Earth. Fluorine substitutes for OH in all micas, but the amount of F is generally higher in Mg-rich micas. Complete F-OH substitution is observed between fluorphlogopite and phlogopite.
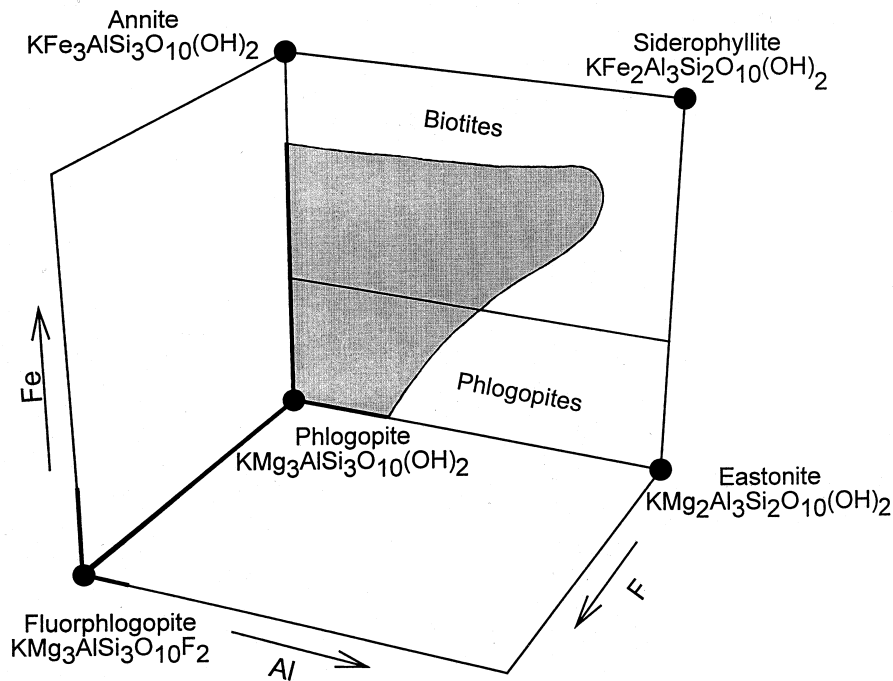
Fig. 1. A schematic diagram showing the end member micas in our calculations, the Al, F, and Fe substitutions involved, and the composition of commonly observed phlogopite and biotite micas on Earth. Modified from Deer et al. (1992).

Biotite and phlogopite generally display random distributions of Fe^{2+} and Mg^{2+} in the octahedral sites. Most samples also have random distributions of Si^{4+} and Al^{3+} in tetrahedral sites, although partially Al-Si ordered micas are also known (Bailey, 1984). Aluminium-Si ordering affects the thermodynamic properties and stability of micas (see Appendix A). Most of our calculations were done for disordered micas because these are commonly observed on Earth.

The various substitutions that occur in micas have important consequences for their thermodynamic stability. For example, substitution of Mg^{2+} for Fe^{2+}, the coupled substitution of Al^3 for Mg^{2+}, Fe^{2+}, and Si^{4+}, and F^- substitution for OH^- increase the thermal stability of phlogopites and biotites up to the limits of the substitutions (e.g., Hewitt and Wones, 1984; Munoz, 1984; Circone and Navrotsky, 1992). In particular, fluorphlogopite has high thermal stability in comparison with other micas. Hammouda et al. (1995) report that the one atmosphere melting point of synthetic fluorphlogopite is 1390–1410°C. In contrast, phlogopite heated at one atmosphere begins to lose structural hydroxyl groups (i.e., dehydroxylate) above about 500°C and the dehydroxylated phlogopite decomposes at 1060–1160°C (Chandra and Lokanathan, 1988; Vedder and Wilkins, 1969). These considerations and prior calculations showing that pure eastonite and fluorphlogopite are stable on Venus (Fegley and Treiman, 1992; Zolotov et al., 1997) suggest that Al- and F-enriched phlogopites should be more stable on Venus that pure phlogopite.

In the next section we calculate how these substitutions influence mica stability on Venus. We focus on three binaries: phlogopite-eastonite, eastonite-siderophyllite, and phlogopite-fluorphlogopite (see Fig. 1), because micas containing eastonite and fluorphlogopite are plausibly stable on Venus. However, we do not consider phlogopite-annite or annite-siderophyllite solutions because these three micas are all very unstable on Venus (Fegley and Treiman, 1992; Zolotov et al., 1997), and hence their solid solutions will also be unstable.

3. Atmospheric structure and composition model

We use the temperature-pressure-elevation profile from the Venus International Reference Atmosphere (VIRA) model (Seiff et al., 1986). The zero level in the VIRA model corresponds to a planetary radius of 6052.0 km, which is ∼0.6 km above the modal radius of 6051.4 km (Ford and Pettengill, 1992).

We use 30 ppmv as the nominal water vapor mixing ratio in Venus' deep atmosphere with an uncertainty range of 15–70 ppmv based on the water vapor contents measured by the Pioneer Venus large probe mass spectrometer (Donahue and Hodges, 1993), by Earth-based and Galileo spacecraft IR spectroscopy (Drossart et al., 1993; Pollack et al., 1993; DeBergh et al., 1995; Meadows and Crisp, 1996), and by the Venera 11, 13, and 14 spectrophotometers (Ignatiev et al., 1997). The corresponding partial pressure of atmospheric H_2O is 2.9×10^{-3} ($10^{-2.54}$)

bars at the modal radius (740 K, 95.6 bars total pressure) and 1.44×10^{-3} ($10^{-2.84}$) bars at the top of Maxwell Montes (660 K, 48 bars total pressure). We assume 5 parts per billion by volume (ppbv) as a nominal mixing ratio for HF with an uncertainty from 1–10 ppbv based on Earth-based spectroscopic data obtained for altitudes greater than 33 km on Venus (Von Zahn et al., 1983; Bézard et al., 1990; Pollack et al., 1993). Based on our previous study of the atmospheric redox state (Fegley et al., 1997), we take a nominal oxygen fugacity (fO_2) of $10^{-20.8}$ bars with uncertainties ranging from $10^{-20.0}$–$10^{-21.7}$ bars at the modal planetary radius (740 K). The adopted fO_2 values are indistinguishable, within the uncertainties of the thermodynamic data, from the fO_2 at the hematite-magnetite boundary at 740 K (Fegley et al., 1997). At 660 K on top of Maxwell Montes we considered a broader fO_2 range due to uncertainty about the redox conditions in the highlands. This uncertainty arises because gas phase chemical reactions are probably quenched at lower elevations on Venus and thus the oxygen fugacity of the Venusian atmosphere in the highlands is not controlled by thermodynamic equilibrium between different gases (Zolotov, 1996; Fegley et al., 1997). We take the lower limit for fO_2 at $10^{-24.7}$ bars at 660 K, which corresponds to the thermochemical equilibrium in the C–O–S–H system (Zolotov, 1996; Fegley et al., 1997). However, redox conditions in the highlands could be even more oxidized than in the lowlands: $fO_2 \geqslant 10^{-20.8}$ bars (Zolotov, 1996; Fegley et al., 1997).

4. Thermodynamic calculations of mica dehydration on Venus

Iron-free micas (i.e., phlogopite and eastonite) on Venus' surface may lose OH and decompose to anhydrous minerals plus water vapor because of the high surface temperature and low water vapor partial pressure in Venus' atmosphere. Following Zolotov et al. (1997) we refer to this overall process as dehydration, to distinguish it from dehydroxylation, which is the loss of structural OH groups *without* decomposition to the thermodynamically stable products. Dehydroxylation is one step during the overall dehydration process.

The dehydration of Fe-free micas is exemplified by phlogopite decomposition to forsterite (Mg_2SiO_4), kalsilite ($KAlSiO_4$), leucite ($KAlSi_2O_6$), and water vapor via the net reaction (Yoder and Eugster, 1954; Wones, 1967):

$$KMg_3AlSi_3O_{10}(OH)_2 = 1\,1/2Mg_2SiO_4$$
$$+ 1/2KAlSiO_4 + 1/2KAlSi_2O_6 + H_2O(g). \quad (1)$$
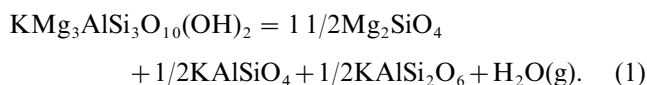
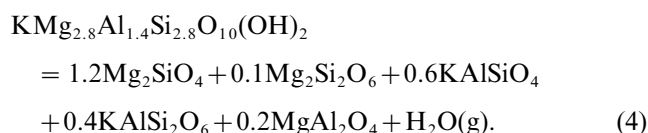Experimental studies (see Yoder and Eugster, 1954; Circone and Navrotsky, 1992) showing that decomposition of aluminous phlogopite also produces spinel ($MgAl_2O_4$), led Zolotov et al. (1997) to model eastonite dehydration to kalsilite, enstatite ($Mg_2Si_2O_6$), and water vapor:

$$KMg_2Al_3Si_2O_{10}(OH)_2 = KAlSiO_4$$
$$+ 1/2Mg_2Si_2O_6 + MgAl_2O_4 + H_2O(g). \quad (2)$$
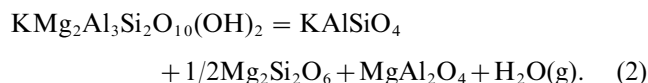
We modeled the dehydration of phlogopite-eastonite (phl-east) micas using the reaction

$$\text{phl-east} = \text{forsterite} + \text{enstatite} + \text{kalsilite}$$
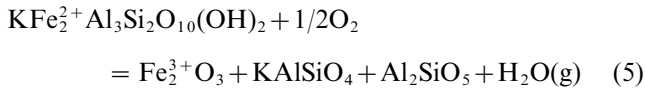$$+ \text{leucite} + \text{spinel} + H_2O(g) \quad (3)$$
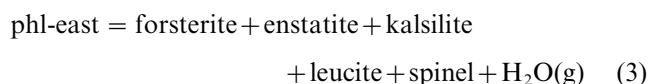
where the formulas for the minerals involved in reaction (3) and subsequent reactions are listed in Table 1. Reaction (3) is the sum of reactions (1) and (2) with the appropriate stoichiometric coefficients depending on the composition of the mica solid solution considered. For example, the dehydration of a mica containing 80 mole% phlogopite and 20% eastonite (phl$_{80}$east$_{20}$) proceeds via the reaction:

$$KMg_{2.8}Al_{1.4}Si_{2.8}O_{10}(OH)_2$$
$$= 1.2Mg_2SiO_4 + 0.1Mg_2Si_2O_6 + 0.6KAlSiO_4$$
$$+ 0.4KAlSi_2O_6 + 0.2MgAl_2O_4 + H_2O(g). \quad (4)$$

Experimental studies of mica phase relations (e.g., Hewitt and Wones, 1984) show that Fe^{2+}-bearing micas are generally less stable than Mg-rich micas and are dehydrated at lower temperatures than Mg-rich micas. In addition, the dehydration of Fe^{2+}-bearing micas also depends on the oxygen fugacity (fO_2). On Venus, dehydration of Fe^{2+} micas (i.e., annite and siderophyllite) should be accompanied by Fe^{2+} oxidation to form magnetite or hematite (Fegley and Treiman, 1992; Zolotov et al., 1997). For example, Zolotov et al. (1997) modeled siderophyllite decomposition to hematite (Fe_2O_3), kalsilite, andalusite (Al_2SiO_5), and H_2O using the net reaction:

Table 1
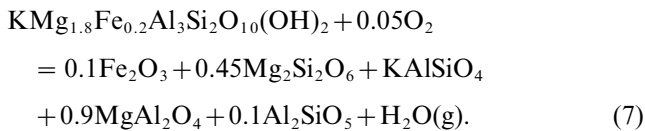Mineral names, formulas, and abbreviations

Abbreviation	Name and ideal formula
and	Andalusite, Al_2SiO_5
ann	Annite, $KFe_3AlSi_3O_{10}(OH)_2$
east	Eastonite, $KMg_2Al_3Si_2O_{10}(OH)_2$
en	Enstatite, $Mg_2Si_2O_6$
fphl	Fluorphlogopite, $KMg_3AlSi_3O_{10}F_2$
fo	Forsterite, Mg_2SiO_4
hem	Hematite, Fe_2O_3
kls	Kalsilite, $KAlSiO_4$
lc	Leucite, $KAlSi_2O_6$
mc	Microcline, $KAlSi_3O_8$
mt	Magnetite, Fe_3O_4
phl	Phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$
sdph	Siderophyllite, $KFe^{2+}_2Al_3Si_2O_{10}(OH)_2$
sp	Spinel, $MgAl_2O_4$

$$KFe_2^{2+}Al_3Si_2O_{10}(OH)_2 + 1/2O_2$$

$$= Fe_2^{3+}O_3 + KAlSiO_4 + Al_2SiO_5 + H_2O(g) \quad (5)$$

which involves both oxidation of Fe^{2+} to Fe^{3+} and dehydration. We modeled decomposition of micas along the eastonite-siderophyllite join using the net reaction

$$east\text{-}sdph + O_2 = enstatite + kalsilite + spinel$$

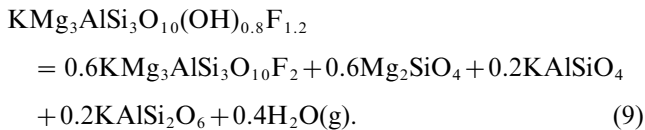$$+ andalusite + hematite + H_2O(g) \quad (6)$$
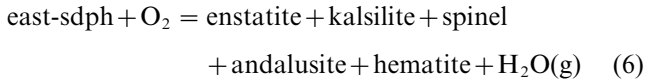
which is the sum of reactions (2) and (5) with the appropriate stoichiometric coefficients for the mica solid solution being considered. For example, the decomposition of a mica containing 90% eastonite and 10% siderophyllite ($east_{90}sdph_{10}$) proceeds via the net reaction

$$KMg_{1.8}Fe_{0.2}Al_3Si_2O_{10}(OH)_2 + 0.05O_2$$

$$= 0.1Fe_2O_3 + 0.45Mg_2Si_2O_6 + KAlSiO_4$$

$$+ 0.9MgAl_2O_4 + 0.1Al_2SiO_5 + H_2O(g). \quad (7)$$

Substitution of F for OH increases the thermal stability of phlogopites (Deer et al., 1963). Experimental studies by Litsarev et al. (1992) show that F–OH phlogopites thermally decompose to humite minerals such as norbergite ($Mg(F,OH)_2Mg_2SiO_4$) when they are heated in air, but thermodynamic data for norbergite and other humite minerals are poorly known, and in some cases unavailable. However, prior calculations show that pure fluorphlogopite is stable on Venus' surface at the observed HF abundance of 1–10 ppbv (Lewis, 1970; Fegley and Treiman, 1992), so the decomposition of phlogopite-fluorphlogopite micas was modeled using the reaction

$$phl\text{-}fphl = fluorphlogopite + forsterite$$

$$+ leucite + kalsilite + H_2O(g) \quad (8)$$
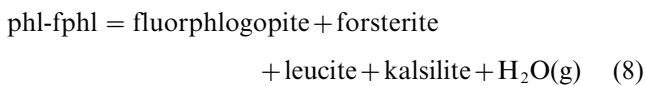
which is based on reaction (1) for phlogopite dehydration. Again, the stoichiometric coefficients in reaction (8) depend on the composition of the mica solid solution, and in the case of a mica containing 40 mole% phlogopite and 60% fluorphlogopite ($phl_{40}fphl_{60}$) the reaction is

$$KMg_3AlSi_3O_{10}(OH)_{0.8}F_{1.2}$$

$$= 0.6KMg_3AlSi_3O_{10}F_2 + 0.6Mg_2SiO_4 + 0.2KAlSiO_4$$

$$+ 0.2KAlSi_2O_6 + 0.4H_2O(g). \quad (9)$$

The stabilities of mica solid solutions were evaluated by comparing the equilibrium water vapor fugacity (f_{H_2O}) for a dehydration reaction to the observed H_2O partial pressure in Venus' atmosphere. The mica is stable if the equilibrium H_2O fugacity is less than or equal to the atmospheric H_2O partial pressure, and is unstable if the equilibrium H_2O fugacity is greater than the atmospheric H_2O partial pressure. At the pressure and temperature conditions in Venus' lower atmosphere, the

partial pressure and fugacity of water vapor are equal because it behaves as an ideal gas (cf Fegley and Treiman, 1992).

The H_2O fugacity in equilibrium with a mica and its dehydration products was calculated from the equilibrium constant for a dehydration reaction. The equilibrium constant, in turn, was calculated from the Gibbs free energy ($\Delta_r G^o$) for the reaction. This procedure is easily illustrated using reaction (1), the dehydration of pure phlogopite, as an example.

The Gibbs free energy for reaction (1) at any temperature is given by:

$$\Delta_r G_1^0 = \Sigma(\Delta_f G^o)_{products} - \Sigma(\Delta_f G^o)_{reactants} \quad (10)$$

where the Gibbs free energies of formation ($\Delta_f G^o$) of phlogopite and its decomposition products were taken from the literature sources listed by Zolotov et al. (1997). The equilibrium constant is

$$K_1 = exp\left[-\Delta_r G_1^o/(RT)\right] = \frac{a_{lc}^{0.5}a_{kls}^{0.5}a_{fo}^{1.5}}{a_{phl}}f_{H_2O} = f_{H_2O} \quad (11)$$

where a_i is the thermodynamic activity of mineral i, f_{H_2O} is the equilibrium fugacity of water vapor, R is the ideal gas constant, and the abbreviations for mineral names are listed in Table 1. Because the activities of pure crystalline solids are unity, the equilibrium constant for reaction (1) is equal to the equilibrium H_2O fugacity. The 2σ uncertainty of the equilibrium H_2O fugacity was then calculated from the tabulated uncertainties in thermodynamic data for phlogopite and its decomposition products as described by Zolotov et al. (1997).

The equilibrium water vapor fugacities for the decomposition of the mica solid solutions (eqns 3, 6, and 8) were calculated in an analogous fashion. The $\Delta_f G^o$ values for the mica solid solutions were calculated from the $\Delta_f G^o$ for the end-member micas using thermodynamic models of the solid solutions. These calculations are described in the Appendix. The Gibbs energies of reaction for equations (3), (6), and (8) were then calculated as a function of the composition of the mica solid solution. The $\Delta_f G^o$ values for water vapor and the product minerals were taken from Robie and Hemingway (1995).

5. Results for pure micas

Before describing the results of our calculations for mica solid solutions, we first briefly review the stabilities of pure micas on Venus' surface (Zolotov et al., 1997). Eastonite is stable over Venus' entire surface because the equilibrium H_2O fugacity for eastonite dehydration is always less than the observed H_2O partial pressure in Venus' atmosphere. However, phlogopite is unstable because the H_2O partial pressure in Venus' atmosphere is lower than the equilibrium H_2O fugacity needed to stabilize phlogopite (see Table A–2). The Fe^{2+}-bearing

micas annite and siderophyllite are unstable because (1) the atmospheric H_2O pressure is much less than the equilibrium H_2O fugacity required for either mica to be stable, and (2) the atmospheric oxygen fugacity is much higher than that needed to prevent oxidation of the micas to either magnetite or hematite. We now present the results of our calculations for stability of mica solid solutions.

6. Results for mica solid solutions

6.1. Phlogopite-eastonite

As shown in Fig. 2, micas along this join do not form complete solid solutions. Instead there is a large range of compositions (inside the asymmetrically shaped curve) between which the solid solution is thermodynamically unstable and the mica separates into two coexisting phases: a phlogopite-rich mica and an eastonite-rich mica. The compositions of the two coexisting phases are those at the left and right side of the curve. For example, at Venus surface temperatures of 660–740 K, the eastonite-rich mica contains > 98 mole% eastonite, while the phlogopite-rich mica contains ∼ 20–24 mole% eastonite.

The eastonite-rich micas are stable over Venus' entire surface, while the phlogopite-rich micas are only stable in the cooler highland regions. The latter point is illustrated in Fig. 3, which shows the H_2O concentration required for phlogopite and phlogopite-rich micas to be stable as a function of elevation (and temperature) on Venus' surface. The composition of the phlogopite-rich micas is also a function of temperature, as can be seen

from Fig. 2, with more eastonite being able to dissolve in phlogopite at higher temperatures.

Figure 3 shows that pure phlogopite is unstable over Venus' entire surface because the concentration of H_2O in Venus' atmosphere is less than that needed to prevent phlogopite decomposition via reaction (1). However, the stability of phlogopite-rich mica is greater than that of pure phlogopite because lower H_2O concentrations are needed to stabilize the solid solution. For example, micas containing ∼ 20 mole% eastonite are stable in the highlands at elevations of ∼ 9 km and above, although within the uncertainties in the thermodynamic properties of the solid solutions, slightly more eastonite-rich micas may also be stable at lower elevations. In any case, the calculations show that Al substitution increases the stability of phlogopite in agreement with the experimental data on Al-enriched phlogopites and biotites (Rutherford, 1973; Hewitt and Wones, 1975; Robert, 1976; Circone and Navrotsky, 1992).

6.2. Eastonite-siderophyllite

Eastonite and siderophyllite apparently form a complete range of solid solutions. Figure 4 illustrates the calculated stability fields for eastonite-rich micas at 740 K on Venus. Micas containing more than about 82 mole% eastonite can be stable, while micas containing less eastonite are unstable at this temperature because the atmospheric H_2O concentration is too low and the oxygen fugacity is too high. Figure 5 illustrates similar calculations for 660 K in the highlands. Micas containing up to 20–25% siderophyllite may be stable at this temperature. However, as discussed earlier, the atmospheric fO_2 in the Venusian highlands is uncertain, and is probably more oxidizing than predicted by complete gas phase thermochemical equilibrium (Zolotov, 1996; Fegley et al., 1997). Oxygen fugacities significantly greater than those shown will lead to oxidation of the siderophyllite component in the solid solution.

6.3. Phlogopite-fluorphlogopite

Figure 6 shows the maximum phlogopite contents of these micas as a function of water content at 740 and 660 K. Depending on the atmospheric water content, micas containing up to ∼ 46% phlogopite may be stable at 740 K, while micas with up to ∼ 80% phlogopite may be stable at 660 K. Figure 7 shows a similar calculation where we took the atmospheric water content at 30 ppmv (our nominal value) and computed the maximum amount of phlogopite that could be dissolved in the solid solution as a function of temperature. About 33–64% phlogopite can be dissolved in fluorphlogopite from 740 − 660 K. The calculated phlogopite contents may be 20% lower or 10% higher depending on the ordering of cations in the different sites in the mica crystal structure. Despite these
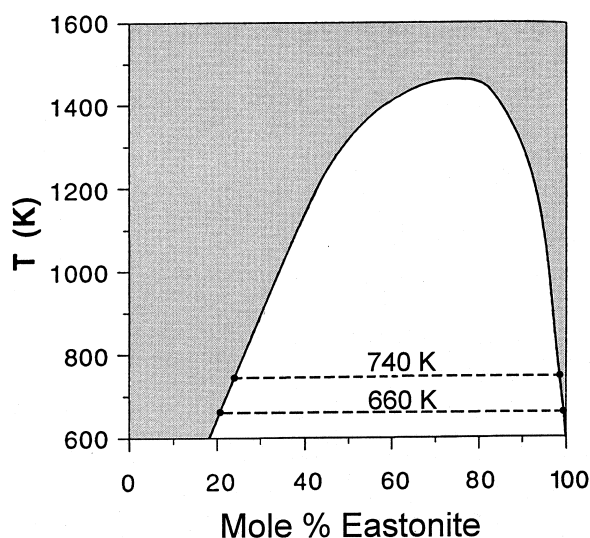

Fig. 2. A phase diagram for phlogopite-eastonite micas showing where the two micas form a complete solid solution (shaded region) or exist as two separate phases. The compositions of the coexisting micas at 660 and 740 K in the two phase region are given by the dots on the curve. Modified from Circone and Navrotsky (1992).
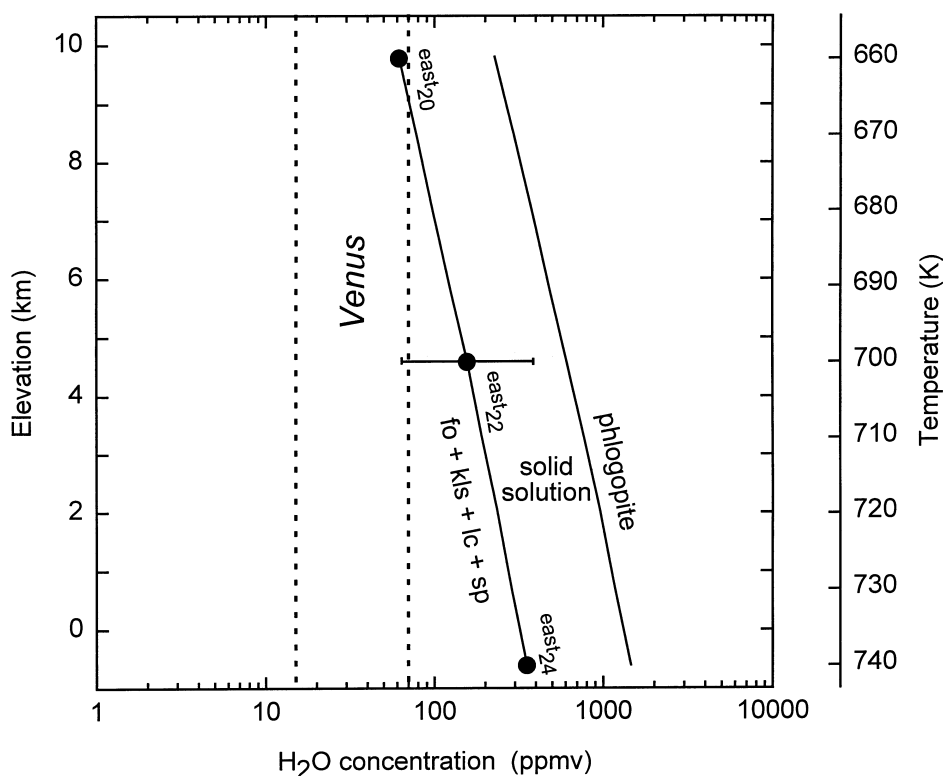
Fig. 3. The stability of phlogopite and phlogopite-eastonite micas on Venus' surface as a function of elevation (i.e., temperature), and concentration of water vapor. The vertical dashed lines show the observed water vapor content (15–70 ppmv) in Venus' sub-cloud atmosphere. Phlogopite is stable on and to the right of the diagonal line labeled phlogopite, while the mica solid solution is stable on and between the two diagonal lines. The black dots show the eastonite content (mole%) in the mica solid solution. The error bar shows the 2σ uncertainty in the calculated equilibrium H_2O pressure needed to stabilize the micas. This uncertainty arises from the uncertainties in the thermodynamic data for phlogopite and eastonite, and for the solid solution.

uncertainties, it seems probable that a significant amount of phlogopite can dissolve in fluorphlogopite on Venus' surface.

7. Discussion

Our results show that some mica compositions along all three binary joins may be stable on Venus' surface. We now use these results, terrestrial geology, and petrologic phase equilibria to discuss plausible geological settings where micas may be present on Venus' surface.

7.1. Formation of phlogopitic micas on Venus

As discussed by Zolotov et al. (1997), formation of micas and other hydrous minerals on Venus' surface is unlikely because of kinetic constraints. For example, formation of pure phlogopite via the reverse of reaction (1):

$$1\ 1/2Mg_2SiO_4 + 1/2KAlSiO_4 + 1/2KAlSi_2O_6$$

$$+ H_2O(g) = KMg_3AlSi_3O_{10}(OH)_2 \quad (12)$$
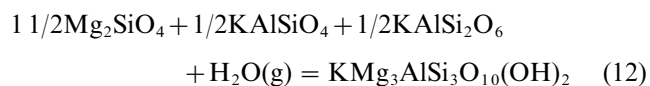
requires the reaction of three different minerals with water vapor to form phlogopite. Ionic diffusion is prob-

ably slow at Venus surface temperatures, especially in the absence of liquid water, so eqn (12) and analogous reactions forming mica solid solutions probably proceed very slowly, if at all, at the relatively low temperatures and pressures on Venus' surface.

Overall, formation of micas in Venus' interior seems more likely that formation of micas on the surface. However, mica formation inside Venus is probably much less favorable than on the Earth due to the dryness of Venus' interior, which plausibly contains two orders of magnitude less water than the terrestrial mantle (see Table VII and associated discussion in Zolotov et al. (1997)). Other factors such as undersaturation of Venusian magmas with water also argue that formation of micas inside Venus will be more difficult and less common than on Earth. On the other hand, crystallization of (initially) water-undersaturated magmas can produce residual melts enriched in water, fluorine, K, and Al. By analogy with Earth, micas may then form during crystallization of these residual, water-saturated melts (e.g., see chapter 12 of Wilson 1989). These qualitative statements point out the need for quantitative theoretical modeling of mica and amphibole stability in Venus' interior and we plan to report such work in the near future.
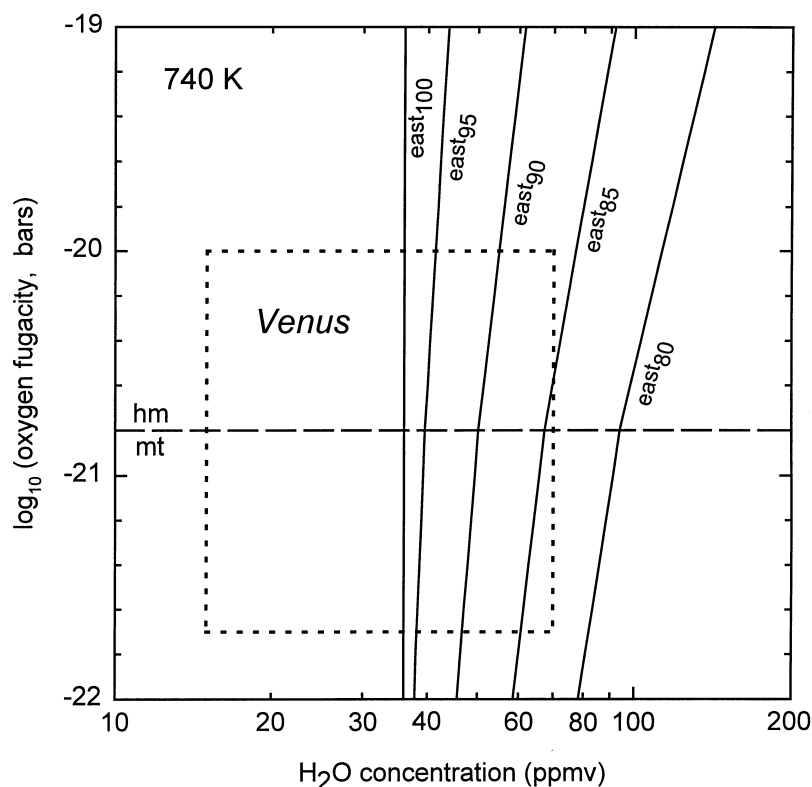
Fig. 4. The stability of eastonite-siderophyllite micas as a function of the oxygen fugacity (fO_2) and water content of Venus' atmosphere at the modal planetary radius where $T = 740$ K and $P = 95.6$ bars. The micas are stable on and to the right of the diagonal lines. The vertical line (east$_{100}$) is the stability line for pure eastonite, which is only a function of the water content and not of the oxygen fugacity (see reaction (2) in the text). The box shows the observed water content (15–70 ppmv) and calculated fO_2 (Fegley et al., 1997) for Venus' atmosphere at 740 K and the horizontal dashed line shows the fO_2 of the magnetite-hematite phase boundary at the same temperature.

Conversely, the proposed deficiency of quartz-bearing rocks on Venus (e.g., Hess and Head, 1990; Kargel et al., 1993) favors the formation of phlogopite because calculations and experiments show that the presence of quartz decreases the melting point of phlogopite and also decreases thermal stability of phlogopite in metamorphic reactions (e.g., Wood, 1976; Wones and Dodge, 1977; Bohlen, 1983; Clemens et al., 1987; Clemens, 1995; Yoder and Kushiro, 1969; Zolotov et al., 1997). The presence of K-rich rocks on Venus is another favorable factor because on Earth phlogopite is a primary mineral in some K-rich rocks such as leucite-bearing igneous rocks (Deer et al., 1963; 1992), and it is also characteristically found in kimberlites (Kushiro et al., 1967; Wilson 1989). Potassium-rich rocks have been found by gamma ray spectroscopy at the Venera 8 landing site and by gamma ray spectroscopy and X-ray fluorescence spectroscopy at the Venera 13 landing site (Vinogradov et al., 1973; Surkov et al., 1984). We return to this point later when discussing geological settings on Venus where micas may occur. For now, we conclude that any micas on Venus probably formed in the interior and were then brought to the surface. We now explore in some more detail the geological factors that influence formation of the different mica solid solutions studied.

7.2. Phlogopite-eastonite micas on Venus

As discussed earlier, thermodynamic modeling shows that phlogopite-rich micas containing $\sim 20\%$ eastonite are stable in the lower temperature highlands regions of Venus and eastonite-rich micas containing $< 2\%$ phlogopite are stable over Venus' entire surface. The formation (magmatic or metamorphic) of these micas in Venus' interior requires an Al-rich environment. The high $(K + Al)/Si$ ratios in alkaline igneous rocks, which are suggested to be present at the Venera 8 and 13 landing sites, and possibly elsewhere on Venus (Kargel et al., 1993), favor Al substitution in phlogopites.

However, at present there are no data that support the existence of an Earth-like, Al-rich continental crust on Venus. This raises the question of whether or not eastonite and eastonite-rich micas are likely to be widespread on Venus because natural occurrences of pure eastonite are very rare on Earth (Livi and Veblen, 1987). Almost pure eastonite should be formed by unmixing of phlogopite-eastonite micas with compositions falling inside the two phase region of Fig. 2. We have not found any descriptions of eastonite formation via this mechanism in the literature. Either natural eastonite-rich micas do not form via unmixing, or very fine lamellae, which can
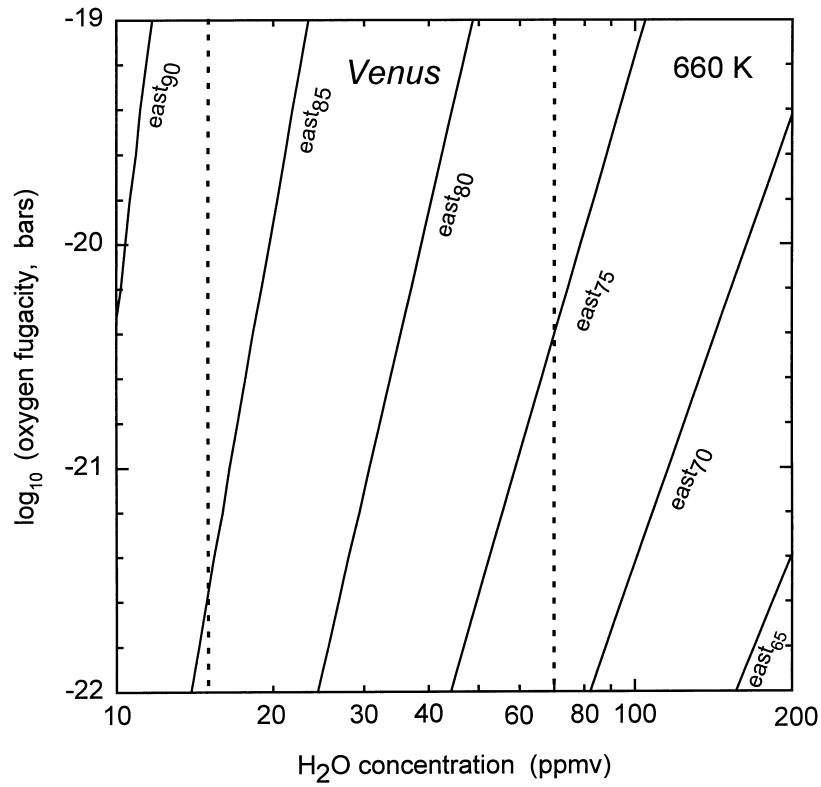
Fig. 5. The same as in Fig. 4, but for the upper part of Maxwell Montes where $T = 660$ K and $P = 48$ bars.
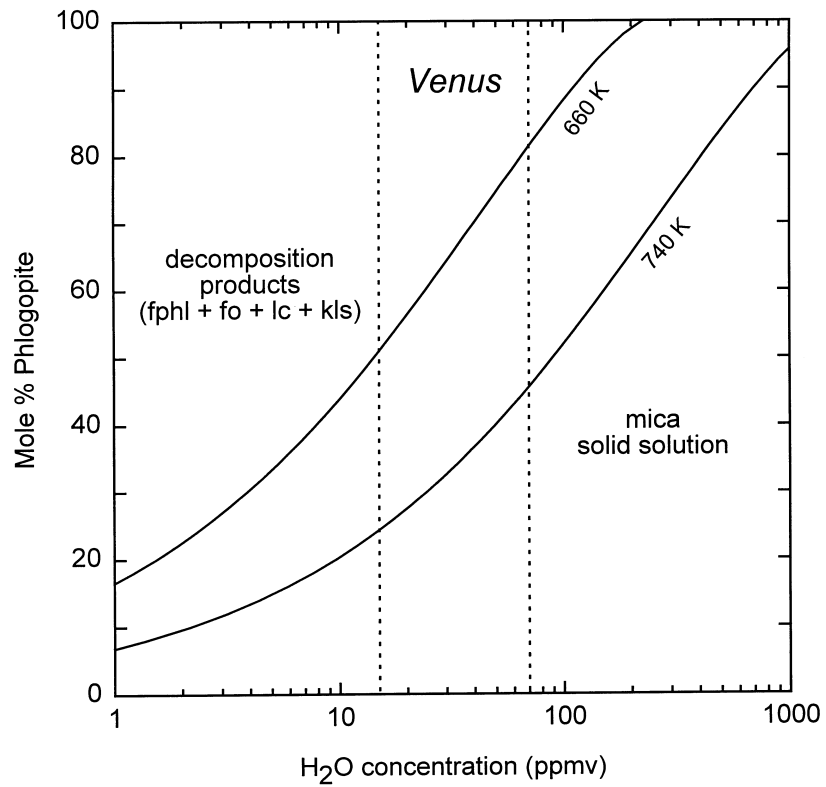

Fig. 6. The stability of phlogopite-fluorphlogopite micas on Venus' surface as a function of composition and atmospheric water content at 740 and 660 K. The micas are stable on and below the two curves. More phlogopite can be dissolved in the micas at lower temperatures.
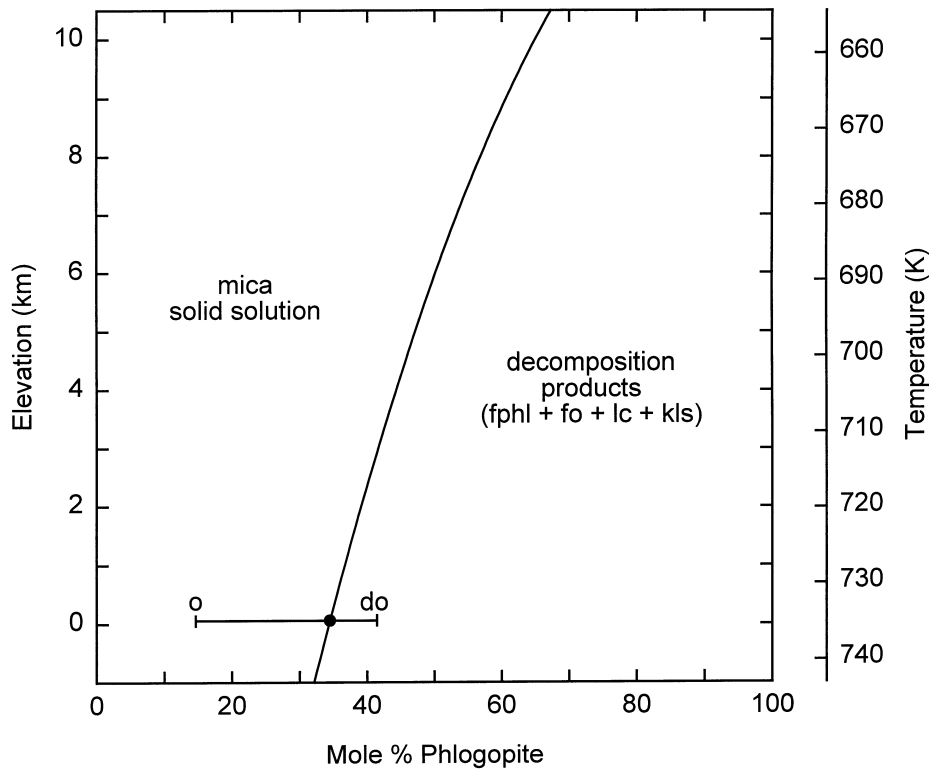
Fig. 7. The composition of phlogopite-fluorphlogopite micas as a function of elevation (i.e., temperature) for 30 ppmv H_2O. The error bar shows the effect of Al, Si ordering on the position of the equilibrium line for ordered (o), and disordered (do) micas. The amount of phlogopite dissolved in the micas increases with increasing elevation (i.e., decreasing temperature), and with increased disordering.

only be seen using transmission electron microscopy, are formed. In any case the available data indicate that pure eastonite and eastonite-rich micas are uncommon on Earth, and probably are also uncommon on Venus. However, Al-substituted phlogopites are more common on Earth (Deer et al., 1963) and are probably present on Venus as well.

7.3. Iron-bearing micas

Experimental studies of mica phase relations show that the substitution of Fe^{2+} for Mg^{2+} decreases phlogopite stability against dehydration along the phlogopite-annite join (Hewitt and Wones, 1984). We found similar behavior in our calculations for eastonite-siderophyllite micas, where increasing siderophyllite (i.e., Fe^{2+}) content destabilized the micas (see Figs 4 and 5). It is difficult to argue for an iron poor environment on Venus because X-ray fluorescence (XRF) spectroscopy shows 9.3, 8.8, and 7.7 mass % FeO at the Venera 13, 14, and Vega 2 landing sites, respectively. (The iron detected by the XRF experiments is reported as FeO, but the oxidation state is actually unknown.) The presence of iron is one of the most important factors (after the dryness and high temperature of Venus' atmosphere and interior) which suppress the formation and stability of phlogopitic micas

on Venus. Thus, the amounts of Fe which are likely to be in micas on Venus is of interest.

The trends observed for Fe/Mg substitution in terrestrial micas provide some guidance. Phlogopites with low Fe/Mg ratios are generally found in alkaline rocks while phlogopites with high Fe/Mg ratios are generally found in acidic (i.e., silica-rich) rocks (e.g., Deer et al., 1992). The total Fe content of a rock also influences the Fe content of the micas. Thus, terrestrial phlogopites from marbles usually contain less Fe^{2+} in comparison with phlogopites from other rocks. The Fe/Mg ratios in biotites generally increase from marbles (metamorphic rocks), to ultramafic (mantle) rocks, to basalts. On Venus we expect a similar trend with the caveat that only Al-enriched phlogopites are stable. As discussed above, we expect Al-enriched phlogopites to be formed in alkaline rocks, which on Earth generally contain micas with low Fe/Mg ratios. Phlogopites with high Fe/Mg ratios are also unstable against dehydration. Thus, we expect phlogopites with low Fe/Mg ratios on Venus, although the exact Fe/Mg ratio is difficult to constrain.

7.4. Phlogopite-fluorphlogopite micas

Lewis (1970) proposed that the HF abundance in Venus' atmosphere is buffered by mineral assemblages

containing fluorphlogopite. Fegley and Treiman (1992) reached the same conclusion and also proposed that solid solutions of phlogopite in fluorphlogopite could be stable on Venus' surface. Figures 6 and 7 show that several percent to several tens of percent phlogopite could indeed be present in F–OH phlogopite on Venus' surface.

On Earth, the F/OH ratio in phlogopites and biotites increases with increasing temperature and grade of metamorphism (e.g., Munoz and Ludington, 1974; Guidotti, 1984). In part this is due to concentration of F in the more thermally stable micas, but this trend also reflects the higher thermal stability of F-micas versus their OH counterparts. The F/OH ratio of terrestrial phlogopites and biotites also increases as the Mg/Fe ratio increases, but apparently F/OH is decreased with increasing Al substitution (Guidotti, 1984). These correlations suggest that the high temperature of Venus' lithosphere and the expected low Fe content of stable micas should allow the formation of F-rich phlogopites.

7.5. Phlogopite Al-Si ordering on Venus

As mentioned earlier and discussed in the Appendix, the ordering state of micas influences their thermodynamic stability with disordered micas being more stable than partially or completely ordered micas. Most of our calculations in this paper are for disordered micas, because on Earth natural phlogopites and other micas generally have a disordered Al-Si distribution (Bailey, 1984; references in Clemens et al., 1987). Furthermore, phlogopite samples synthesized at 400–850°C (Clemens et al., 1987; Circone and Navrotsky, 1991) also show disordered or partially disordered structures.

However, should we expect ordered, partially ordered, or disordered micas on the surface of Venus? In the laboratory, the ordering state of micas can be determined using infrared spectroscopy, X-ray diffraction, and nuclear magnetic resonance spectroscopy of ^{29}Si (Bailey, 1984; Circone and Navrotsky, 1991; Rossman, 1984). On a future lander or automated balloon mission to Venus, infrared reflectance spectroscopy or powder X-ray diffraction could be used to determine whether or not any micas are present (cf Zolotov et al., 1997), and possibly to also constrain the ordering state. Some more details about the detection of hydrous minerals on Venus by spacecraft experiments are given by Zolotov et al. (1997).

7.6. Plausible geological settings for micas on Venus

Where should we expect to find micas on Venus today? As noted earlier, mica formation via chemical weathering may be very difficult on Venus' present surface because of the relatively low temperatures and absence of water. Both of these factors mitigate against rapid ionic diffusion and thus against mica formation reactions such as eqn (12). Thus, we should expect to find micas in bedrock rather than in soils formed by chemical weathering on Venus today.

However, most of the work on mica formation and decomposition has been done in hydrothermal bombs under pressure and temperature conditions far removed from those on Venus' surface. Although we argue that mica formation via gas-solid reactions is very slow on Venus, there are no experimental studies to show whether or not this is actually the case. Furthermore, as discussed by Zolotov et al. (1997), (metastable) dehydroxylated micas may persist on Venus for some time. The dehydroxylated micas may also be stabilized by substitution of F into the vacant OH sites. Thus, it is important for future lander, penetrator, and/or automated balloon missions to determine whether or not micas (and other hydrous silicates) are present in soil, in bedrock, or in both soil and bedrock. But where should these missions look?

On Earth, phlogopites are common in alkaline igneous rocks, ultramafic mantle rocks, and metamorphosed limestones and dolomites (Deer et al., 1963; 1992). The high potassium contents measured at the Venera 8 and Venera 13 landing sites have been interpreted as evidence for leucite-bearing or alkaline igneous rocks at two locations (e.g., Kargel et al., 1993). Taking these interpretations at face value leads us to suggest that micas may be found in these regions, which should be considered as targets for future spacecraft exploration.

Some phlogopite-bearing rocks may also be exposed in the highly tectonically deformed and elevated tessera terrain, which resides on $\sim 8\%$ on Venus' surface (Ivanov and Head, 1996). Tectonic deformations of tessera generally ceased before the formation of surrounding volcanic plains, but the rocks exposed on tessera terrain could be significantly older, and hence might be formed during a (possibly) wetter era of Venus' history. In this regard we note that the D/H ratio measured by the Pioneer Venus large probe mass spectrometer indicates that earlier in its history Venus had at least 0.1% as much water as found in Earth's oceans (Donahue et al., 1982).

The composition of the tessera is unknown. But if we accept the arguments of Nikolaeva et al. (1992) and Sukhanov (1992), tessera could be composed of feldspar-rich (i.e., Al-rich) material, analogous to the terrestrial continental crust. Pure eastonite and very eastonite-rich micas require a high Al chemical potential and should occur in Al-rich terrain. However, eastonite is relatively rare on Earth (see Livi and Veblen, 1987), even though the terrestrial continental crust is Al-rich. On the other hand, micas along the eastonite-phlogopite join are more common on Earth and by analogy are potential hydrous phases in Al-rich regions of Venus' lithosphere.

The tessera may also be the best place to find mica-bearing metamorphosed rocks on Venus because the tessera are not covered by basalt. The elevated, and hence cooler, tessera terrain favors formation of Mg-rich car-

bonates such as magnesite (e.g., Fegley and Treiman, 1992; Zolotov and Volkov, 1992). By analogy with Earth (Deer et al., 1963), phlogopite might be formed by metamorphic reactions such as

$$3MgCO_3 + KAlSi_3O_8 + H_2O(g)$$
$$= KMg_3AlSi_3O_{10}(OH)_2 + 3CO_2(g) \quad (13)$$
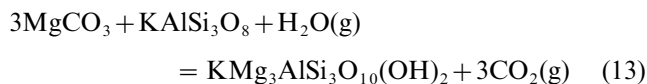
involving magnesite and K-bearing feldspar. However, even if micas are not present in the tessera, this terrain represents an interesting site for future spacecraft exploration, in particular spacecraft equipped with geochemical instrumentation such as imaging infrared reflectance spectrometers, X-ray diffractometers, and X-ray fluorescence spectrometers.

8. Summary

Table 2, which is based on this work and that of Zolotov et al. (1997) for pure micas, summarizes our results. The micas stable in the Venusian lowlands are eastonite, eastonite-rich solid solutions with phlogopite or siderophyllite, fluorphlogopite, and fluorphlogopite-rich solid solutions with phlogopite. Although eastonite and eastonite-rich micas are thermodynamically stable against dehydration, they may be relatively uncommon on Venus because eastonite formation requires a high Al chemical potential (i.e., Al-rich rocks). Even though Earth has an Al-rich continental crust, eastonite and eastonite-rich micas are rarely observed. The fluorphlogopite-rich solid solutions with phlogopite may be more common. The same suite of micas are also stable in the Venusian highlands, although more phlogopite and more siderophyllite can be tolerated in the mica solid solutions at the lower temperatures in the highlands regions. Some micas, such as the Fe^{2+} end-members annite and siderophyllite, and several dioctahedral micas, are unstable anywhere on Venus' surface and are not expected to be present.

Finally, the present work suggests several lines of enquiry that can be pursued to improve our knowledge of mica formation and stability on Venus. These topics include:

(1) Theoretical modeling of the stability of micas in Venus' interior. This is important for constraining mica formation and also for constraining formation of silica undersaturated rocks via the breakdown of deep crustal or mantle phlogopite during melting.
(2) Theoretical modeling of mica formation during hypothesized cooler, wetter epochs on Venus. At present essentially all the studies of atmosphere-surface interactions on Venus are for the present climate and the effects of cooler; wetter climates have not been considered.
(3) Experimental studies of the dehydroxylation and dehydration of phlogopitic micas as a function of temperature and pressure in CO_2 and CO_2 gas mixtures relevant to Venus. At present, all the experimental work on mica dehydroxylation has been done in other atmospheres (air, inert gas, reducing gases) that are not directly relevant to Venus.

Appendix

Thermodynamic data for mica end-members and solid solutions

Phlogopites are characterized by the distribution of Mg^{2+} over 2 octahedral sites and Al^{4+} and Si^{4+} over three tetrahedral sites. The Al–Si distribution in tetrahedral sites exhibits various stages of ordering which affect the thermodynamic properties. The effect of Al-Si ordering on the standard enthalpy of formation is poorly known. Robie and Hemingway (1984; 1995) evaluated the enthalpy of ordering to be -20 kJ mol^{-1} for phlogopite and fluorphlogopite based on the experimental data of Wood (1976) and Wones and Dodge (1977). According to their evaluation, Al-Si ordered phlogopite has a more negative standard enthalpy and therefore is more stable than the disordered phase. On the other hand, Clemens et al. (1987) critiqued Wood's (1976) and Wones and

Table 2
The stability of common micas on the surface of Venus

Stable micas		Unstable micas
Lowlands	Highlands	
Eastonite-phlogopite (phl$_{<02}$east$_{>98}$)	Phlogopite-eastonite (phl$_{80}$east$_{20}$, phl$_{<01}$east$_{>99}$)	Phlogopite
eastonite	eastonite	Annite
Eastonite-siderophyllite (east$_{>90}$sdph$_{<10}$)	Eastonite-siderophyllite (east$_{>75}$sdph$_{<25}$)	Siderophyllite
Phlogopite-fluorphlogopite (phl$_{<46}$−fphl$_{>54}$)	Phlogopite-fluorphlogopite (phl$_{<80}$−fphl$_{>20}$)	Muscovite
fluorphlogopite	fluorphlogopite	Paragonite
		Margarite

Table A1
Thermodynamic properties for pure micas

Mineral name	Ideal formula	$\Delta_f H^o$(298.15 K) (kJ mol^{-1})	S^o(298.15 K)	$Cp = a+bT+cT^{-2}+dT^{-0.5}$ (J mol^{-1} K^{-1})				Source[a]
				a	b 10^{-3}	c 10^5	d 10^3	
Phlogopite	KMg$_3$AlSi$_3$O$_{10}$(OH)$_2$	-6215.0 ± 3.5	315.9 ± 1.0[or]	863.9	-76.08	3.52	-8.47	CN,CN,RH
			331.8 ± 1.0[po]	863.9	-76.08	3.52	-8.47	CN
			334.6 ± 1.0[do]	863.9	-76.08	3.52	-8.47	CN
Eastonite	KMg$_2$Al$_3$Si$_2$O$_{10}$(OH)$_2$	-6363.0 ± 6.0	317.4 ± 1.2	785.5	-38.03	-21.3	-6.89	CN,CN,HP
Siderophyllite	KFe$_2^{+2}$Al$_3$Si$_2$O$_{10}$(OH)$_2$	-5628.3 ± 4.2	375.0 ± 4.8	815.8	-36.65	-5.65	-7.52	HP,HP,HP
Annite	KFe$_3^{+2}$AlSi$_3$O$_{10}$(OH)$_2$	-5149.3 ± 4.0	415 ± 10	636.6	82.08	-4.86	-3.73	RH,RH,RH
Fluorphlogopite	KMg$_3$AlSi$_3$O$_{10}$F$_2$	-6355.5 ± 4.0	317.6 ± 2.1[or]	492.88	49.1	-65.99	-1.57	RH,RH,RH
			333.5 ± 2.1[po]	492.88	49.1	-65.99	-1.57	TW
			336.3 ± 2.1[do]	492.88	49.1	-65.99	-1.57	RH

[a]The sources of enthalpy, entropy, and heat capacity data, respectively.
[or]ordered, [po]partially ordered, [do]disordered.
CN, Circone and Navrotsky, 1992; HP, Holland and Powell, 1990; RH, Robie and Hemingway, 1995; TW, this work.

Table A2
Equilibrium partial pressure and abundance of H$_2$O for phlogopite dehydration reaction (1) on Venus' surface

Phlogopite Al-Si	Plains[a]		Maxwell Montes[b]	
ordering state	$\log_{10} f_{H_2O}$ (± 0.36)	H$_2$O (ppmv)[c]	$\log_{10} f_{H_2O}$ (± 0.36)	H$_2$O (ppmv)[c]
Ordered	-0.03	9760 (4260–22400)	-1.13	1544 (674–3538)
Partially ordered	-0.86	1140 (630–3310)	-1.96	228 (100–523)
Disordered	-1.01	1020 (446–2340)	-2.11	162 (71–370)

[a]At the modal radius of 6051.4 km where $T = 740$ K and $P = 95.6$ bars. The modal radius is 0.6 km below the zero level (6052 km) in the VIRA model (Seiff et al. 1986).
[b]10.4 km above the modal radius where $T = 660$ K and $P = 48.0$ bars.
[c]The H$_2$O mole fraction and 2σ uncertainties in parenthesis.

Dodge's (1977) data and suggested a small (<6 kJ mol^{-1}) enthalpy of ordering for phlogopite based on the similarity of the low and high temperature phase equilibrium data. Clemens et al. (1987) and Circone and Navrotsky (1992) used high temperature solution calorimetry and measured very similar values for the standard enthalpy of formation for disordered and partially disordered samples. Therefore, the enthalpy of Al-Si ordering could be less than the experimental uncertainty of ~6 kJ mol^{-1} (Clemens et al., 1987). The enthalpy value of -6215 ± 3.5 kJ mol^{-1} by Circone and Navrotsky (1992) based on their and Clemens' et al. (1987) calorimetry, is consistent with enthalpies obtained from phase equilibrium data (Bohlen et al., 1983; Clemens, 1995). We take this value for the $\Delta_f H^o$ at 298.15 K for both ordered and disordered phlogopite.

The standard entropies of disordered phlogopite and fluorphlogopite are higher than those of the ordered phases by a configurational entropy term of 18.7 J mol^{-1} K^{-1} (Circone and Navrotsky, 1992; Clemens et al., 1987; Robie and Hemingway, 1984; 1995). The higher entropy for the disordered phases makes them more stable than

the ordered micas. Indeed, disordered phlogopites occur more frequently than ordered phlogopites (Bailey, 1984). We used S^0_{298} from Robie and Hemingway (1995) for the ordered phase and for the completely disordered phase. We take the S^0_{298} value obtained by Circone and Navrotsky (1992) for their synthetic sample as the entropy of the partially disordered phase.

By analogy with phlogopite we assume zero enthalpy of Al–Si ordering for fluorphlogopite. The enthalpy for ordered fluorphlogopite is taken from Robie and Hemingway (1995). We used S^0_{298} tabulated by Robie and Hemingway (1995) for the ordered phase and the completely disordered phase. We estimated the S^0_{298} for partially disordered fluorphlogopite using the entropy difference of 2.82 J mol^{-1} K^{-1} between the disordered and partially ordered phlogopite samples of Circone and Navrotsky (1992). We used the thermodynamic properties of partially ordered phlogopite for our nominal calculations described in the text. However, Table A–2 demonstrates how the ordering of phlogopite affects its thermodynamic stability against dehydration.

We take the enthalpy of formation for eastonite

($\Delta_f H^{\circ}_{298} = -6363 \pm 6$ kJ mol^{-1}) from high temperature solution calorimetry measurements by Circone and Navrotsky (1992). However, their $\Delta_f H^{\circ}$ value may be uncertain for several reasons. First, they calculated $\Delta_f H^{\circ}_{298}$ for eastonite by extrapolation of their calorimetric data for synthetic phlogopite-eastonite micas to pure eastonite. Second, there are apparently very few natural occurrences of pure eastonite (Livi and Veblen, 1987). This is somewhat surprising considering the high stability predicted from the available calorimetric data. Finally, the preliminary enthalpy of formation given by Holland and Powell (1990), ($\Delta_f H^{\circ}_{298} = -6337$ kJ mol^{-1}) indicates that eastonite is less stable than found by Circone and Navrotsky (1992). We conclude that although eastonite is apparently very stable, future measurements of either its $\Delta_f H^{\circ}_{298}$ or $\Delta_f G^{\circ}_{298}$ are desirable.

The eastonite-phlogopite solid solution is characterized by the substitution of Al^{3+} in 2 octahedral positions, M1 and M2 (where Al^{3+} substitutes for Mg^{2+}) and in three tetrahedral positions, T1–T3 (where Al^{3+} substitutes for Si^{4+}). High temperature oxide solution calorimetry for eastonite-phlogopite solid solution made by Circone and Navrotsky (1992) showed an asymmetric enthalpy of mixing. Those data combined with their evaluations of configurational entropy for their partially Al–Si ordered samples predict an asymmetrically-shaped immiscibility gap below ~ 1470 K (see Fig. 2). The thermodynamic properties of the eastonite-phlogopite solid solution depend on the ordering state of phlogopite. For the nominal case, we apply the model of short range Al,Si ordering developed by Circone and Navrotsky (1992). That model corresponds to a partially Al–Si ordered phlogopite end-member and an ordered eastonite end-member. We use the enthalpy of mixing (ΔH°_{mix}) measured by Circone and Navrotsky (1992) and we calculate the entropy of mixing from

$$\Delta S^{\circ}_{mix} = -2R[X_E \ln X_E + X_P \ln X_P], \qquad (A1)$$

where X_E and X_P are the mole fractions of eastonite and phlogopite, respectively, in the solid solution. The Gibbs free energy ($\Delta_f G^{\circ}_{ss}$) of the solid solution was calculated as a function of composition from

$$\Delta_f G^{\circ}_{ss} = X_E \Delta_f G^{\circ}_E + X_P \Delta_f G^{\circ}_P + \Delta H^{\circ}_{mix} - T\Delta S^{\circ}_{mix}. \qquad (A2)$$

For the eastonite-siderophyllite solution we applied an ideal solid solution model. The enthalpy of mixing for the ideal model equals zero and the ideal entropy of mixing is calculated from equation (A1), where X_P is replaced by X_S, the mole fraction of siderophyllite. The Gibbs free energy of solid solution is calculated from equation (A2), where X_P is replaced by X_S. The activities and mole fractions of the end-members are related by the equations:

$$\ln a_P = -2 \ln X_P, \qquad (A3)$$

$$\ln a_S = -2 \ln X_S. \qquad (A4)$$

We take the same ideal mixing model for phlogopite-fluorphlogopite solid solutions. The thermodynamic data for the end-member micas are summarized in Table A1.

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