VENUS: SURFACE CHEMISTRY AND MODIFICATION PROCESSES,
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In view of the substantial age of most of the Venus surface (~0.5 Gyr, from crater counts [1]), its high temperature, and the chemical reactivity of the atmosphere, it is likely that originally basaltic surface material has been weathered to some depth to a secondary mineral assemblage. The nature of the secondary assemblage can be estimated from thermodynamic principles [2,3]. Phase diagrams applicable to the Venus surface are shown in Fig. 1. These assume atmospheric H$_2$O=100 ppm and SO$_2$=185 ppm, and are cast in terms of the two most important variables: altitude (which controls temperature and pressure), and $\delta$, a measure of the redox potential of the atmosphere, which is unknown. ($\delta$ is the fraction of atmospheric C that exists as CO because there is not enough O to oxidize it to CO$_2$. The smaller $\delta$ is, the more oxidizing the atmosphere.)

Venus mountaintops (altitudes >~2.5 km) display extraordinarily high SAR reflectivity and low microwave emissivity (<0.6). This has been attributed to localized surface material having a high dielectric constant, presumably because it consists of inclusions of electrically conductive minerals dispersed in an insulating matrix in a configuration that constitutes a radar-scattering loaded dielectric [4]. The weathered assemblages of Fig. 1 have the potential for forming such a configuration. Of the conductive minerals shown in Fig. 1a, pyrrhotite is the most promising constituent for a loaded dielectric, because this hexagonal mineral tends to form platy grains. Platy grains are more polarizable than equidimensional grains, and form a more reflective loaded dielectric [5].

If the Venus atmosphere is uniform in composition and thermal structure, the altitude at which the magnetite/pyrrhotite phase boundary is crossed (Fig. 1a) and the radar reflectivity of surface material changes should be the same everywhere. However, this is not the case: the altitude at which the change occurs varies in approximate proportion to the

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**Figure 1.** Stable phase assemblages on the Venus surface consist of plagioclase, orthopyroxene, K-feldspar, rutile, and the minerals shown in these figures. a: Fe minerals; the dotted line corresponds to the value of $\delta$ advocated in this paper, which accounts for the altitude above which surface material on Sapas Mons displays very low emissivity. b: Other minerals. Ad, andalusite; Ah, anhydrite; Cn, corundum; Cr, cordierite; D, diopside; Q, quartz; Sp, spinel.
height of the mountain in question, from \(-2.5\) km on Sapas Mons (height, 4.4 km) to \(-4.75\) km on Maxwell Montes (height, 10.6 km). This may result from modulation of the atmospheric thermal structure by topography, such that high-standing structures are hotter than gas at the same altitude in an atmospheric column over the plains would be. There are also anomalous emissivity effects close to volcanic vents, which may result from local changes in the atmospheric composition caused by continuing emission of volcanic gases [6].

Taking the height of the reflectivity change on Sapas Mons to be most nearly representative of the effect of the normal thermal gradient in the Venus atmosphere (because the small size of Sapas would perturb it least), a value of \(\delta\) for the atmosphere can be deduced: \(-2 \times 10^{-5}\) (Fig. 1a). This corresponds to an oxygen fugacity of \(-10^{21}\) bar at plains level, between the magnetite/hematite and magnetite/wüsite buffers, a redox potential similar to that in the earth's crust. The equilibrium concentration of CO at plains level for this \(\delta\) is \(-12\) ppm, similar to the \(20 \pm 3\) ppm CO concentration found in the atmosphere at an altitude of 22 km by the Pioneer Venus entry probe [7]; species abundances in the lower atmosphere can be understood as having been established by near-equilibrium chemistry at the Venus surface, after which the gas mixed upward with little additional reaction.

It would appear that the magnetite/pyrrhotite and pyrrhotite/pyrite reactions in Fig. 1a constitute atmospheric buffers that would tend to maintain the CO and SO\(_2\) concentrations in the atmosphere at constant values. If volcanic emissions increased the SO\(_2\) concentration of the atmosphere, for example, all other things being equal, it would push the pyrrhotite/pyrite phase boundary to a lower altitude (this cannot be read from Fig. 1a, which assumes a constant SO\(_2\) concentration), causing some pyrrhotite to react to pyrite, which would remove SO\(_2\) from the atmosphere. However, all other things are not equal, because SO\(_2\) is an important greenhouse gas [8]; an increase in atmospheric SO\(_2\) leads to higher temperatures, which shrinks the fields of stability of sulfide minerals, releasing additional SO\(_2\) gas. The system exhibits positive feedback, so it cannot act as a buffer in the traditional sense. Reconnaissance studies show that if volcanic inputs of SO\(_2\) ceased, weathering reactions would gradually lower the concentration of this species and decrease the surface temperature of Venus substantially; pyrite would become the stable Fe mineral at all altitudes, and carbonate and hydrated minerals would become stable under some circumstances. In practice Venus surface material buffers the atmospheric composition only in the crude sense that there is a long-term balance between the rate of addition of SO\(_2\) by volcanoes, and its removal by weathering reactions. The time-averaged SO\(_2\) concentration at which this dynamic balance is struck can vary over the long term, with changes in volcanic activity. In the short term, volcanic activity can cause major upward fluctuations of SO\(_2\) concentration, but since weathering is undoubtedly slow, there is nothing that can cause similar downward fluctuations.