Space Sci Rev (2017) 212:1511–1540
DOI 10.1007/s11214-017-0370-8

Venus Surface Composition Constrained by Observation and Experiment

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Received: 7 February 2017 / Accepted: 21 April 2017 / Published online: 3 August 2017

Abstract New observations from the Venus Express spacecraft as well as theoretical and experimental investigation of Venus analogue materials have advanced our understanding of the petrology of Venus melts and the mineralogy of rocks on the surface. The VIRTIS instrument aboard Venus Express provided a map of the southern hemisphere of Venus at ∼1 μm allowing, for the first time, the definition of surface units in terms of their 1 μm emissivity and derived mineralogy. Tessera terrain has lower emissivity than the presumably basaltic plains, consistent with a more silica-rich or felsic mineralogy. Thermodynamic modeling and experimental production of melts with Venera and Vega starting compositions predict derivative melts that range from mafic to felsic. Large volumes of felsic melts require water and may link the formation of tesserae to the presence of a Venus ocean. Low emissivity rocks may also be produced by atmosphere-surface weathering reactions unlike those seen presently.

High 1 μm emissivity values correlate to stratigraphically recent flows and have been used with theoretical and experimental predictions of basalt weathering to identify regions of recent volcanism. The timescale of this volcanism is currently constrained by the weathering of magnetite (higher emissivity) in fresh basalts to hematite (lower emissivity) in Venus' oxidizing environment. Recent volcanism is corroborated by transient thermal anomalies identified by the VMC instrument aboard Venus Express. The interpretation of all emissivity data depends critically on understanding the composition of surface materials, kinetics of rock weathering and their measurement under Venus conditions.

Venus III
Edited by Bruno Bézard, Christopher T. Russell, Takehiko Satoh, Suzanne E. Smrekar and Colin F. Wilson

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Extended theoretical studies, continued analysis of earlier spacecraft results, new atmospheric data, and measurements of mineral stability under Venus conditions have improved our understanding atmosphere-surface interactions. The calcite-wollastonite CO_2 buffer has been discounted due, among other things, to the rarity of wollastonite and instability of carbonate at the Venus surface. Sulfur in the Venus atmosphere has been shown experimentally to react with Ca in surface minerals to produce anhydrite. The extent of this SO_2 buffer is constrained by the Ca content of surface rocks and sulfur content of the atmosphere, both of which are likely variable, perhaps due to active volcanism. Experimental work on a range of semiconductor and ferroelectric minerals is placing constraints on the cause(s) of Venus' anomalously radar bright highlands.

Keywords Venus · Mineralogy · Crust · Geochemistry

1 Introduction

Planetary surface composition can be assessed via remote sensing, by in situ measurements by landers or rovers or by the analysis of returned samples. The Venusian atmosphere is a considerable obstacle to measurements of surface composition by any of these techniques. It prohibits the high-resolution imaging of the surface at visible—thermal wavelengths that has revolutionized the study of the mineralogy of Mars, Mercury and the Moon. The high Venus surface temperature (740 K) places severe limits on the lifetime of landers. No Venus meteorites have yet been recognized in the terrestrial collection—the delivery of a Venus meteorite to Earth is highly unlikely due to the large escape velocity of Venus and the thick atmosphere (Gladman et al. 1996). Long-lived in situ or sample return missions will require investment in several key technologies to operate in the Venus environment (Sweetser et al. 2000; Cutts et al. 2007; VEXAG 2014; Glaze et al., this issue).

Despite these challenges, new orbital data, experimental and theoretical work on the mineralogy and chemistry of materials under Venus conditions, and the reexamination of Venera data have allowed advances in our understanding of the composition of the Venus surface. The European Space Agency's Venus Express (VEx) orbiter carried two instruments, the Visible and Infrared Thermal Imaging Spectrometer (VIRTIS) and Venus Monitoring Camera (VMC) that measured radiance through an atmospheric spectral window at $\sim$1 micron. This signal is dominated by surface emission and contains information that can be related to mineralogy. This orbital dataset provides, for the first time, the ability to measure the distribution of surface radiance and derived emissivity and to relate this signature to the surface morphology and stratigraphy derived from the continued detailed geological mapping of the Magellan SAR data. The interpretation of these data depends critically on our knowledge of the radiance of minerals at high-temperatures and our understanding of the composition of Venus rocks and their expected weathering products in the Venus environment.

Advances have been made using both theoretical modeling and experiment to understand the predicted petrology and mineralogy of the Venus surface. Thermodynamic modeling and experimental investigation of Venus analogue rocks guided by the major element chemistry of the Venera and Vega landers allows the calculation of Venus mantle potential temperatures as well as predicts a broad range of melt types from basaltic to silicic compositions on Venus. Improved measurements of the Venus atmosphere from VEx, improved thermodynamic modeling of atmosphere-surface interactions and new experiments on the fate of surface minerals under a range of Venus-like atmospheres have placed new constraints on reasonable equilibrium reactions that may occur and may buffer the Venus atmosphere. New experimental work and observations of regional variability have refined possible candidate minerals of high permittivity that cover most Venus mountaintops.

In this paper, we review the constraints on Venus surface composition placed primarily by the VIRTIS instrument and improved analyses of surface-atmosphere reactions. This includes a summary of current laboratory work on the expected mineralogy and weathering products of likely Venus surface materials. Finally, we discuss some implications of these measurements for Venus evolution and activity.

2 Geochemistry and Petrology of Venusian Rocks

During the period 1972–1985, 5 Venera and 2 VEGA landers measured geochemistry of the surface at 7 locations on Venus. The Venera and VEGA X-ray Fluorescence (XRF) and gamma-ray chemical analyses were discussed in the *Venus II* volume and others (Grimm and Hess 1997; Treiman 2007). Those chemical analyses are all consistent with basaltic rocks, including tholeiitic and highly alkaline types (Treiman 2007). Four of the landers only returned abundances of the radioactive elements Th, U, and K, which vary enormously; those at the Venera 8 site are high enough to suggest granitic rocks but would also be consistent with highly alkaline basaltic lavas (e.g., Nikolayeva et al. 1992). Unfortunately, the Venera and VEGA analyses are quite imprecise and the instrument could not quantify abundances of sodium, which is crucial for understanding the nature and origin of igneous rocks.

Some advance in understanding of the Venera and VEGA analyses has come from comparison of their overall geochemistry and trends to those seen from laboratory experiments of terrestrial basalts (Filiberto 2014). Tholeiitic Venus basalts, like those at the Venera 14 and VEGA 2 sites, would be consistent with melting of peridotite in the shallow mantle; perhaps the most comparable Earth environment would be an oceanic hot-spot volcano. Alkaline basalt, like that analyzed by Venera 13, would be consistent with melting at much greater depth ($\sim$18–27 kbar) of a “marginally hydrous and substantially carbonated source region” (Filiberto 2014). Mantle potential temperatures derived from modeling of the Venera 14 data are consistent with the modern terrestrial mantle (Lee et al. 2009; Weller and Duncan 2015; Shellnutt 2016; Filiberto and Treiman 2017). These two basalts may have distinctive different Ti contents (Filiberto 2014), which could imply strong chemical fractionations, (e.g., loss of ilmenite) in the Venus’ mantle. As on Earth, a range of melting environments may exist and should be expected.

Shellnutt (2013) has shown through thermodynamic modeling that silicic (phonolitic, rhyolitic and andesitic) rocks can be derived from the differentiation and partial melting of rocks of Venera 13 and 14 compositions. The melt composition was found to depend critically on assumptions about Na and water content, neither of which was measured by the Venera landers; presumably melt composition would also depend on halogen content as well, although this was not modeled. As on Earth, the generation of felsic liquids from mafic magmas requires fractionation on the order $\sim$90% (Spulber and Rutherford 1983) and thus copious amounts of melting would be required to generate significant volumes of silicic melts.

The notion that silicic igneous rocks, granitic or andesitic, may be present at Venus’ surface dates to the earliest detailed radar maps. Ishtar Terra was compared to a continent on Earth, that is, low-density silicic material ‘floating’ in a denser mafic mantle (Phillips and Malin 1984). A similar argument has been made for tessera terrain, which are structurally deformed materials that cover 8% of the surface and are often found in high standing plateaus

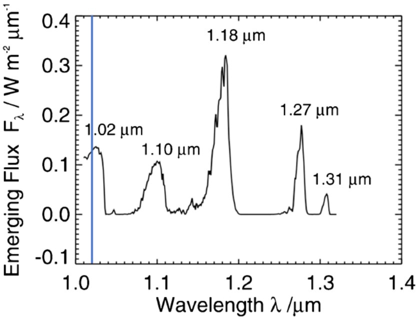

Fig. 1 Modeled spectrum of NIR windows at VIRTIS-H spectral resolution (Drossart et al. 2007; Tsang et al. 2008). Line indicates VIRTIS M channel discussed in this study. A full discussion of Venus atmospheric windows can be found in Taylor et al. (1997). Figure after Mueller et al. (2008)

(Nikolayeva et al. 1992; Romeo and Turcotte 2008). Pancake domes and festoon flows appear to have viscous morphologies consistent with siliceous lavas (e.g., Pavri et al. 1992; Moore et al. 1992). The implications of abundant silicic (e.g., granitic) material on Venus would be profound, as abundant granites require abundant water (Campbell and Taylor 1983) and a plate recycling mechanism, neither of which are apparently operating today (although see Davaille et al. 2017).

The Venera and VEGA spacecraft likely landed on plains units, which exhibit morphologies consistent with basaltic lava flows (Weitz and Basilevsky 1993). Thus it is generally assumed that the bulk of the plains, which cover ∼80% of the surface, are basaltic. These plains are weathering under an atmosphere of CO_2 and sulfur and halogen species at a temperature of 740 K. This assumption underlies the observational and experimental constraints on the mineralogy of Venus, which we now discuss.

3 Mineralogy of Venus

3.1 Near-infrared Observations of Venus

3.1.1 Theory

It is theoretically possible to relate thermal emission from the Venus surface to mineralogy. There are several near-infrared spectral windows in the Venus atmosphere through which radiation from below the cloud deck (25–45 km) can be detected (Allen and Crawford 1984; Carlson et al. 1991; Crisp et al. 1991; Baines et al. 2000; Fig. 1). Radiation observed through 1.0, 1.1 and 1.18 µm windows contains a large component of surface emission where the 1.0 µm window is less affected by atmospheric gaseous absorption/emission than the other two windows (Meadows and Crisp 1996; Fig. 1).

The observed nighttime radiation must be corrected for stray sunlight, limb darkening, and variable cloud opacity and cloud reflections (Meadows and Crisp 1996; Hashimoto and Sugita 2003; Mueller et al. 2008; Kappel et al. 2016). The data need also be corrected for surface temperature. The surface temperature of Venus is strongly constrained by the thick atmosphere and its high heat capacity and capability to transport heat (Stone 1975, Lecacheux et al. 1993). Descent probes at various local times and latitudes recorded nearly the same temperature in the lower atmosphere, closely following the adiabatic lapse rate (Seiff et al. 1985). This horizontally uniform temperature means that surface temperature is strongly controlled by surface topography (Lecacheux et al. 1993). Thus, the surface thermal emission can be corrected for surface temperature using Magellan

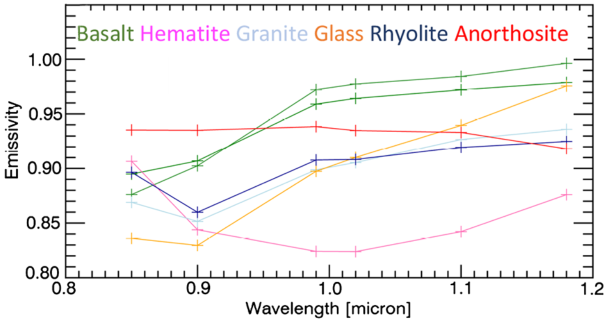

Fig. 2 Spectra of Venus analogue samples at all known atmospheric surface windows of Venus. Samples represent a suite of crustal differentiation and thus different Fe and Si concentrations. Hematite is a predicted surface weathering product of basalt. Additional spectral analysis techniques allow for robust identification of subtle spectral differences

radar altimetry (Lecacheux et al. 1993, Meadows and Crisp 1996; Hashimoto et al. 2008; Helbert et al. 2008; Mueller et al. 2008; Smrekar et al. 2010; Basilevsky et al. 2012; Kappel et al. 2016). This correction is most robust for the regions where topography is smooth over the ~10 km Magellan altimeter footprint.

The resulting surface emissivity provides an opportunity to assess the composition of surface materials. In common silicate minerals at room temperature, 1 μm reflectance is controlled by crystal field spectra of transition metal ions in the crystal lattice. As Fe^{2+} is the most common transition metal in silicates, 1 μm reflectance is dominated by and positively correlated to ferrous iron content, where olivine ($(Mg, Fe)_2SiO_4$) and pyroxenes ($(NaCa)(Mg, Fe, Al)(Al, Si)_2O_6$) have low reflectance, and quartz (SiO_2) and feldspars (generally AT_4O_8, where $A = Ca$, Na or K and $T = Si + Al$) have high reflectance (e.g., Hunt and Salisbury 1970). At room temperature, reflectance is inversely related to emissivity e, via Kirchoff's Law:

$$e = 1 - r \tag{1}$$

where $r =$ reflectivity. At visible and near-infrared wavelengths, reflectance also depends on particle size, where smaller particle sizes typically have higher reflectance and thus lower emissivity (e.g., Adams and Filice 1967).

Recent investigation into the effects of high temperatures (500 °C) of komatiites in reflectance (Maturilli et al. 2014) and a variety of minerals and rocks in emission (Helbert and Maturilli 2009; Helbert et al. 2015) had suggested that the changes in the spectra are complex and significant laboratory work is required fully characterize temperature effects on the spectra of minerals and rocks in this wavelength range. A new experimental setup at the Planetary Spectroscopy Laboratory at DLR now allows for the first time to obtain emissivity measurements of Venus analogue materials at Venus surface temperatures for all atmospheric windows (Helbert et al. 2017). Figure 2 shows measurements of Venus analogue samples, confirming that the near infrared windows allow for the determination of and distinctions between minerals. A full database of emissivity spectra for a wide range of analogues obtained at Venus surface temperatures will support the data analysis for VIRTIS, VMC and future orbital and lander missions.

3.1.2 Observations

Hashimoto et al. (2008) measured the night side surface emission from orbit using the 1.18 μm channel on the Galileo NIMS instrument. They noted a general trend of low emissivity at higher surface elevations measured in data integrated over a 250-km region. This relationship has been confirmed in the VIRTIS data observing at 1.02 μm at a spatial resolution of ~100 km (Mueller et al. 2008; Haus and Arnold 2010). The VIRTIS

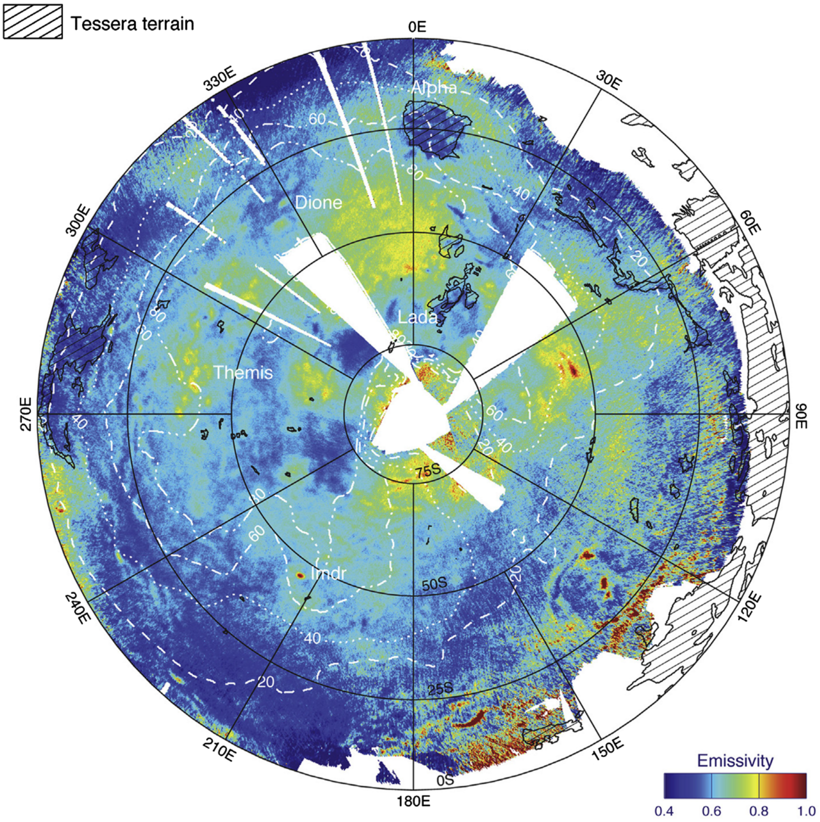

Fig. 3 Map of VIRTIS surface emissivity at 1.02 μm. An average surface emissivity of 0.62 is used here. Tessera terrain is indicated by the striped areas (Tanaka et al. 1997). Contours indicate number of VIRTIS images acquired in each area; more images results in reduced noise and other potential variable effects. White areas are data gaps. Low emissivity values are associated with Alpha Regio. High emissivity values are associated with the Mylitta Fluctus/Lada Terra and Imdr, Themis, Dione Regions. Modified from Smrekar et al. (2014)

data are often reported as brightness anomaly, which is the difference between the measured flux and the global or local average (Mueller et al. 2008; Helbert et al. 2008; Kappel et al. 2016). As plains dominate the Venus surface generally and the southern hemisphere in particular, the average emissivity is reasonably assumed to measure the average plains signature. VIRTIS imaged the bulk of the southern hemisphere of Venus and detected both high and low flux anomalies correlated with geomorphologic features (Fig. 3).

High Emissivity Anomalies Relatively high 1 μm emissivity flux values ($\leq 12\%$ above average) are spatially associated with coronae, volcanoes and lava flow fields in several regions in the southern hemisphere of Venus (Mueller et al. 2008; Helbert et al. 2008; Smrekar et al. 2010; Kappel et al. 2016; D'Incecco et al. 2017). The geographically largest of these anomalies is in Lada Terra and correlates with digitate and lobate plains on southern flank of Quetzalpetlatl corona and the flows of Mylitta Fluctus with adjacent flows associated with edifices along the Lada Terra rift (Helbert et al. 2008; Mueller et al. 2008). Coronae generally (e.g., Stofan et al. 1992) and the flows of Quetzalpetlatl (Magee and Head 1995) and Mylitta Fluctus (Roberts et al. 1992) in particular, are interpreted to form due to mantle upwelling and melting. The flows associated with the high emissivity values at Quetzalpetlatl and Mylitta Fluctus are mapped at the top of their local stratigraphic column, indicating they are relatively young volcanic units (Ivanov and Head 2006; Kumar and Head 2013).

Positive flux anomalies are also associated with number of volcanic edifices and coronae in Imdr, Themis and Dione Regionnes (Smrekar et al. 2010; Kappel et al. 2016; D'Incecco et al. 2017). Smrekar et al. (2010) and D'Incecco et al. (2017) observe that the anomalies are correlated with digitate and sheet flows at the summit of flanks of these edifices. These flows are also mapped to be the locally stratigraphically youngest units including some flows that postdate radar-dark parabola deposits associated with the most recent impact craters (ca. 10% of the average surface crater age; Izenberg et al. 1994).

The lander data and weathering reactions described in Sect. 3.2.1 below suggest that the surface of Venus is dominated by basalts weathered to hematite and other secondary phases. Thus the positive emissivity anomalies here and in Lada Terra are interpreted to represent relatively unweathered and geologically young basalts. Fresh basalts are shown to have higher emissivity than hematite at 1.02 µm at both Earth and Venus conditions (Fig. 2). Estimates of reasonable resurfacing rates give an upper bound for the average age of these basalts at 2.5 Ma (Smrekar et al. 2010).

Low Emissivity Anomalies Relatively low 1 µm thermal emission for mapped tessera units compared to global average have been noted in both VEx VIRTIS (Mueller et al. 2008; Helbert et al. 2008; Gilmore et al. 2015) and VMC data (Basilevsky et al. 2012). Since the plains are presumed to be basaltic by extrapolation from the Venera lander data (Weitz and Basilevsky 1993) and morphology (e.g., Guest et al. 1992), the lower emissivity values observed for the highlands are consistent with non-plains mineral assemblages including felsic rocks (Hashimoto et al. 2008; Mueller et al. 2008; Gilmore et al. 2015).

In addition to mineralogy, other factors could be contributing to the relatively low 1 µm emissivity signal of the tesserae such as roughness or sedimentation. These factors may be controlled at Alpha Regio tesserae, the largest contiguous region of tesserae imaged by VIRTIS. The western boundary of Alpha Regio is morphologically classified as tessera terrain, however, small volcanoes and radar-smooth regions amongst the tectonic structures show that this boundary comprises plains units that have been sequentially deformed and uplifted to the level of the adjacent tessera terrain (Gilmore and Head 2000). Western Alpha provides us deformed plains, presumable basaltic, adjacent to the main body of Alpha tesserae whose composition is unknown. The colocation of these deformed units in Alpha allow us to interpret emissivity signatures that are independent of macroscopic roughness, elevation and local mass wasting processes and thus likely to be dominated by mineralogy. The NIR flux anomaly value of western Alpha is similar to the local plains, Eve corona and the average plains value, suggesting that these materials share a presumably mafic mineralogy. The remainder of Alpha tessera has a distinctly lower emissivity signature than western Alpha and the average plains value, consistent with relatively Fe-poor and high-Si minerals.

A low emissivity flux is also observed in the VMC data for the summit of Tuulikki Mons volcano (Basilevsky et al. 2012). This has been interpreted to result from felsic mineralogies, potentially related to a steep-sided dome at the summit (Basilevsky et al. 2012). High-silica lavas have been proposed for steep sided-domes to explain their apparent high viscosity (Pavri et al. 1992). Low emissivity anomalies associated with Shiwanokia Corona (Kappel et al. 2016) may also indicate variations in original lava composition and/or weathering.

3.2 Chemical Weathering at the Venus Surface

Chemical interactions between the Venus surface and its atmosphere have important effects on both (Urey 1952), as is true for any terrestrial planet with a thick atmosphere (i.e., more than an exosphere). For Venus, these interactions are substantially different from those of Earth and Mars because of its absence of water and because Venus' surface is so hot, at ~740 K.

We can divide the field of atmosphere-surface interactions into three threads of inquiry: controls on the chemistry of Venus' atmosphere, the effects on mineralogy of the surface, and effects on radar properties of the surface. These threads have been studied theoretically since the beginnings of planetary sciences, and studied through acquired data in the 'golden age' of spacecraft exploration of Venus: Pioneer Venus, the Venera and VEGA landers, and the Magellan orbiter. Much of this work was reported at length in the *Venus II* book (Fegley et al. 1997a; Wood 1997). Here, we will recapitulate those results, and emphasize the work done since *Venus II*: extended theoretical studies; continued analysis of earlier spacecraft results (especially Magellan), and new data, primarily from the Venus Express spacecraft.

3.2.1 Chemistry of Venus' Atmosphere and Surface-Atmosphere Interaction of Major Species

The idea that the composition of Venus' atmosphere is controlled by chemical reactions at its surface dates famously to Urey (1952), who proposed that the pressures of gases at the Venus surface could be controlled by mineral devolatilization reactions. Urey's idea for Venus was generalized to consideration of mineral-gas reactions that could control or buffer oxidation state (e.g., CO/CO_2 ratio), abundance of sulfur-bearing gas species, and halogen-bearing species (e.g., Lewis 1968; Mueller 1969), and the concept of mineral buffering was explored in detail in a series of papers by Fegley and colleagues (e.g., Fegley and Prinn 1989; Fegley and Treiman 1992; Fegley et al. 1997a, Fegley 2004).

CO_2 Buffer Urey (1952) suggested equilibria of this type as potential buffers,

$$\underset{\text{calcite}}{CaCO_3} + \underset{\text{quartz}}{SiO_2} = \underset{\text{wollastonite}}{CaSiO_3} + \underset{\text{gas}}{CO_2}, \tag{2}$$

but dismissed them for Venus because its surface was considered too cool (~560 K) for them to represent surface conditions. However, the reaction was resurrected with the recognition that Venus' surface was far hotter than previously estimated (740 K; Adamchik and Draper 1963), and that its surface pressure and temperature were consistent with equilibrium (2). The hypothesis that reaction (2), now called 'the Urey reaction' buffered the CO_2 content of the Venus was explored in detail by Lewis (1968), who found that it alone, among many plausible decarbonation equilibria, was consistent with conditions at the Venus surface. Following Fegley's works (cited above), equilibrium (2) was broadly accepted as the control on CO_2 pressure of the Venus atmosphere.

However, studies since the *Venus II* book have contested and refuted the hypothesis that equilibrium (2) buffers the CO_2 content of the Venus atmosphere. Challenges have come from many directions: estimated planetary abundance of carbon, geological conditions required to producing abundant calcite + quartz, the instability of calcite on the Venus surface and the concept of buffering in an adiabatic atmosphere.

The first of these challenges was a simple estimate of the mass of carbon on Venus compared to that of the Earth. The total mass of carbon in the Venus atmosphere is comparable to that of the Earth's crust and atmosphere (Taylor 2006; Halliday 2013). This similarity suggests, within the paradigm of non-stochastic planetary accretion, that essentially all of Venus' carbon is in its atmosphere, leaving little in surface rocks to buffer the atmosphere.

For equilibrium (2) to operate on the scale of a whole planetary atmosphere, Venus' surface must contain significant abundances of quartz and calcite in intimate contact, and of wollastonite, across the planet and at all elevations (Hashimoto and Abe 2005). The early students of Venus surface-atmosphere reactions did not recognize the geological implications and difficulty of such a widespread surface mineralogy. An abundance of quartz implies the presence of widespread silicic igneous rocks, like granite, and/or sediments derived from them. To form masses of pure quartz, or of pure quartz mixed with calcite, requires (on Earth) multiple cycles of erosion, chemical weathering, and deposition (Pettijohn et al. 1986). On Earth, calcite is most abundant as chemical sediment from water, and although most recent sedimentary calcite is of biologic origin, (Tucker and Wright 1990), that need not have been true in Earth's distant past (Grotzinger and Kasting 1993), or in general. Wollastonite forms essentially only by reaction of calcite + quartz or calcite plus silica-bearing aqueous fluids. Based on Earth analogues, then, an abundance calcite, quartz, and/or wollastonite on Venus would be possible only if it had widespread silicic magmas and extensive aqueous chemical processing. To date, there is no geomorphic evidence for such a history.

Even if Venus had produced abundant carbonate at its surface in past epochs, equilibrium (2) cannot operate today because calcite is unstable with respect to anhydrite, $CaSO_4$, in the Venus surface atmosphere. The thermochemical instability of calcite and other Ca-bearing phases was recognized soon after S gases were discovered in the Venus atmosphere (e.g., Barsukov et al. 1982; Volkov et al. 1986; Fegley and Treiman 1992; Zolotov 2007), via reactions like

$$\underset{\text{calcite}}{CaCO_3} + 1.5\,\underset{\text{gas}}{SO_2} = \underset{\text{anhydrite}}{CaSO_4} + \underset{\text{gas}}{CO_2} + 0.25\,\underset{\text{gas}}{S_2}\,. \tag{3}$$

This reaction is fast on laboratory timescales (Fegley and Prinn 1989; Radoman-Shaw et al. 2017), and presumably would go rapidly to completion at Venus' surface.

Perhaps the last nail in the 'Urey reaction' coffin is the recognition that equilibria like (2) cannot buffer CO_2 abundances in a planetary atmosphere. The problem is that a potential buffer like (2) must act within an atmosphere with an adiabatic lapse rate (i.e., change in temperature with pressure). The effect of this constraint is to make equilibria like (2) unstable: a small perturbation in temperature or CO_2 pressure would not be damped out as in a true buffer, but would be amplified to catastrophe (Bullock and Grinspoon 1996; Hashimoto et al. 1997; Hashimoto and Abe 2005; Treiman and Bullock 2012). This criterion has a firm thermochemical basis (Treiman and Bullock 2012) and can be generalized to any mineral devolatilization that releases a radiatively active gas species, like CO_2 or H_2O.

Oxidation State—Fe Oxides Oxidation state is the principal control on the iron oxide minerals that might be present on Venus, i.e. magnetite at lower oxidation state and hematite at higher. That equilibrium, can be cast in terms of carbon gas species as

$$2\,\underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{gas}}{CO_2} = 3\,\underset{\text{hematite}}{Fe_2O_3} + \underset{\text{gas}}{CO}\,. \tag{4}$$

The CO/CO_2 ratio of Venus' near-surface atmosphere is close to that of equilibrium (4) (Zolotov 2007), so "The correspondence of atmospheric redox conditions to the conditions of the magnetite–hematite equilibrium is not likely to be accidental and could reflect ongoing magnetite-to-hematite transition … (and) slowly reacting ferric oxides may maintain the redox conditions in the near-surface atmosphere, where the majority of air mass is located."

One could reasonably expect that ferrous iron in basalt would weather to form magnetite or hematite or both.

Another potential product of oxidative alteration on Venus is maghemite, Fe_2O_3 in the spinel structure like magnetite, but it has not been evaluated as a potential product (or intermediary) of surface-atmosphere interaction. Maghemite and magnetite form a solid solution, and maghemite is a common metastable oxidation product of magnetite, while hematite is the thermochemically stable product. One can readily imagine that all three oxides might be found in weathering basalts on Venus' surface, and so act as the oxidation state buffer of reaction (4). Basalt on the Venus' surface will start reacting rapidly with the atmosphere, and would likely form surface layers rich in oxides of iron and of divalent cations (Cook et al. 1990; Treiman and Allen 1994; Cook and Cooper 2000; Burkhardt and Scherer 2006). One would expect that magnetite would form next to basalt glass, being influenced by the glass' abundance of Fe^{2+}. The magnetite could oxidize to maghemite solid solution under further influence of Venus' atmosphere, and eventually could recrystallize to hematite as oxidation was complete and recrystallization could proceed. This process would imply, given that hematite is the end-product, that reaction (4) operates primarily to hold the oxidation state of the Venus atmosphere at the hematite-magnetite buffer and offsets some other process acting to oxidize the atmosphere.

Apparently, Donahue et al. (1982) was the first to suggest that the surface of Venus might be rich in iron oxides, as products of basalt oxidation following the loss of atmospheric H to space. Reflectance spectra provided the first direct evidence of iron oxides at the Venus surface (Pieters et al. 1986). The reflectance of Venus surface materials in visible light wavelengths is consistent with that of hematite (Pieters et al. 1986; Yamanoi et al. 2009), although this inference depends on how one calculates the color of incident sunlight filtered through the Venus atmosphere. Rock at the Venera 9 and 10 sites was distinctly reddish (and reflective in the near-infrared) suggesting the presence of hematite, while rock at the Venera 13 and 14 sites was dark gray through the near-infrared, consistent with basalt. In Venera and VEGA images of Venus' surface, finer-grained material is 'redder' (Shkuratov et al. 1987), which would be consistent with more complete weathering of that material to hematite (Zolotov 2007).

Despite this evidence, the identity of iron oxide minerals on the Venus surface is not certain. The Venera 13 and 14 missions included a direct measure of the oxidation state of the Venus atmosphere, the KONTRAST experiment (Florensky et al. 1983), in which the colors of several vanadium salts would change with the oxidation state of the near-surface atmosphere. That experiment was compromised by dust on the plates of vanadium salts, but its results are consistent with oxidation states for both magnetite and hematite (Fegley et al. 1997a, 1997b; Fegley 2004; Zolotov 2007). However, a preponderance of magnetite, not hematite, is suggested by compositions and abundances of C and S-bearing gases near the surface (Hashimoto and Abe 2005; but see Zolotov 2007). These results are not necessarily inconsistent, as one could imagine abundant magnetite just beneath the surface, overlain by an optically thick layer (a few micrometers) of hematite.

The kinetics of iron oxide formation on Venus basalt is of considerable interest, both as an indicator of the reactions' effectiveness in buffering atmospheric oxidation state, and as a possible chronometer. Reflectance spectra suggest that Venus basalts have weathered to different degrees (or different products), as described above (Pieters et al. 1986). Similarly, as mentioned in Sect. 3.1.2, Smrekar et al. (2010) interpreted variations in the near-infrared emissivity of lava flows as representing varying degrees of weathering—stratigraphically younger flows have higher emissivities, which is consistent with less surface hematite. Although there are few laboratory measurements of emissivity (or reflectance) in this wavelength and temperature range (Yamanoi et al. 2009; Helbert et al. 2017), one can make a rough estimate of the rate of hematite formation on Venus basalt by extrapolating the results of Cooper et al. (1996) on oxidation of a terrestrial basalt; compositions and experimental conditions are far from those of Venus surface basalts, so any application to Venus must be considered speculative. Their results predict a diffusion constant for divalent cations (including Fe^{2+}) during the oxidation of basaltic glass of $D = 1.5 \times 10^{-16}\ cm^2\ sec^{-1}$ for Venus surface temperature, which would imply that formation of an optically thick coating of hematite (10 μm) on basalt glass would require <1 million years. This is very rapid in geological terms, and would suggest that Venus is volcanically active now (Smrekar et al. 2010); it would be important to calibrate this weathering reaction for appropriate Venus conditions and compositions!

Oxidation State—Sulfur Compounds The sulfur chemistry of the Venus atmosphere is complex, involving many gas species in S–O–C–H (SO_2, COS, H_2S, S_2, S_3, S_4, S_8), photochemical and thermochemical reactions in the gas phase (which may be kinetically inhibited), reactions with condensed phases (solids, H_2SO_4-rich cloud droplets), and significant variations with both elevation and time. In S-bearing gases, S can have a wide range of oxidation states, from highly reduced (H_2S), to neutral (S_2) to highly oxidized (SO_2).

Because S-bearing gas species are reactive and so abundant in the Venus atmosphere, there has been much study of S-bearing solids at Venus' surface as potential buffers of (or products of) atmosphere chemistry. The presence of abundant SO_2 in the Venus atmosphere invited speculation that it might be buffered by reactions with the surface. Such buffering is possible in theory (Treiman and Bullock 2012), both for a simple reaction like (3) and more complex reactions like

$$\underset{\text{pyrite}}{3\,FeS_2} + \underset{\text{gas}}{16\,CO_2} = \underset{\text{magnetite}}{Fe_3O_4} + \underset{\text{gas}}{6\,SO_2} + \underset{\text{gas}}{16CO} \tag{5}$$

(e.g., Hashimoto and Abe 2005). In reaction (5), a strong greenhouse gas (CO_2) is consumed, and is replaced by a radiatively inactive gas (CO) and a smaller proportion of a weak greenhouse gas (SO_2). Thus, forward progress of reaction (5), forced by an increase in temperature, will tend to decrease temperature by decreasing the strength of the greenhouse effect (Treiman and Bullock 2012).

However, no known reactions are suitable as SO_2 buffers at Venus' surface conditions. Common silicate and oxide minerals of Fe, Mg, Al, Na, and K will remain stable and not form sulfate minerals. Only Ca in silicate minerals will react with the Venus atmosphere to form the sulfate mineral anhydrite (Barsukov et al. 1982; Fegley and Treiman 1992), e.g.,

$$\underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{gas}}{SO_2} \rightarrow \underset{\text{anhydrite}}{CaSO_4} + \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{quartz}}{SiO_2} \tag{6}$$

and

$$\underset{\text{anorthite}}{CaAl_2Si_2O_8} + \underset{\text{gas}}{SO_2} \rightarrow \underset{\text{anhydrite}}{CaSO_4} + \underset{\text{andalusite}}{Al_2SiO_5} + \underset{\text{quartz}}{SiO_2}\,. \tag{7}$$

Basaltic glass is calculated to react with atmospheric SO_2 to form anhydrite, cordierite, ($(Mg, Fe^{2+})Al_4Si_5O_{18}$), low-Ca pyroxene, silica, and Fe-oxide (Sidorov 2006; Treiman and Schwenzer 2009). In all these cases, however, equilibria involving anhydrite would occur at much lower SO_2 than in the current Venus atmosphere, i.e. SO_2 is not currently buffered by atmosphere-surface chemistry.

Although anhydrite formation by these reactions is favored strongly by thermochemistry, the rates of the reactions are essentially unknown. Despite this ultimate instability of Ca-bearing silicates in the Venus atmosphere, the Venus surface materials analyzed by the Venera and VEGA mission are not fully altered, i.e. they have not gained enough S to have converted all their Ca to $CaSO_4$, i.e. the molar ratio S/Ca in those rocks is significantly less than unity (Prinn 1985; Zolotov and Khodakovsky 1989; Fegley and Treiman 1992; Fegley 2004; Zolotov 2007). This fact suggests that formation of $CaSO_4$ on Venus' surface is relatively slow (on Venus geological timescales), and so is not likely to be an effective sink for atmospheric SO_2, especially on the decadal timescales of SO_2 variation in Venus' middle atmosphere (Marcq et al. 2013). However, there have been no laboratory determinations of the rates of reactions (6) and (7). Diopside pyroxene does react with SO_2-bearing gas at temperature to form anhydrite (Fig. 1b of Fegley and Prinn 1989; Aveline et al. 2011), and plagioclase feldspar does react with SO_2-bearing gas at temperature (Aveline et al. 2011). But, available data do not define the rates of either reaction, and cannot be extrapolated to Venus physical conditions and timescales.

The case for sulfide minerals at the Venus surface, and the possibility that they buffer atmospheric S gases, is more complicated and less definitive. The controversy surrounding pyrite, FeS_2, on the Venus highlands will be discussed below. Here, we note that pyrrhotite, $Fe_{1-x}S$ is not stable at the Venus surface (Klose et al. 1992) relative to pyrite, and consider only one potential buffering reaction. The stability of pyrite at the Venus surface was studied by Barsukov et al. (1982) and Hashimoto et al. (1997), Hashimoto and Abe (2005), who suggested that the canonical SO_2 and CO abundances of the Venus surface atmosphere are consistent with buffering by equilibrium (5) and that this reaction acts as a buffer of CO and SO_2 in the Venus atmosphere. This model is problematic with respect to the variable abundances of CO and SO_2 in the Venus atmosphere (see above), and also with respect to the stability of magnetite. As noted above, the mass of available evidence suggests that hematite rather than magnetite is the stable iron oxide at the Venus surface; in this case, reaction (5) is not useful.

Temporal variations in SO_2 abundances in Venus' mid-atmosphere (cloud tops) may be important for surface-atmosphere chemistry. The abundance of SO_2 at Venus' cloud tops has varied by a factor of $\sim$100 on decadal timescales (Esposito 1984; Marcq et al. 2013), and have been explained as rapid inputs of S-rich gas from the deep atmosphere (upwellings or volcanic eruptions) followed by photochemical breakdown and/or conversion to H_2S and which has been ascribed to occasional injections of S-rich gas from volcanic eruptions. Such temporal variability in SO_2 in the mid-atmosphere suggests that Venus' deep atmosphere may also be significantly variable on similar timescales, especially if volcanic eruptions are involved (Esposito 1984). Alternatively, SO_2 variations observed on decadal timescales may be a result of climatic variability (Marcq et al. 2013).

Halogen Gases Both HCl and HF have been detected spectroscopically in the Venus atmosphere, and several workers have considered whether their abundances might be buffered by surface-atmosphere reactions (e.g., Mueller 1968; Lewis 1970; Fegley and Treiman 1992). The masses of Cl and F in the Venus atmosphere are far lower than expected of the planet as a whole (Zolotov 2007) assuming non-stochastic accretion processes, implying that most of the planet's halogens are in its solid material and thus available in to buffer abundances in the atmosphere. Fegley et al. (1992, 1997a, 1997b) suggested several solid-gas reactions that could buffer halogen hydride gases to reasonable levels in the Venus atmosphere. Their most likely potential buffer of HF is potassium feldspar and enstatite pyroxene to form the mica fluorphlogopite ($KMg_3(AlSi_3)O_{10}F_2$), quartz, and H_2O gas (Lewis 1970); these are reasonable starting minerals in a basaltic rock, and reasonable products such as might be found in metamorphic rocks on Earth. However, decomposition/reaction rates for fluorine-bearing silicates are slow at Venus surface conditions (Johnson and Fegley 2003a, 2003b), suggesting that such buffering mineral assemblages, if present, can operate only over geological timescales. On the other hand, potential reactions that could buffer HCl in the Venus atmosphere to its current levels involve mineral assemblages that are exceedingly rare on Earth, like nepheline ($(Na, K)AlSiO_4$) + albite ($NaAlSi_3O_8$) + sodalite ($Na_8Al_6Si_6O_{24}Cl_2$; Fegley et al. 1992; Fegley 2004). Such mineral assemblages cannot be completely excluded, but it seems unlikely that they (being so rare on Earth) would be abundant enough on Venus to buffer its entire atmosphere.

Water The abundance of hydrogen (including deuterium) in the Venus atmosphere is very low, ~30 ppm volume near its surface and (could conceivably be buffered by chemical reactions at its surface), although much of the atmosphere's hydrogen is taken up in and conceivably buffered by cloud droplets rich in H_2SO_4 (Fegley 2004). No end-member hydrous silicate minerals for which there is thermochemical data can serve as buffers for the water content of Venus' atmosphere, including all end-member amphiboles and micas (Zolotov et al. 1997; Zolotov 2007). However, some mixed-anion mixed cation micas, like F–OH phlogopite ($KMg_3(Si_3Al)O_{10}(F, OH)_2$)/eastonite ($KMg_2Al[Al_2Si_2O_{10}](OH)_2$) could be stable at high elevations (Zolotov et al. 1997, 1999), and could conceivably act to buffer atmospheric H_2O. However, decomposition/reaction rates for hydrous silicates are slow at Venus surface conditions (Johnson and Fegley 2000, 2002), suggesting that such buffering mineral assemblages, if present, can operate only over geological timescales.

3.2.2 Highlands Radar Anomalies

The first Pioneer Venus data show that many high elevations on Venus had distinctly elevated values of radar reflectivity (Masursky et al. 1980; Pettengill et al. 1980, 1988; Garvin et al. 1985) and thus low values of radar emissivity (Ford and Pettengill 1983). These results were confirmed by returns from the Magellan spacecraft at greater spatial resolution, in both radar reflectivity and emissivity (Tyler et al. 1991; Pettengill et al. 1992; Klose et al. 1992). The Magellan data shows that, at least for some areas, the transition to radar-bright (low emissivity) surfaces occurs over a small altitude range, with elevations above ~4.75 km (with respect to mean planetary radius of 6051.8 km) being significantly brighter than lower elevations. Similar but unfortunately limited results were obtained in bistatic radar mode by the Venus Express spacecraft (Simpson et al. 2009), before its radar system failed. The anomalous radar properties at high elevations imply material(s) with unusual electrical properties, and considerable effort has been devoted to discovering those materials.

The nature of the radar-reflective material at Venus' high elevations is presently constrained only by its radar properties and the chemistry of the Venus surface and atmosphere. The low emissivity implies that the bulk relative dielectric constant, ε, of the Venus highlands must be high, $\varepsilon > 50$ (even ~100 over Maxwell Montes), while the lowlands have $\varepsilon \approx 5$ which is typical of dry rock (including basalt; Pettengill et al. 1988, 1992; 1997). Bistatic radar observations of Maxwell Montes imply a large imaginary component to its relative dielectric constant, $-i100 \pm i50$ (Pettengill et al. 1997; Simpson et al. 2009) which implies that its high-ε material is lossy, i.e., like a semiconductor in which much of the incident radar energy is dissipated.

Semiconductor Materials Quests for the identity of the radar-reflective material at Venus' high elevations were active when the *Venus II* book was written and published. The first suggested materials were iron sulfides, especially the semiconductor mineral pyrite FeS_2 as a weathering product of basaltic rock (Pettengill et al. 1992; Ford and Pettengill

1983), although relatively large proportions of pyrite would be required to match the observed permittivity. Weathering at lower elevations (higher temperatures) would presumably have produce a mineral product with a low permittivity, like magnetite, and the transition from magnetite to pyrite (e.g., reaction (5)) would lead to a sharp transition in permittivity, a "snow line." Later, Klose et al. (1992) and Wood (1997) championed the idea of pyrite, and argued that the constituent elements of pyrite were readily available (Fe from basalt, S from the atmosphere), and that pyrite was a stable and expected weathering product, given the observed abundances of SO_2 and COS (at a single time, averaged over the lower atmosphere) and the assumption of equilibria among C–O–S gases.

However, B. Fegley and colleagues objected strongly to the presence of pyrite, arguing that the Venus atmosphere was too oxidizing for its formation (Fegley and Treiman 1992; Fegley et al. 1992, 1995a, 1995b, 1997a, 1997b; Hong and Fegley 1997, 1998). Their argument relied on the abundances of S_3 measured by the Venera 11–14 landers from the Venera 13 and 14 spacecraft (mixing ratios of $1.5\text{–}8 \times 10^{-11}$) between 5 and 25 km elevation and calculated abundances of other S gas species (Fegley et al. 1997b). Their calculations showed that pyrite would not be stable at the measured S_3 abundances, over a wide range of possible oxidation states, and the inference that C–O–S gases are kinetically inhibited from equilibration at Venus' higher altitudes. Experiments by Fegley et al. (1995a, 1995b) showed that pyrite reacts rapidly to hematite under a model Venus atmosphere, but their experimental design was flawed (Wood and Brett 1997).

Other semiconductor materials have been evaluated, ranging from tellurium and germanium (Pettengill et al. 1996) to a wide range of halide and chalcogenide compounds (sulfides, selenides etc.; Brackett et al. 1995). For such compounds to be present in abundances to match the radar properties of the Venus highlands would require significant enrichments above what could be expected in Venus surface rocks themselves (Brackett et al. 1995). To solve this problem, Brackett et al. (1995) modeled elemental transport from Venus' high-temperature lowlands through the atmosphere to the cooler highlands. Some potential compounds are no longer considered candidates, e.g. tellurium itself, because they are thermochemically unstable (Shaefer and Fegley 2004). Others, for which thermochemical data are lacking, have been shown unsuitable in laboratory experiments (Kohler et al. 2012, 2013, 2014; Guandique et al. 2014). The semiconductor materials thus far studied that still considered suitable as of this writing include Bi, Hg, S and Te compounds including tellurobismuthite (Bi_2Te_3), and coloradoite (HgTe) (Kohler et al. 2014, 2015; Guandique et al. 2014; Port et al. 2016; Port et al. 2017).

Other Materials In parallel with these discussions of pyrite, other potential high-ε semiconductors were evaluated. Fegley et al. (1992) considered and rejected ilmenite and rutile ($FeTiO_3$, TiO_2) as possible high-ε phases, and found that the mineral perovskite, $CaTiO_3$, might be suitable because of its very high ε value. However, perovskite is very rare in terrestrial igneous rocks, and is uncommon even where it does occur such as in strongly silica-undersaturated rocks like carbonatites. To achieve the high ε values of the Venus highlands would require perovskite abundances of 10 s of percent by mass, and there is no evidence, at this point, that Venus' rocks or highlands contain such rocks.

Geological investigations of the Ovda Regio highlands suggested a different sort of materials with high relative permittivity—ferroelectrics. Detailed mapping of the Ovda highlands (Shepard et al. 1994; Arvidson et al. 1994) showed that radar emissivity decreased (and reflectivity increased) with increasing elevation, but that there was a precipitous increase in emissivity (decrease in reflectivity) above elevations of ∼6056 km, as one approached Ovda's highest elevations. These results have been confirmed at smaller spatial scales with Magellan SAR reflectivity and stereo elevations (Harrington and Treiman

2015). Similar changes in emissivity/reflectivity are seen on most near-equatorial highlands at ~6056 km: Theia Mons, Devana Chasma, Ganis Chasma, and Tepev Mons (Campbell et al. 1994, 1999). Ozza Mons shows similar changes in emissivity but at a slightly lower elevation of ~6054 km (Campbell et al. 1999). Of the equatorial highlands of this elevation, only Maat Mons does not show this emissivity pattern (Campbell et al. 1999).

The altitudinal changes in emissivity/reflectivity in the near-equatorial highlands are consistent with those of a ferroelectric substance (Shepard et al. 1994)—one with a crystal structure that maintains a permanent electric dipole moment. As a ferroelectric substance is heated, it may change to para-electric (without a permanent dipole) at its Curie-Weiss temperature; at that temperature (i.e. elevation on Venus), the substance's permittivity rises enormously, followed (as temperature continues to rise) by a gradual decline in permittivity to normal values (Shepard et al. 1994). Because the intrinsic permittivity of a ferroelectric compound can be so large (e.g., 10^5), rock would need only contain ~0.1–10% of a suitable ferroelectric mineral (depending on its crystal shape) to have the radar properties of these Venus highlands (Shepard et al. 1994).

Despite the attractiveness of a ferroelectric substance in explaining the radar properties of near-equatorial highlands, no likely substance has been identified. Shepard et al. (1994) listed several substances, all of which are exceedingly rare or unknown in terrestrial basaltic rocks (like $KNbO_3$ and $PbTa_2O_6$). In fact, very few minerals are ferroelectric at room- and high-temperatures, which makes the widespread occurrence of low-emissivity regions even more peculiar. A possible ferroelectric phase in Venusian rocks would be apatite, $Ca_5(PO_4)_3$(F, Cl, OH), which can be a minor constituent of igneous rocks (Treiman et al. 2016). The structure of apatite and its solid solutions involve many subtle complications (Hughes and Rakovan 2002), and some varieties of chlorapatite are ferroelectric; measured Curie-Weiss temperatures are near 350 °C or above 400 °C (Rausch 1976; Bauer and Klee 1993), and it is not clear whether higher Curie-Weiss temperatures are possible. Similarly, it is possible that anhydrous calcium phosphates (related to merrillite ($Ca_{18}Na_2Mg_2(PO_4)_{14}$), and whitlockite ($Ca_9(Mg, Fe^{++})(PO_4)_6(PO_3OH)$)) could be ferroelectric at Venus surface conditions (Lazoryak et al. 2004). It is also possible that thin films of bulk paraelectric materials might act as ferroelectrics (Lang et al. 2013). Clearly, much work remains.

Although most researchers ascribe these changes in permittivity to a ferroelectric substance, Campbell et al. (1994, 1999) have ascribed them to physical changes associated with weathering. They invoke porosity variations caused by temperature-dependent chemical weathering (of unspecified nature), which is consistent with the observed enhancements of linear radar polarization in these areas. However, the regions of enhanced linear polarization are not coincident with those of high ε at Theia and Tepev Mons (Carter et al. 2006), suggesting that these properties are not reflecting the same material characteristic or phenomena.

Different Properties, Different Processes The attentive reader will have noted that explorations of semiconductor and similar materials in the Venus highlands have focused on Maxwell Montes, while explorations of ferroelectric materials have focused on Ovda Regio. In fact, the radar properties of Maxwell Montes and Ovda Regio (and other near-equatorial highlands) are distinctly different and therefore must have different causes (Treiman et al. 2016). Both Maxwell and Ovda (Fig. 5) do show gradual increases in radar backscatter coefficient (radar brightness) from ~0.05 in the lowlands plains up to ~0.15 at 4 km above the datum (6051 km radius), but at higher elevations their radar behavior diverges totally (Fig. 5). In Ovda and other equatorial highlands, radar backscatter coefficient increases

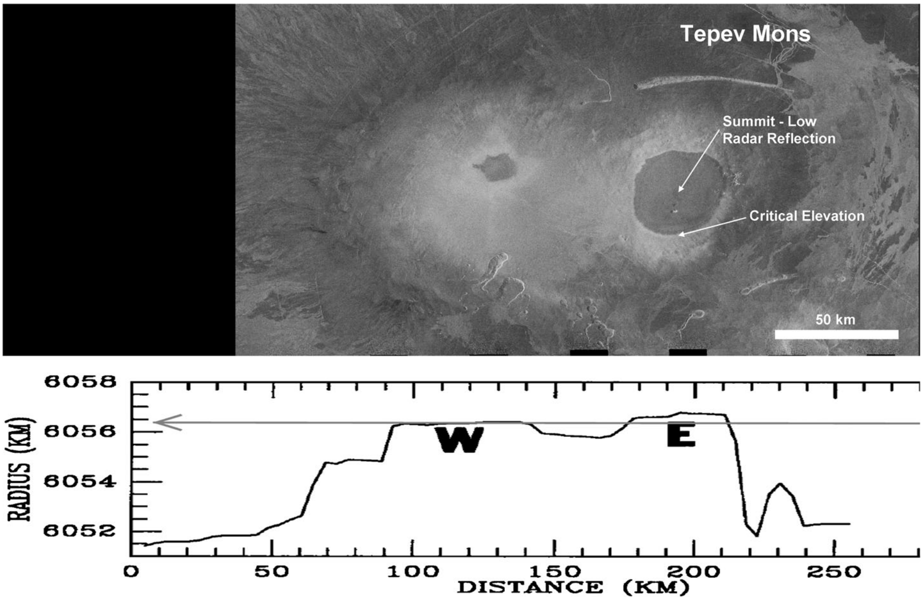

Fig. 4 Tepev Mons in SAR with elevation profile from Campbell et al. (1994). A change from increasing radar brightness to radar dark materials with elevation correspond to changes in dielectric properties of the surface, from Treiman et al. (2016)

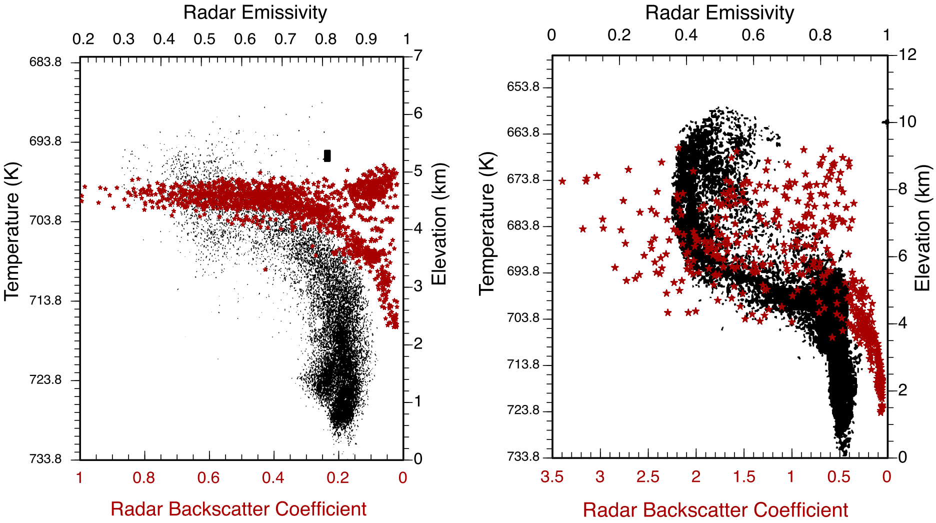

Fig. 5 Comparison of radar backscatter (*red*) and radar emissivity (*black*) on Ovda and on Maxwell, from Treiman et al. (2016)

asymptotically with increasing elevation to >1 at ~4.7 km (~6055.7 km radius), and then drops precipitously to values <0.1 again. There is no indication in Ovda or other equatorial highlands that the radar backscatter coefficient changes with further increase in altitude (e.g. Tepev Mons, Fig. 4). On Maxwell Montes, however, radar backscatter coefficient and emissivity continue their trend of slow change from the lowland plains up to ∼5 km above the datum. At approximately that elevation, radar backscatter jumps up to ∼2, the so-called snow line (Fig. 5), with a concomitant decrease in emissivity from ∼0.8 to ∼0.5. Both backscatter and emissivity values for Maxwell show significantly more scatter than for Ovda, which certainly represents the extreme roughness of the Maxwell highlands (Head et al. 1985; Ford and Pettengill 1992) superimposed on variations in material properties. On Maxwell, there is no evidence at all for a precipitous decrease in radar backscatter at any elevation, although backscatter does appear to decrease slightly at Maxwell's highest elevations (Fig. 5).

From these data, it seems impossible that the radar properties of Maxwell and Ovda could have the same causes. If there were ferroelectric substances near the surface of Maxwell, we should see at some elevation a precipitous drop in radar reflectance and in increase in emissivity. Those features are not observed at Maxwell, so its surface materials do not contain whatever mineral in suitable abundance to be visible.

Similarly, if the Ovda area were being weathered to form a semiconductor material, that should appear as a snow line (whether ferroelectric materials are also present). No snow line is observed, so Ovda's surface materials cannot contain the same semiconductor substance(s) as does Maxwell.

The causes of this difference between Maxwell Montes and Ovda Regio (and the other near-equatorial highlands) are entirely unknown, but one can speculate on differences in rock composition or in atmosphere composition. It has been suggested that Ishtar Terra could be a 'continent' composed of silicic igneous rocks (e.g., granite, granodiorite; Phillips and Malin 1984; see Campbell and Taylor 1983); the near-equatorial volcanoes are generally considered as basaltic, while there is uncertainty about the rock types in tesserae like Ovda and others (e.g., Ivanov 2001; Hashimoto et al. 2008; Basilevsky et al. 2012; Romeo and Capote 2011). The low-elevation Venus atmosphere has been considered to be well-mixed and homogeneous, but the recent recognition of massive polar vortices at the cloud tops (e.g., Garate-Lopez et al. 2013) raise the possibility that the near-surface atmosphere near the poles (as Maxwell is) might be different from that near the equator. Again, much work remains.

4 Implications for Venus Composition and Geologic History

4.1 Does Venus have Differentiated Crust?

The relatively low radiance flux anomaly and derived 1 µm emissivity measured for several regions of tessera terrain by VIRTIS, VMC and Galileo NIMS are consistent with several rock types for the tesserae that include, but are not limited to, felsic mineralogies.

4.1.1 Tesserae may be Felsic

The lower than global average 1 µm emissivity values for tesserae are consistent with felsic mineralogies due to the lower Fe content of these rocks relative to basalts. Most granitoid rocks on Earth form via hydrous melting of mantle, continental crust and/sediments (e.g., Campbell and Taylor 1983; Brown 2013). In modern settings, this occurs primarily at subduction zones and zones of crustal collision. The chemistry of Archean granitoids is consistent with melting of hydrated basalts and eclogites within the lower crust (e.g., Martin et al. 2005). Each of these mechanisms require both water and a plate recycling mechanism

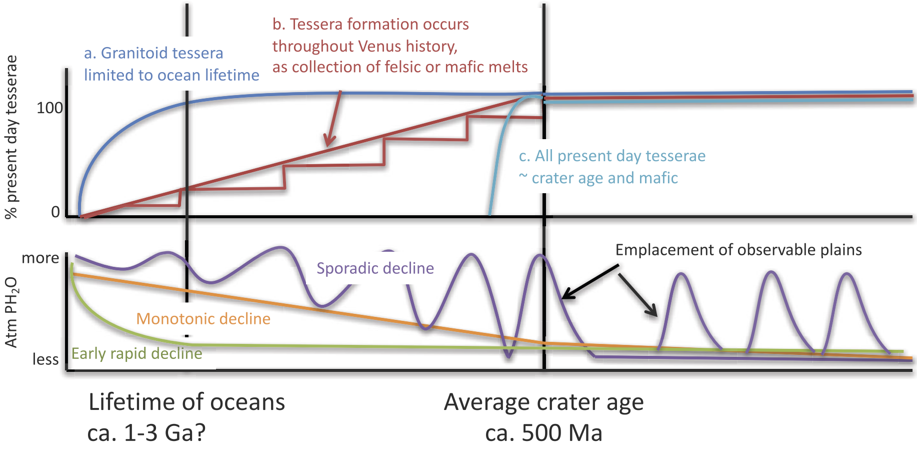

Fig. 6 Schematic diagram of tessera formation (*upper panel*) and atmospheric H_2O (*bottom panel*). Several models of water loss can be envisioned including early, rapid loss (e.g., Kasting and Pollack 1983), monotonic decline (e.g., Grinspoon 1993), or sporadic decline such as that predicted in catastrophic overturn models (e.g., Grinspoon and Bullock 2007). (**a**) The formation of continents' worth of felsic tesserae terrain is limited to the lifetime of oceans on Venus. (**b**) Tessera terrain could be produced by the aggregation of small volumes of felsic melt or weathering of mafic melts. (**c**) Tesserae formed just prior to plains emplacement. Recent volcanism may contribute to steady or sporadic influx of volatiles into the atmosphere resulting in changing weathering regimes

to allow the production of the volumetrically significant volumes of felsic melts that comprise the bulk of Earth's continental crust. In this scenario tessera formation would be tied to ocean lifetime and the tesserae would be relicts of that era (Fig. 6a).

Silicic magmas can also be produced by the differentiation of mafic melts (e.g., Spulber and Rutherford 1983) under conditions of low water content. This mechanism has been invoked to explain the limited occurrence of felsic rocks on the Moon (Hagerty et al. 2006; Glotch et al. 2010), Mars (Whitaker et al. 2005; Wray et al. 2013; Rogers and Nekvasil 2015), asteroidal meteorites (Bonin 2012 and references therein) and Venus (Shellnutt 2013; Filiberto 2014). The efficiency of this process is low, where the volume of felsic melts formed via fractional crystallization of mafic magma is $\sim$10% of the parent melt volume (Spulber and Rutherford 1983). Assuming an average crustal thickness of tesserae of 20 km, consistent with admittance estimates (Anderson and Smrekar 2006), yields a total volume of tesserae crust of $\sim 7 \times 10^8$ km^3. This could be formed via the differentiation of $\sim 7 \times 10^9$ km^3 of mafic melt, which is an order of magnitude more melt than is estimated to be preserved in the lavas of the present-day plains of Venus (Ernst et al. 2007). This implies that if tesserae were granitoids formed via this process, they would have had to form from magmatism that exceeds and thus precedes the eruption of the current Venus plains. This would argue that the tesserae may have formed through the bulk of Venus history (Fig. 6b) and were assembled into their present-day configuration. The identification of fold belts at tesserae boundaries is consistent with lateral compression and obduction of materials at tesserae boundaries (Gilmore 2009; Romeo and Capote 2011) which supports this mechanism, whatever the composition of the tesserae. This and the widespread distribution of low-lying tesserae inliers amongst the plains suggest tesserae terrain may have been more widespread than what is visible today.

4.1.2 Tesserae may be Mafic

As described in Sect. 3.2 the chemical weathering of mafic rocks on Venus today occurs in a low P_{H_2O} environment and is predicted to produce hematite and anhydrite. With higher atmospheric P_{H_2O}, the weathering of basalts might go to completion where in the top 10 s of microns, all Fe is converted to hematite and all Ca in pyroxene and plagioclase is converted to anhydrite. McCanta et al. (2014) show that basalts weathered under SO_2-rich volcanic gases in Hawaii alter to amorphous silica and sulfates, which have high 1 µm reflectance (and thus low emissivity) in spectra collected under terrestrial conditions (Milliken et al. 2008; Cloutis et al. 2006). Massive volcanic outgassing, as has been invoked to produce the Venusian plains, has been modeled to lead to cloud formation and a temporary reduction in surface temperatures (Bullock and Grinspoon 2001). Such an extinct low-temperature, high P_{H_2O} environment should favor the production of carbonates via the weathering of Ca and Mg silicates (Zolotov 1996). Such carbonates, if formed, are predicted to react with the present-day atmosphere to form sulfate minerals (Fegley and Prinn 1989; Zolotov et al. 1997) with high 1 µm reflectance (Cloutis et al. 2006).

It is also possible that the tesserae comprise basalts weathered on a Venus with an active hydrological cycle. At the current oxidation state, we would expect basalts to weather to ferric oxides, phyllosilicates such as smectites and chlorites and potentially amphiboles (e.g., Eggleton et al. 1987; Ferry et al., 1987; Bain et al. 1980; Johnson and Fegley 2000). Experiments and thermodynamic modeling show that hydrous silicates can form on Venus at >40 ppm atmospheric H_2O at current pressure and temperatures (Cathala et al. 2017). At room temperature, the spectra of phyllosilicate minerals that lack ferrous iron are dominated by vibrational features in the infrared and have high reflectance (low emissivity) at 1 µm (e.g., Hunt and Salisbury 1970). Hydrated phyllosilicates are not stable under current surface conditions of high temperatures and low water content and are predicted to break down via dehydration, oxidation and/or sulfitization (Zolotov et al. 1997), nevertheless, the smectites saponite and montmorillonite retain high reflectance values at 1 µm even when dehydrated under present-day Venus temperatures (Bruckenthal and Singer 1987; Gavin and Chevrier 2010).

4.2 Tesserae and Venus Evolution

The Venus surface has a population of ∼1000 impact craters which yield an average crater retention age of ∼300 Ma (Strom et al. 1994) to ∼1 Ga (McKinnon et al. 1997). The apparent spatial randomness of the crater population on the surface of Venus and rarity of obvious volcanically embayed craters (Phillips et al. 1992; Schaber et al. 1992) can be produced by a geologically rapid emplacement of that surface (e.g., Schaber et al. 1992) by varying methods (e.g., Turcotte et al. 1999; Arkani-Hamed 1993; Parmentier and Hess 1992). Alternatively, the crater record has been modeled to result from steady state geologic processes that are a consequence of secular cooling of the planet (Phillips et al. 1992; Solomon 1993; Herrick 1994; Solomatov and Moresi 1996). These "catastrophic" vs. "equilibrium" models depend critically on the number of geologically modified craters and the assumptions made about the rate and extent of volcanic resurfacing in models of the crater size-frequency distribution (e.g., Campbell et al. 1999; Herrick and Sharpton 2000; Bjonnes et al. 2012; Romeo 2013; O'Rourke et al. 2014; Ivanov and Head 2013). Perhaps the most critical observation is whether dark-floored craters have suffered volcanic infilling and embayment which supports continuous resurfacing (Herrick and Sharpton 2000; Herrick and Rumpf 2011).

Regardless of the resurfacing model, the apparent average crater age of ∼300–1000 Ma is the single datum in the stratigraphic column of Venus. The bulk of the surface including the plains and volcanoes was emplaced since that time. Here we describe a timeline for Venus based on a mean resurfacing age, the time before, and the time since, in context of surface composition (Fig. 6).

The tesserae are consistently stratigraphically older than the plains with a crater age 1 to 1.4× the global average (Ivanov and Basilevsky 1993; Gilmore et al. 1997). The lack of widespread deformed craters or crater-like features within the tesserae shows that this age is certainly the last deformation age, but there are no constraints on the formation age of tessera materials. The tesserae are our only record of an earlier period in the history of the planet. Confirmation of specific rock types in the tesserae would provide critical insights into an early period of Venus' history.

4.2.1 Venus as Earth—Hydrated Plate Recycling

As described above, the formation of significant volumes (continents' worth) of granitoid magmas can occur via several mechanisms, but each of these mechanisms requires both water and a plate recycling mechanism for formation. If we assume that Venus and Earth had similar volatile inventories at the outset as it suggested by models for accretion (e.g., Morbidelli et al. 2012), the high D/H ratio of the Venusian atmosphere (Kumar and Taylor 1984; de Bergh et al. 1991; Krasnopolsky 2010) is consistent with the loss of a significant inventory of water over the history of the planet. There is debate about the volume and rate and mechanisms of water loss, yielding estimates of the lifetime of a Venus ocean that range from 600 Ma (Kasting and Pollack 1983) to ∼2 Ga (Grinspoon and Bullock 2007) or ∼3 Ga (Way et al. 2016). Although our knowledge of interior volatiles is limited even on Earth, Venus appears to have lost less of its original volatile inventory than Earth (Kaula 1999; O'Rourke and Korenaga 2012).

Thus, if all tesserae are confirmed to be granitic, they may be relicts from an earlier era, possibly from an ancient period when Venus had oceans (Fig. 6a). As on Earth, any felsic crust should be buoyant to instability and thus once formed should persist through time. Romeo and Turcotte (2008) present a model where remnant continental crust on Venus can survive multiple, periodic subduction events that may trigger global plains emplacement (Turcotte et al. 1999). Confirmation of granitic tesserae terrain would elevate their importance for future investigation as they may have formed on a more habitable Venus.

We note that a Venus with felsic crust would also have implications for atmospheric-surface interactions and buffering reactions that affect atmospheric species, water vapor abundance, pressures and temperatures. For example, Schaefer and Fegley (2011) consider three types of Venus-sized exoplanets: a hot atmosphere with a mafic surface, a cold atmosphere with a mafic surface and a cold atmosphere with a felsic surface, and show that only in the first case can they produce a planet with temperature and CO_2 partial pressure greater than present-day Venus. It is clear that further study of Venus critically informs our understanding of the generation of Earth-sized planets and the position and duration of the habitable zone.

4.2.2 Venus as Venus—Delamination of a Single-Plate

As described above, the melting and differentiation of mafic magmas can produce felsic melts. Increased volatile content enhances melt production by depressing the solidus. At issue is whether the dry atmosphere and surface of Venus necessitates a dry mantle. Smrekar et al. (2007) argue that the interior likely retains a primordial volatile content that is modified through time by melting. Elkins-Tanton et al. (2007) elaborate on this idea by proposing that Venus may have active recycling in the form of plume volcanism and lithospheric delamination providing a range of melting environments and source regions and a mechanism to recycle volatiles within the mantle. They show that a wide range of melt compositions can be produced from the melting of perioditic to eclogitic sources regions hydrated to varying degrees—a mechanism that has been invoked to explain the production the granitoids in the Archean (Martin et al. 2005). This provides a means to produce granitoids throughout Venus history as a consequence of convection on a one-plate planet.

The recognition of a range of felsic melt compositions associated with spatially limited domains in the tesserae might support formation by the collection over time of relatively meager volumes of felsic melts associated with mafic differentiation (e.g., Shellnutt 2013). In this scenario, the continental-size tesserae plateaus observed today may have been formed piecemeal throughout geologic history and represent a range of formation ages (Fig. 6b), and perhaps compositions, later reset by deformation ca. the average crater retention age. The differences between the weathering products of Maxwell and Ovda (Sect. 3.2.2), the assembly of tesserae of varying morphology (Ivanov 2001; Straley and Gilmore 2007) and the complex history of plateaus on Earth all caution us to remember that all tesserae are not necessarily alike. This may be a consequence of such an incremental formation mechanism.

4.2.3 Venus in Catastrophe

The rapid, global emplacement of volcanic plains as described in catastrophic resurfacing models will release large quantities of gases into the atmosphere and thus alter planetary climate. Bullock and Grinspoon (2001) used a numerical climate model to investigate the consequences of a massive influx of H_2O and SO_2 into the Venusian atmosphere accompanying global volcanic eruption 600–1100 Ma that lasted 10–100 Ma. Their models predict an initial cooling period of 100–300 Ma due to the formation of clouds followed by an increase in surface temperatures for 200–500 Ma after resurfacing. An effect of this climate perturbation is to temporarily alter the weathering regime and consequent mineralogy of the surface.

Given the stratigraphic position of tessera terrain, the catastrophic resurfacing model predicts that the tesserae and the earliest erupted (and observable?) plains would have weathered under conditions of higher atmospheric P_{H_2O}. An increase of atmospheric water vapor would oxidize the surface materials and act to speed the kinetics of all chemical reactions, thereby significantly weathering the surface. Higher water content will also change the stability fields the minerals produced by atmospheric/surface reactions (Zolotov 2007). As discussed in Sect. 4.1.1, enhanced weathering of basalts under an enhanced P_{H_2O} atmosphere may produce surface minerals consistent with the low emissivity seen in the VIRTIS data. Such tesserae could be the relicts of plains materials older than the average age deformed and incorporated into tessera terrain (Fig. 6a, b, c).

We note that each of the above scenarios may apply to tessera inliers, which are spatially limited regions of tesserae that often lie at plains elevations. Several papers have suggested that they may be relaxed earlier plateaus, or the result of small scale melting events. If these inliers are more relaxed tesserae, that could be due to: (1) formation on early Venus, when the lithosphere was hotter, (2) formation in the presence of more water that lead to a weaker composition, (3) greater/longer dehydration after formation, (4) more relaxation during a hotter climatic period. These inliers are a reminder that all tesserae are not necessarily of similar composition, age or origin. Higher resolution maps enabled by new measurements of tessera morphology, topography and emissivity will greatly enhanced our understanding of the diversity of this terrain.

4.3 Is Venus Active?

There are several indirect but independent lines of evidence that support ongoing volcanism on Venus, which is expected by analogy with Earth. The relatively fresh basalts inferred from the VIRTIS data by Smrekar et al. (2010) are interpreted to yield ages of no more than 2.5 Ma; this would presumably also apply to any high 1 µm emissivity flows (e.g., Helbert et al. 2008; D'Incecco et al. 2017). This estimate is based on crater degradation ages, rates of resurfacing and rate of basalt weathering, each of which is loosely constrained. The absence of enhanced microwave reflectivity at the summit of Maat Mons has been interpreted by Klose et al. (1992) to result from young flows resurfacing at rate greater that the chemical process responsible for this phase change. Again, experimental work is required to assess the reactants and kinetics of this transition.

As discussed in Sect. 3.2.1, the amount of atmospheric SO_2 today is higher what it is predicted to be if equilibrated with the surface, requiring a sulfur source in the past ca. 1–10 Mya (Fegley and Prinn 1989; Bullock and Grinspoon 2001). Fluctuations in SO_2 abundance were measured by Pioneer Venus orbiter (Esposito 1984) and by Venus Express (e.g., Marcq et al. 2013), consistent with variable input via volcanism. As noted in Sect. 3.2.1, it is wise to consider the effects of such variable inputs to the chemistry and geographical distribution of surface-atmosphere interactions.

Transient high emissivity anomalies have been detected in the VMC data spatially associated with the Ganiki Chasma rift zone in northern Atla Regio (Shalygin et al. 2015). The magnitude of the anomalies exceeds what is predicted from surface emissivity alone and is attributed to elevated temperatures consistent with those expected for lava flows as observed by VMC. This area contains stratigraphically young flows and faults, some of which are superposed onto parabola deposits. The transient nature, and the locations of these anomalies supports their interpretation as lava flows and are possible evidence of active volcanism on Venus.

Lastly, Whitten and Campbell (2016) use Magellan data to show that some tessera slopes have a radar-dark backscatter near impact craters. They interpret this to represent sedimentary mantles derived from the airfall deposits associated with impact craters. Mantling deposits in the tesserae are also seen in circular polarized Arecibo data (Campbell et al. 2015). Provocatively, Whitten and Campbell (2016) also see radar-dark slopes in tesserae that lack a nearby crater. They interpret that this material represents the parabola deposit from a crater removed by volcanic resurfacing in the past 80 My, thus, providing independent evidence of recent volcanic activity of Venus.

5 Conclusions

Since the *Venus II* book, we have made several important strides in the understanding of the planet's surface. The VIRTIS instrument enables for the first time the measurement of broad-scale inferred mineralogy of the Venus surface. Surface units can now be defined in terms of their 1 µm emissivity and show variation that distinguish units within tesserae, the plains and recent lava flows. Tesserae are found to differ from the plains in a manner consistent with felsic or weathered materials and require formation in an era different than today. Measurement of Venus analogue rocks under Venus conditions will help verify these observations.

The surface of modern day Venus weathers at 740 K under a 92 bar CO_2 atmosphere encircle by clouds comprised of several sulfur species. Basalt surfaces are predicted to undergo several reactions including the oxidation of Fe and precipitation of anhydrite. The VIRTIS observations of correlations between high emissivity anomalies and stratigraphically young flows supports the experimental prediction that Venus basalts are oxidizing over time. Improved measurement of the kinetics of surface-atmosphere reactions is critical to constrain their products and speed which may differ geographically due to variations in surface and/or atmospheric composition.

Independent lines of evidence suggesting a volcanically active Venus drive investigations of renewed mapping, modeling and new observations of the surface radar, topography, gravity and infrared wavelengths. These techniques are also required for addressing the critical question of the origins of tesserae which may have formed on a more clement and potentially habitable Venus. Every effort should be applied to study this important planet.

Acknowledgements We appreciate discussions with Justin Filiberto, John Grotzinger, and Bruce Fegley. We thank the reviewers who provided very helpful comments.

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