Carbonate–Sulfate Volcanism on Venus?

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Received April 4, 1994; revised September 12, 1994

Venusian canals, outflow channels, and associated volcanic deposits resemble fluvial landforms more than they resemble volcanic features on Earth and Mars. Some canals have meandering habits and features indicative of channel migration that are very similar to meandering river channels and flood plains on Earth, venusian outflow channels closely resemble water-carved outflow channels on Mars and the Channeled Scabland in Washington, collapsed terrains at the sources of some venusian channels resemble chaotic terrains at the sources of martian outflow channels, venusian lava deltas are similar to bird’s-foot deltas such as the Mississippi delta, and venusian valley networks indicate sapping. The depositional fluvial-type features (deltas, braided bars, and channeled plains) are generally among the smoothest terrains at the Magellan radar wavelength (12.6 cm) on Venus. These features suggest the involvement of an unusual lava, unexpected processes, and/or extraordinary eruption conditions. Possibly the lava was an ordinary silicate lava such as basalt or a less common type of silicate lava, and conditions unique to Venus or to those particular eruptions may have caused an unusual volcanological behavior. We have developed the alternative possibility that the lava had a water-like rheology and a melting point slightly greater than Venus’ surface temperature, thus accounting for the unusual behavior of the lava. Unlike silicate lavas, some carbonatites (including carbonate–sulfate-rich liquids) have these properties; thus they can flow great distances while retaining a high fluidity, significant mechanical erosiveness, and substantial capacity to transport and deposit sediment. Venustian geochemistry and petrology are consistent with extensive eruptions of carbonatite lavas, which could have crustal and/or mantle origins. Venus’ atmosphere (especially CO₂, HCl, and HF abundances) and rocks may be in local chemical equilibrium, which suggests that the upper crust contains large amounts of calcite, anhydrite, and other salts. Chemical analyses indicate, according to some models, that Venustian rocks may contain 4–19% calcite and anhydrite. Mixtures of crustal salts could melt at temperatures a few tens to a few hundred Kelvins higher than Venus’ surface temperature; hence, melting may be induced by modest endogenic or impact heating. Salts may have many of the same geologic roles on Venus as water and ice have on Mars. A molten salt (carbonatite) “aquifer” may exist beneath a few hundred meters to several kilometers of solidified salt-rich “permafrost.” Many geologic features can be explained by carbonatite magmatism: (1) impact melting of crustal salts can explain crater outflows, (2) small, sustained eruptions from molten salt aquifers can explain sapping valleys, (3) large, sustained eruptions may explain canali and their flood plans, and (4) catastrophic outbursts may have formed outflow channels and chaotic terrain. Landforms created by carbonate-rich lavas would be thermally stable on Venus’ surface, though some minerals may weather to other solid substances. © 1994 Academic Press, Inc.

I. INTRODUCTION

Magellan synthetic aperture radar images (12.6 cm wavelength) of Venus show volcanic features unmatched elsewhere in the Solar System for variety, freshness, and abundance (Head et al. 1992). Thick, steep-sided domes and flows were formed by eruptions of highly viscous and perhaps siliceous lavas (McKenzie et al. 1992, Moore et al. 1992, Pavri et al. 1992). Evidence for lavas of moderately low viscosity (probably mafic silicate lavas) is widespread; it includes small volcanic cones, shields, huge lava flow fields, lunar-type sinuous rilles, and lava plains (Baker et al. 1992, Guest et al. 1992, Head et al. 1992, Roberts et al. 1992). Mafic silicate lavas dominate Venus’ surface, according to interpretations of Magellan, Venera, and VEGA data (Surkov et al. 1983, 1986; Garvin et al. 1984; Basilevsky et al. 1985; Barsukov et al. 1986; Barsukov 1992; Kargel et al. 1993). Although there
may be a considerable overlap of major types of lava on Venus and Earth, some lavas that are rare or exotic on Earth may be common on Venus. For instance, Hess and Head (1990) suggested that a dry venusian mantle should yield large amounts of silica-undersaturated ferrobasalt and ultramafic lava and minor amounts of siliceous lava compared to what the Earth’s mantle generates. A possibility that carbonatite volcanism might occur on Venus was suggested by Sill (1984). Such unusual lavas may have important implications for venusian volcanology and might explain some of the more peculiar Venussian volcanic landforms.

Some venusian volcanic landforms resemble terrestrial fluvial counterparts more than any terrestrial volcanic features. This paper summarizes some characteristics of these venusian features and develops a possible origin—they may have been produced by unusually fluid, low-temperature lavas of an extraordinary composition, such as molten mixtures of carbonates, sulfates, and other salts (Kargel et al. 1991, Baker et al. 1992, Komatsus et al. 1992b, Gregg and Greeley 1994, Komatsus and Baker 1994, Treiman 1994a). This possibility is raised because there are indications that these solids may be present on Venus’ surface in substantial amounts (Table 1) and that they may melt to a low-viscosity liquid at temperatures just slightly higher than Venus’ surface temperatures. Furthermore, Venus is known to have strongly silica-undersaturated mafic silicate lavas similar to some on Earth that are petrogenetically related to and commonly associated with carbonatites. We are not presently concerned with the logical alternative that Venus’ fluvial-type features might have been formed by ordinary mafic silicate lavas erupted under extraordinary conditions (Komatsus et al. 1992a, b; Head et al. 1992; Gregg and Greeley 1993; Kargel et al. 1993).

This work (1) presents new observations of venusian volcanic landforms produced by low-viscosity lavas, (2) reinforces proposed fluvial analogies of these features, (3) summarizes the stability of solid and molten salts (including carbonatite lavas), (4) reviews the physical chemistry of carbonatite, and (5) presents selected models illustrating possible Venussian magmatic processes involving carbonatite. The term “carbonatite,” following terrestrial volcanological usage, may include lavas that contain high abundances of noncarbonate salts (especially sulfates, but also chlorides, fluorides, and phosphates) and certain silicate and oxide phases.

II. LOW-VISCOSITY VENUSIAN LAVAS AND THEIR VOLCANIC LANDFORMS

Lunar-Type Sinuous Rilles: A Familiar Volcanic Landform without Fluvial Analogues

Venusian sinuous rilles are similar to those on the Moon and Mars (Baker et al. 1992, Komatsus and Baker 1994), which suggests formation by similar volcanic processes and thermophysically comparable lavas. Sinuous rilles typically (1) are 10–300 km long; (2) are several hundred meters to several kilometers wide; (3) have large depth to width ratios; (4) narrow and shallow downstream until they fade completely; (5) commonly have long stretches of straight channels (suggesting tectonic control) or, where meanders occur, their loops are tight and commonly have cuspatc inner bends; (6) have almost no channel bifurcations, braided bars, levees, crevasse splays, or cutoff meander loops (oxbows); and (7) do not have meander scroll bars or terminal lava deltas comparable with those of venusian canali.

Evidence for Lateral Migration of Canali: Meanders, Oxbows, and Scroll Bars

Canali (singular, canale), known only on Venus, are an unusual class of channels characterized by (1) lengths generally >500 km, and in one case >6800 km (the longest channel in the Solar System); (2) widths of ~1–5 km; (3) small ratios of depth to width compared with other types of volcanic channels; (4) little longitudinal variation in depths and widths (Baker et al. 1992; Komatsus et al. 1992b, 1993; Komatsus and Baker 1994); (5) evidence of lateral channel migration, such as mature meander patterns, abandoned meanders, meander scroll ridges, and cutbanks; and (6) an absence of cuspatc inner bends of meanders.

<table>
<thead>
<tr>
<th>TABLE I</th>
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<td>Modeled Abundances of Calcium Salts in Venussian Rock Samples</td>
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<tr>
<th>Sample site</th>
<th>Calcite (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Anhydrite (wt%)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Total calcium salts (wt%)</th>
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<tr>
<td>Venera 13</td>
<td>4.3 ± 4.3</td>
<td>2.8 ± 1.7</td>
<td>7.1 ± 4.6</td>
</tr>
<tr>
<td>Venera 14</td>
<td>3.0 ± 3.0</td>
<td>1.5 ± 1.3</td>
<td>4.5 ± 3.3</td>
</tr>
<tr>
<td>VEGA 2</td>
<td>10.5 ± 10.5</td>
<td>8.0 ± 2.6</td>
<td>18.5 ± 10.8</td>
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<sup>a</sup> Calculated from oxide abundances given by Surkov et al. (1983, 1986). The calculated amounts of calcium salts would contain ~50% of the CaO of the Venera 13 sample, 20% of the CaO in the Venera 14 sample, and 90% of the CaO in the VEGA 2 sample. The remaining CaO possibly is sited primarily in perovskite and silicate phases such as diopside and plagioclase, which apparently incompletely reacted to form the calcic salts. Alternatively, smaller fractions of CaO plus some fraction of certain other components, such as MgO, Na2O, and K2O, may be contained in complex carbonate–sulfate–rich mixtures.

<sup>b</sup> Calculated on the assumption that mass deficits in X ray fluorescence analyses (after addition of calculated amounts of Na) are due to bound CO₂ (which was not analyzed) in the form of CaCO₃.
FIG. 1. Magellan SAR image of a meandering reach of a canal. The channel has an average width of about 1900 m. Narrow levees are barely resolved in some places. Lineaments running from left to right are tectonic fractures that in some places seem to superpose (postdate) the channel and in other places are cut by (predate) the channel. F-MIDR35S157.1. Center of image near lat 33.1°S, long 157.9°. Scene is 63 × 106 km. Resolution 75 m/pixel. North at 11 o'clock.

Figure 1 shows a meandering reach of a canal. The overall meander pattern is highly asymmetric and is similar to that of many terrestrial river channels, such as the Rouge River, Quebec (Lapointe and Carson 1986). The mean width of the canal is 1900 m, and the wavelength of major meanders is ~19 km. The channel traverses the bottom of a broad lowland trough at an elevation of about 1100 m in the area shown in Fig. 1. Along-valley gradient is ~1 m per kilometer (0.1%), a value comparable to those of the Arkansas and Missouri rivers and other streams of the Great Plains of North America. The volcanic plains of Fig. 1 are very smooth in SAR images (resolution ~100 m); root-mean-square (rms) slope of this area is only 1.6°, indicating that this terrain is among the smoothest on Venus at scales equivalent to and larger than Magellan's radar wavelength (12.6 cm). Radar reflectivity is ~14% and emissivity is ~0.84 in this area, both fairly typical values for regions at this elevation.

A conservative interpretation of Fig. 1 is shown in Fig. 2; a liberal interpretation was given by Kargel (1994). The plains adjoining many canali have many features interpretable as cutoff meander loops (oxbows) and meander scroll ridges (point bars); some of these are visible in the reproduced image in Fig. 1 and are mapped in Fig. 2. These features and the mature, asymmetric meander pattern suggest extensive channel migration. Evidence for channel migration, though not shown by all canali, is extremely significant, because it implies that there was a rough balance between deposition and erosion; a similar balance is rarely if ever observed among silicate lava streams, and no such balance is inferred from the characteristics of lunar-type sinuous rilles.

The small topographic relief of oxbows and meander scrolls on Venus is a characteristic shared by meander scars on the flood plains of terrestrial rivers; meander scars are progressively buried by overbank flood deposits. By direct analogy to terrestrial flood plains, the canali plains of the Venusian lowlands may include large components of point-bar and flood-plain deposits. Flood plains are also suggested by crevasse splays (described below).

Baker et al. (1992) and Komatsu and Baker (1994) observed that the meander habits of canali are similar to those of terrestrial river channels. Additional support for the riverine analogy of canali is given in Fig. 3, which shows that the meander habits of canali resemble those of terrestrial rivers on alluvial plains and may be distinguished from sinuous rilles and terrestrial lava tubes.
Hickin (1974) observed that terrestrial river meanders commonly have minimum radii of curvature ($r_m$) roughly twice the channel width ($w$). He noted that initially straight rivers are unstable, but hypothesized that too tight meander bends are also unstable; he suggested that as $r_m/w$ of a meander decreases, erosion on one bank and deposition on the other forces the channel to migrate and causes $r_m/w$ to stabilize at the critical minimum value of $\approx 2$. We have observed a similar clustering of $r_m/w$ (Fig. 3), but the dispersion of $r_m/w$ in our selection of rivers is greater than Hickin observed. A full analytical explanation for the causes and limits of river meanders has not been developed, but Hickin (1974) noted that as water flows through curved pipes, the minimum frictional resistance to flow is achieved for $r_m/D = 2$, where $D$ is pipe diameter. The meander behavior of rivers is thought to be related to a similar minimization of total resistance to flow at about twice the meander radius (Hickin 1974). Venusian canali commonly have $r_m/w \approx 2$, indicating a high maturity of the meander pattern.

The meander wavelength of terrestrial rivers is closely related to the bank-full discharge rate (Schumm 1977). The calculated discharge rate of the canale of Fig. 1 approximately fits the empirical relationship observed for terrestrial rivers (unlike venusian lunar-type sinuous rilles). This aspect will be considered under Discussion. The depth of the canale shown in Fig. 1 was determined by using a radarclinometric program called MGNSCARP, written by R. Kirk. The program can determine the height of a spatially unresolved scarp or the height and average slope of a resolved scarp. Measurements of the canale at four points along one meander
loop (~15 km east of the eastern edge of Fig. 1) gave depths of 16, 19, 20, and 42 m, or an average of 24 m. The average slope of the canale’s bank is ~6°. The depth: width ratio of this canale is ~0.013, a value typical of low-gradient rivers meandering through coarse alluvium (Schumm 1977). The depth of this canale is similar to the depth ~50 m of another canale measured by analysis of radar foreshortening (Komatsu et al. 1992b). By contrast, lunar-type sinuous rilles on the Moon and Venus have depth: width ratios generally in the range of 0.07 to 0.2 (i.e., much deeper than most river channels).

**Levees and Crevasse Splays**

Levees occur along some canali but generally not along lunar-type sinuous rilles. Levees form along the banks of terrestrial lava and river channels by accretion of solidified lava or fluvial sediment. The usual absence of levees of lunar-type sinuous rilles and the other characteristics of these channels suggests a formation primarily by erosion.

Crevasse splays are subsidiary river channels and sheetflood deposits often due to point failures of a channel’s levee. Channelized lava flows do not as commonly form crevasse splays. Like terrestrial rivers, venusian outflow channels and canali commonly have crevasse splays and sheetflood deposits tied to point sources (Fig. 4; see also Fig. 21 in Baker et al. 1992), seeming to imply the presence of levees, even where none are observed in Magellan images. The observed features further indicate that the spilled liquids maintained capacities to erode channels and to spread invasively across low-gradient plains, thus implying that they were lavas of low viscosity.

**“Fluvial” Lava Deltas of Canali and Outflow Channels**

Outflow channels (the “compound channels” of Baker et al. 1992) and canali commonly terminate in lava deltas (Figs. 5, 6). The term “outflow channel” is used here to refer descriptively to a class of channels that exhibit a complex morphology consisting of multiple braided channels and longitudinal bars. This term is commonly applied to large martian channels that have strong morphological similarities to the venusian outflow channels but have distinct origins involving outbursts of (presumably) water instead of lava.

Perhaps the best known outflow channel on Venus terminates in the spectacular delta of Kallistos Vallis, near Ammavaru (Fig. 5), which resembles the classic bird’s-foot fluvial delta (e.g., the Mississippi River delta) more than any other landform on Earth (including other types of fluvial deltas and volcanic deltas; Leeder 1982, Coleman et al. 1986, Greeley 1987). The Kallistos and Mississippi deltas have nearly straight distributary channels, and overbank splays are abundant along some of the major distributaries of both deltas. It may be significant that the Mississippi delta is dominated by fluvial sedimentation in a low-energy body of water, unlike many other deltas, whose morphologies commonly are controlled by sediment redistribution by waves or tides (Leeder 1982).

The source of Kallistos Vallis is a complex set of collapse depressions and fractures near an elevation of 1300 m; the channels descend to an elevation of 800–900 m in the region of the braided bars and delta. The average gradient is ~1 m per kilometer, although there is virtually zero gradient in the region of the braided bars and delta. By analogy with the Mississippi delta, the regional topographic relations of the delta of Kallistos Vallis suggest that it may have prograded into a lava lake that formed as lava ponded against and then drained through a low saddle in the north-trending ridge shown in Fig. 5A.

Kallistos Vallis and its delta have an average rms slope of only 1.8°, indicating a very smooth surface comparable to some of the smoothest pahoehoe lavas and other smooth terrains on Earth (Campbell and Campbell 1992). Hence, this area has very few cobbles, boulders, corrugations, or steep slopes. The lava that spilled across the natural dam, having rms slopes as high as 7°, is much rougher than the deltaic lava. The Kallistos delta appears as a discrete feature of relatively low radar reflectivity (~10%).

The volcanic delta shown in Fig. 6 terminates in a closed basin where ponding apparently occurred. The channel has a source near an elevation of 1600 m; about 800 km downstream the channel terminates in the delta of Fig. 6 near an elevation of ~400 m, indicating a comparatively steep channel gradient of ~2.5 m per kilometer (0.25%). This delta has a different morphology than that of the Kallistos delta. Instead of a small number of large and fairly straight distributary channels, the delta of Fig. 6 has numerous anastomosing distributaries. Like the Kallistos delta, the rms slopes all along the banks of the canale, in the delta region of Fig. 8, and in the area of ponded lava near the delta are very low (generally 1.6° to 3.0°), again indicating very smooth surfaces. The radar emissivity of the delta and pond area is very low, ranging from 0.82 to 0.83 (i.e., lower than most areas of Venus at this elevation), and the radar reflectivity of these areas is accordingly moderately high (~14%) for this elevation.

The delta illustrated in Fig. 6 may have formed by sediment deposition in a temporary lava lake. This delta is morphologically similar to the arctic periglacial deltas of the Yukon, Mackenzie, and Lena Rivers (Coleman et al. 1986). Permafrost and seasonal river icings are thought to be important controls on delta morphology of each of these terrestrial analogs (Coleman et al. 1986). The delta of Fig. 6 also is similar to certain terrestrial...
FIG. 4. Crevasse splays and overbank flood (lava) deposits associated with point sources on canali. (A) Magellan SAR image of a main channel and an anatomosing system of overbank crevasse splays. F-MIDRP.1950565:1. North end (source?) of rille near lat 10.9°S, long 67.5°. Scene 37 × 50 km. Resolution 75 m/pixel. North up. (B) Overbank flood deposits (moderately radar bright material, "F," no visible relief) spilled from a discrete point source of a canale ("S"), which probably indicates levee rupture. Also note channel anastomoses ("A"). The channel has no visible depth; it may be completely filled with radar-bright material. The terminal reach of the canale flares out, merging with radar-bright plains. Adjoining smooth, radar-dark plains embay or are superposed by low cratered shields, such as that at "V." Probable wrinkle ridges deform the dark plains and the radar-bright deposits of the canale. F-MIDRP.05N318:1. Center near lat 5.7°N, long 318.6°. Scene 253 × 182 km. Resolution 75 m/pixel. North up.
FIG. 4—Continued
FIG. 5. Spectacular outflow channel and flow complex of Kallistos Vallis, near Ammavaru, the largest such compound channel system on Venus. (A) This Magellan SAR image captures almost the entire volcanic channel system, including most of the source ("S"), a reach dominated by braid bars ("B"), a terminal delta ("D"), and an area where lava formerly ponded and spilled through a breach in a large tectonic ridge ("R") and finally spread out in another lava distributary network ("N"). Large overbank splays form subdeltas that were erupted from breaches in a major distributary channel just downstream of "D." C1-MIDRP.45S032;1. Center of image at lat 46.0°S, long 23.8°. Scene 535 × 780 km. Resolution 75 m/pixel. North up. (B) Magellan SAR image of a braided reach of the outflow channel shown in (A). An area of large braided bars is noted by "B." Note that the distributary channels have low sinuosities, like the major distributaries of the Mississippi delta. F-MIDRP.50S021;1. Scene 104 × 151 km. Resolution 75 m/pixel. North up. (C) Magellan SAR image of part of the lava delta of the outflow channel system. Lava plains embay fractured terrain in the upper half of the image. The left (west) edge of this scene joins the right (east) edge of (B) without overlap, but the scale of (C) is larger. The main channel is 10 km wide just west of the point where it begins to flare into distributaries. F-MIDRP.30S021;1. Scene 130 × 190 km. Resolution 75 m/pixel. North up.
FIG. 6. Magellan SAR image showing the lava delta at the terminus of a canale. F-MIDRP.45N019:1. Scene 71 × 94 km. Center of image near lat 44°N, long 18°. Resolution 75 m/pixel. North up.
inland fluvial fans and deltas built where streams lose their carrying capacity due to (1) infiltration of water, (2) evaporation of water, (3) reduced precipitation and run-off, and (4) decreased stream gradient. Baker (1986) described Landsat images of several possible analogs, including the inland delta of the Niger River, Mali; the Kosi Fan, India and Nepal; and Taquari Fan, Brazil. The Venusian lava stream may have lost its carrying capacity because of lava crystallization. The inland deltaic style of deposition could only occur if the precipitated lava was efficiently deposited on the channel bed (had solids remained suspended, they would have caused the lava to congeal and overflow the channel, thus forming a normal lava flow).

Streamlined Bedforms of Canali and Outflow Channels

Venusian outflow channels are hundreds to over a thousand kilometers long. Remarkably, they closely resemble water-formed catastrophic flood channels on Mars and Earth. Venusian outflow channels, exemplified by the spectacular compound channel and flow complex near Ammavaru (described in detail by Baker et al. 1992), are most notable for their huge scale. They consist of multiple anastomosing channels and large streamlined bars (Fig. 5A, B). The braided bars, which also occur in some canali, are streamlined, similar to the bars of terrestrial and especially martian river channels (see Fig. 16 in Baker et al. 1992).

Chaotic Terrain and Other Collapse Features at Channel Sources

Venusian volcanic outflow channels and canali commonly originate at volcanic depressions or tectonic fractures. The outflow channel system of Kallistos Vallis, near Ammavaru, originated at a complex set of fractures and caldera-like depressions (Fig. 5A) that resembles the sources of outflow channels on the west side of the Elysium volcanic province on Mars. Some venusian channels have chaotically collapsed terrain at their sources that resembles chaotic terrain at the sources of the Chryse (fluvial) outflow channels on Mars. Figure 7 shows a region of venusian chaos and the proximal reach of its outflow channel (see also Fig. 14 in Baker et al. 1992 for another example). The chaotic terrain here consists of several modified coalesced fractures that form a large graben, whose central part is smooth; it apparently was flooded by lava. Slumping, collapse, and sapping appear to have widened the graben, so that the walls have a series of arcuate reentrants. The floor near the edges of the graben contains a chaotic jumble of blocks, each typically 600–2000 m across. The main area of chaos is 13 × 40 km, comparable with the smaller areas of martian chaotic terrain that apparently formed by catastrophic groundwater withdrawal. By analogy, this region on Venus is interpreted to have experienced (1) a sudden withdrawal of large amounts of lava from a shallow, subsurface reservoir, (2) contemporaneous catastrophic collapse of the overlying rock, and (3) erosion of the outflow channel by the rapid drainage. The distal reach of this volcanic complex consists of large, relatively radar-bright, channel-fed lava flows.

Sapping Features

Baker et al. (1992) and Komatsu et al. (1992a) reported valley networks and other features on Venus that appear to have formed by sapping. Subsidiary channels associated with the chaotic terrain shown in Fig. 7B, each theater-headed and 5 to 10 km long, appear to be small examples of sapping valleys. Though many possible sapping-valley networks on Venus are quite large (Baker et al. 1992, Komatsu et al. 1993), they are neither as abundant nor as widespread as those on Earth and Mars. Sapping implies the existence, at least locally and transiently, of shallow aquifers of a liquid of fairly low viscosity that reached the surface at low rates of discharge and was able to flow for tens of kilometers without solidifying.

Crater Outflows

Crater outflows on Venus (e.g., Fig. 8) have been interpreted as impact melt (Komatsu et al. 1991, Schaber et al. 1992, Chadwick and Schaber 1993) or atmospheric fluidization of crater ejecta (Schultz 1992). Venusian crater outflows, though commonly very extensive laterally, are very thin (their thickness generally cannot be measured from Magellan images). Their original extreme mobility is indicated by their capacities to flow great distances on low gradients and to make abrupt turns into and through narrow fractures and around small obsta-

FIG. 7. Venusian outflow channel and chaotic terrain at its source. (A) This scene shows almost the entire volcanic system, including the chaotic source ("S"), a reach of anastomosing channels and braided bars ("B"), and a vast, radar-bright, channel-fed lava flow field ("F"). Some of the fractures oriented N–S cut the channels and flow field and others serve as the source of this volcanic system; all fractures oriented NE–SW in the lower half of the image are embayed by the flow field. From F-Map 065210. Scene 288 × 390 km. Center of image near lat 40°S, long 202°. Resolution 75 m/pixel. North up. (B) Chaotic terrain at the source of the outflow channel (left center) and the proximal region of braided bars (lower right). Probable sapping valleys ("V") appear to have eroded headward into fractured plains adjacent to the chaotic terrain. Also note streamlined bars of many sizes ("B"). Enlarged from (A). Scene 77 × 105 km.
FIG. 8. Magellan SAR image of an irregularly shaped impact crater and its ejecta outflow. The outflow is extremely thin (no visible thickness) and runs into and then out of fractures.
icles. Hence, crater outflows had very low effective viscosities and very low yield strengths.

Compositions and Flow Processes of Possible Low-Viscosity Lavas

The origin of canali and other venusian fluvial-like features has been discussed in terms of many possible lavas: tholeiite basalt, lunar-type Fe–Ti basalt, komatiite, kimberlite, maﬁc alkaline lava, carbonatite, and sulfur (Head et al. 1992; Kargel et al. 1991, 1993; Baker et al. 1992; Komatsu et al. 1992a, b; Gregg and Greeley 1993). A good hypothesis should explain two aspects: the unusual forms of the fluvial-like venusian features and the extraordinary lengths of some of them. Both aspects can be explained by an unusual lava of low viscosity and low melting point. Alternatively, lava discharge rates may have been unusually high, so that even ordinary basalt might have behaved hydrodynamically like water, thus producing fluvial-like landforms. We suggest that lunar-type sinuous rilles may have been formed by lavas completely distinct from the lavas that formed canali and compound outﬂow channels.

The characteristics of sinuous rilles suggest that thermal and/or mechanical erosion by a hot, low-viscosity, silicate lava was directed into the entire wetted perimeter. The usual absence of evidence for lateral channel migration suggests that lunar-type sinuous rilles were stably positioned. Their stability was probably caused by deep erosional entrenchment and widening of the channel to both sides (Komatsu and Baker 1994). Widening of a stable, sinuous, river-like channel would cause the inside bends of normal meanders (e.g., \( r_m/w = 2 \)) to evolve into cusps (e.g., \( r_m/w = 0.5 \)). Erosion of both banks implies that deposition within rilles, even on the inside banks of meanders, was inhibited, except near the channels’ distal ends where they simply ﬁlled up under ﬂoods of lava.

Sinuous rilles on the Moon were probably eroded by Fe–Ti-rich basaltic lavas (Hulme 1973, Greeley and Spudis 1986), which have viscosities an order of magnitude less than that of common terrestrial basalts (McBirney and Murase 1970, Weill et al. 1971). A venusian lava similar to olivine leucite was analyzed by Venera 13 and may be abundant on Venus; it would have had a viscosity lower than that of ordinary basalt and close to that of lunar Fe–Ti basalt (Kargel et al. 1993), and it may have produced sinuous rilles. Komatiite lavas have even lower viscosities, two to four orders of magnitude lower than the viscosity of ordinary basalt; large effusions of komatiite could explain some aspects of the venusian fluvial-like channels. However, as explained below, a cool, low-viscosity lava such as carbonatite might better explain the origins of canali, outﬂow channels, and other ﬂuvial-type features.

Komatsu et al. (1992b) modeled the rates of flow, cooling, and congelation of basaltic lava in venusian channels. Basalt could not have easily ﬂowed through the whole length of preexisting canali (much less eroded them) unless other processes or special conditions were involved. At discharge rates high enough to make the lava ﬂow thousands of kilometers, basalt would tend to overﬂow and bury the channel; discharges low enough to allow basalt to remain channelized would result in the lava freezing, thus locking and burying the channel, after ﬂowing typical distances to one to hundreds of kilometers. This model explains why basaltic lava channels on Earth and the Moon are relatively short (hundreds of meters to thousands of kilometers) and tend to narrow, shallow, and fade downstream.

Similarly, komatiite cannot easily account for all the characteristics of canali. Erupting komatiite is extremely hot and fluid; consequently, it can effectively erode channels, but its high temperature causes it to cool even more rapidly than basalt. Hence, even if komatiite theoretically can form channels thousands of kilometers long, one predicts that large longitudinal changes in lava rheology would be reﬂected in longitudinal variations of morphology (not observed for canali). However, the complexities of natural lava ﬂows and the uncertain eruption conditions make it premature to rule out formation of canali by komatiite or other silicate lavas (Komatsu et al. 1992b, Gregg and Greeley 1993, Kargel et al. 1993).

Venus’ ﬂuvial-type volcanic landforms and their associated plains tend to be extremely smooth at scales comparable to and larger than the Magellan radar wavelength, as indicated by rms slopes that commonly are lower than 2°. The interpretation of the smoothness of Venus’ ﬂuvial-like landforms is ambiguous, because lavas ranging from natrocarbonatite to basalt can exhibit smooth pahoehoe textures (Krafft and Keller 1989, Keller and Krafft 1990, Campbell and Campbell 1992). The smoothness also is consistent with ﬁne-grained sediments, as might be produced on a volcanic ﬂood plain or on volcanic sand and gravel bars.

The ﬂuvial analogs of river-like canali imply ﬂow regimes that were partly erosional and partly depositional (Baker et al. 1992, Komatsu et al. 1993, Kargel 1994, Komatsu and Baker 1994). Volcanic sedimentary deposits of outﬂow channels and canali may consist of sediment eroded from the channel’s banks and crystalline precipitates of the lava. Some canali, unlike that shown in Fig. 1, do not have river-like meanders or obvious evidence of channel migration. These canali, in contrast to the highly meandering ones, may not have been active for a period sufﬁcient for channel adjustment and development of a mature meander pattern.

Natrocarbonatite streams on the shield volcano Oldoinyo Lengai, Tanzania, exhibit hydrodynamic behav-
ior like that of water streams, thus producing highly sinuous channels and bird's-foot deltas; photographs also show what appear to be cutbanks, cutoff meanders, and other features in common with typical channels and sediment deposits of fluvial streams (Fig. 1 of Kraf\textsuperscript{t} and Keller 1989; Figs. 4, 7, and 8 of Keller and Kraf\textsuperscript{t} 1990; see also Dawson et al. 1990). These natrocarbonatite features are perhaps the best terrestrial volcanic analogs of the venusian landforms described above, although they occur on different scales. Besides the fluvial-like aspects, the natrocarbonatite flows of Oldoinyo Lengai also include large expanses of spectacular pahoehoe lavas that may have the smoothness required by the venusian features. Some terrestrial silicate lavas also form volcanic sedimentary deposits, such as the lava stream bed and flood plain deposits of ultramafic nodules in a large komatiite flow of the Archean Perseverance Ultramafic Complex (Western Australia, Barnes et al. 1988). Basaltic flows rarely form volcanic sedimentary deposits of much significance; an exceptional dunite xenolith bed occurs in a basaltic lava tube on Hualalai Volcano, HI (Jackson et al. 1981).

Sapping requires a ground fluid close to the surface that can remain liquid following extrusion long enough to transport downstream all the rock debris produced by fluid flow and mass wasting. The active sapping agent on Venus may have been analogous to water on Mars (solid at the surface, but liquid at shallow depths). Multicomponent molten salts such as natrocarbonatite are possible sapping agents. In contrast, a high-temperature lava such as komatiite or basalt could not easily have produced sapping features.

Crater outflows are consistent with a widespread presence of a liquid reservoir in Venus' upper crust, or of a solid with a melting point close to Venus' surface temperature (Fig. 8). Impacts might induce melting or entrain in the ejecta a preexisting ground fluid (Komatsu et al. 1991). Carbonatite would have the necessary high mobility to explain the outflows. This fluidization mechanism is analogous to the hypothesized fluidization of ejecta on Mars and Ganymede by impact melting and vaporization of ground ice (Barlow and Bradley 1990).

The most compelling terrestrial analogs of venusian fluvial-like volcanic landforms involve liquids (water, carbonatite, and komatiite) two to four orders of magnitude less viscous than common basalt. These analogs do not rule out formation of the venusian features by basaltic or other types of silicate lavas, but the analogs establish a basis for consideration of possible carbonatite volcanism on Venus. Before returning under Discussion to the geology of low-viscosity volcanism, we present thermochemical and thermophysical aspects related to the stability and physical behavior of carbonates and other salts on Venus.

III. ATMOSPHERE–SURFACE CHEMICAL REACTIONS ON VENUS

Venus is unique among the terrestrial planets in possessing both a substantial atmosphere and a high surface temperature. Because of Venus' hot surface, several elements (C, S, F, and Cl), which are found dominantly in the Earth's oceans and crust, are present in the atmosphere of Venus. Earth-based radio observations of Venus provided the first evidence of a hot surface (Mayer et al. 1958), which was later confirmed by the Mariner 2 microwave radiometer (Barath et al. 1963). Because Venus' massive CO$_2$ atmosphere was already known, Mueller (1963) observed that the deduced surface temperature of $\sim$700 K "... corresponds with those attained during moderately high degrees of metamorphism on Earth. It is therefore possible that large parts of the atmosphere of Venus are partially equilibrated with the surface rocks. From this assumption, it therefore follows that the composition of the atmosphere should reflect the mineralogical character of the rocks."

Mueller's assertion must be qualified because of somewhat different physicochemical conditions on Venus' surface and in Earth's crust, and because it is not known with certainty that the present atmosphere and conditions have prevailed throughout recent geologic time. However, his concept of atmosphere–surface chemical interactions generally remains valid (Fegley and Treiman 1992, Fegley et al. 1992). Below we discuss current theoretical models of atmosphere–surface interactions in Venus, particularly gas–solid buffer reactions that may control the atmospheric abundances of CO$_2$, HCl, and HF.

This discussion incorporates the latest abundance data (Bézard et al. 1990, Dalton et al. 1993, Pollack et al. 1993) and recent thermodynamic data for the phases involved in the buffers (Fegley and Treiman 1992).

The buffering reactions appear to involve several minerals typically found in terrestrial carbonatites and related alkaline volcanic rocks (see Hogarth 1989, Mariano 1989, Woolley and Kempe 1989). Possible implications are that (1) carbonatite magmatism may have substantially affected the composition and density of the venusian atmosphere, and/or (2) weathering interactions of the atmosphere with igneous rocks may have formed salts that readily remelt to form carbonate-rich magmas.

**Carbon Dioxide Buffers**

Carbon dioxide is the most abundant gas (96.5 ± 0.8%) in Venus' atmosphere (von Zahn et al. 1983). The CO$_2$ pressure at the surface is about 92 bars. Urey (1952) originally suggested that a reaction among wollastonite, calcite, and quartz,

$$\text{CaSiO}_3 + \text{CO}_2 = \text{CaCO}_3 + \text{SiO}_2,$$

(1)
buffers, or controls, the CO$_2$ pressure in planetary atmospheres. However, Urey dismissed reaction (1) as irrelevant to Venus because the observed CO$_2$ pressure exceeds that generated by this reaction at the low surface temperature that Venus was then thought to have. A decade later, when Venus was discovered to have a hot surface, investigators realized that reaction (1) and other carbonate–silicate equilibria probably control Venus' atmospheric CO$_2$ abundance (Mueller 1963; Lewis 1968, 1970; Vinogradov and Volkov 1971). The observed CO$_2$ pressure on Venus intersects the expected CO$_2$ pressure resulting from the buffer reaction at a temperature of 740 ± 30 K (Table II), corresponding to an altitude of 0 ± 4 km. In other words, the calcite + quartz + wollastonite assemblage appears to be thermodynamically stable over most or all of the surface of Venus and may be regulating the CO$_2$ pressure. This conclusion was reached independently over the past 30 years by Mueller (1963), Lewis (1968, 1970), Vinogradov and Volkov (1971), Lewis and Kreimendahl (1980), and Fegley and Treiman (1992). However, Klose et al. (1992) claimed that equilibrium (1) is irrelevant to Venus and that calcite is unstable. We agree only in that anhydrite is more stable than calcite (Fegley 1988, Fegley and Prinn 1989). As discussed below, anhydrite should replace calcite and other calcic minerals such as diopside across the entire surface of Venus, except that the kinetics of these reactions are very slow. The issue of kinetics in anhydrite formation was raised by von Zahn et al. (1983) and was studied experimentally by Fegley (1988, 1990) and Fegley and Prinn (1989). Calcite converts to anhydrite only on very long geologic time scales; hence, igneous calcite is metastable on Venus. Some of the pertinent reaction kinetics are unknown to establish whether calcite or anhydrite is initially formed by weathering on Venus. Venera and VEGA XRF data show a clear excess of CaO over SiO$_2$ at three sites (Barsukov et al. 1986, Surkov et al. 1986), indicating that anhydrite is not the only calcic phase; others may be calcite, perovskite, and Ca-silicates.

One of us (B.F.) believes that there are unresolved problems with the PHEQ code used by Klose et al. (1992). Their calculations disagree with experimental results and thermodynamic calculations by others, particularly regarding the stability of pyrite and pyrrhotite on Venus (Fegley and Treiman 1990; Treiman and Fegley 1991; Fegley et al. 1993, 1994; Klingelhöfer et al. 1994). Although not relevant to venusian geochemistry, calculations by Wood and Hashimoto (1993) using the PHEQ code also disagree with calculations of the condensation of troilite (FeS) (Larimer 1967, Lewis 1972, Lauretta and Fegley 1994). A problem with the global equilibrium calculations of Klose et al. (1992) is that they implicitly assume that minerals at any two surface locations can equilibrate with one another. However, the reactant mineral assemblages that should be considered in buffering equilibria are those expected to coexist in a single rock or in related rock types, rather than in unrelated rocks that

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log$_{10}$ $K = A + B/T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ buffers</td>
<td></td>
</tr>
<tr>
<td>(1) CaCO$_3$ + SiO$_2$ = CaSiO$_3$ + CO$_2$</td>
<td>$7.97$</td>
</tr>
<tr>
<td>(2) 2CaMg(CO$_3$)$_2$ + SiO$_2$ = 2CaCO$_3$ + Mg$_2$SiO$_4$ + 2CO$_2$</td>
<td>$17.9$</td>
</tr>
<tr>
<td>(3) Mg$_2$SiO$_4$ + CO$_2$ = MgSiO$_3$ + MgCO$_3$</td>
<td>$-8.85$</td>
</tr>
<tr>
<td>(4) 2MgSiO$_3$ + CaMgSi$_2$O$_6$ + 2CO$_2$ = CaMg(CO$_3$)$_2$ + 4MgSiO$_3$</td>
<td>$-17.04$</td>
</tr>
<tr>
<td>HCl buffers</td>
<td></td>
</tr>
<tr>
<td>(5) 12HCl + 6CaSiO$_3$ + 5Na$_2$[Al$_2$SiO$_5$]Cl = 17NaCl + 6CaAl$_2$Si$_2$O$_6$ + 6H$_2$O + 3NaAlSi$_3$O$_8$</td>
<td>$-20.17$</td>
</tr>
<tr>
<td>(6) 2HCl + 9NaAlSi$_3$O$_8$ = Al$_2$O$_3$ + NaAlSi$_3$O$_8$ + 2Na$_2$[Al$_2$SiO$_5$]Cl + H$_2$O</td>
<td>$-13.56$</td>
</tr>
<tr>
<td>(7) 2HCl + 8NaAlSi$_3$O$_8$ = 2Na$_2$[Al$_2$SiO$_5$]Cl + Al$_2$O$_3$ + 5SiO$_2$ + H$_2$O</td>
<td>$-14.92$</td>
</tr>
<tr>
<td>HF buffers</td>
<td></td>
</tr>
<tr>
<td>(8) 2HF + 3Mg$_2$SiO$_4$ + KAl$_2$Si$_3$O$_8$ = KMg$_2$AlSi$_2$O$_8$F$_2$ + 3MgSiO$_3$ + H$_2$O</td>
<td>$-6.23$</td>
</tr>
<tr>
<td>(9) 2HF + NaAlSi$_3$O$_8$ + 2CaMgSi$_2$O$_6$ + Mg$_2$SiO$_4$ + MgSiO$_3$ = NaCaMg$_2$Al$_2$Si$_3$O$_8$F$_2$ + H$_2$O</td>
<td>$-6.93$</td>
</tr>
<tr>
<td>(10) Na$_2$CaMg$_2$Si$_3$O$_9$(OH)$_2$ + 2HF = Na$_2$CaMg$_2$Si$_2$O$_6$F$_2$ + 2H$_2$O</td>
<td>$?$</td>
</tr>
</tbody>
</table>

may be thousands of kilometers apart. By contrast, Fegley and Treiman (1992) and other workers assumed local chemical equilibrium and predicted that calcite and wollastonite are stable (or metastable) on Venus.

Calcite, besides occurring in sedimentary and metamorphic rocks, constitutes a few percent of many alkaline igneous rocks, such as nepheline–syenites, melilite–nephelinites, okaites, ijolites, and melteigites (e.g., Johanssen 1938). Calcite is a major phase in kimberlites (e.g., Mitchell 1986) and carbonatites. Wollastonite occurs with calcite in many of the same rocks, and it occurs with quartz in carbonatites (Deer et al. 1963, Sorensen 1974, Hogarth 1989).

The possible occurrence on Venus of any specific alkaline rock is difficult to assess because chemical analyses of venusian rocks did not include Na. However, the reported abundances of other elements indicates that mafic feldspatoideal rocks are present on Venus (Barsukov et al. 1986, Volkov et al. 1986) and may be more common than on Earth (Kargel et al. 1993). Finally, all existing XRF analyses are consistent with the presence of carbonates and sulfates (Table I). These factors suggest that the assemblage calcite + quartz + wollastonite is present on Venus and may be buffering the partial pressure of atmospheric CO₂. Carbonatites may be the best rock type for providing the necessary mineral assemblage.

Two studies of carbonate–silicate buffers show that three other carbonate–silicate mineral assemblages involving calcite, dolomite, and magnesite may be stable on Venus, but only in the cooler regions above 5 km elevation (Lewis 1970, Fegley and Treiman 1992). These assemblages are formed by reactions 2–4 in Table II. Although not unique to carbonatites, all of the solid reactants involved, with the exception of enstatite, are commonly found in carbonatites and related mafic alkaline rocks (Hogarth 1989), and enstatite is found in these rocks as a major component of other pyroxenes.

Hydrogen Halide Buffers

Two other reactive gases, HCl and HF, may be buffered by reactions with Venus’ surface (Fegley and Treiman 1992). Connes et al. (1967) discovered HCl and HF on Venus and reported abundances of 0.6 ppm HCl and 5 ppb HF at the cloud tops. Their spectroscopic data were later reanalyzed by Young (1972), who derived abundances of 0.4 ppm HCl and 10 ppb HF. DeBergh et al. (1989) reported 0.4 ppm HCl at the cloud tops. Bézard et al. (1990) and Pollack et al. (1993) analyzed IR spectra of Venus’ nightside and derived abundances of 0.5 ppm HCl and 1–5 ppb HF in the middle atmosphere below the clouds. These data show no evidence for gradients in the vertical distribution of HCl and HF (Dalton et al. 1993).

Shortly after the discovery of HCl and HF on Venus, Mueller (1968, 1969) and Lewis (1968, 1970) proposed that the hydrogen halides are buffered by atmosphere-surface chemical equilibria. Fegley and Treiman (1992) supported the idea of a surface-buffered atmosphere but noted that Lewis’ (1970) buffer reactions involve unrealistic mineral assemblages. Fegley and Treiman (1992) used phase equilibria and terrestrial petrology as a guide and proposed new potential buffers. They emphasized that the observed abundances of HCl and HF appear to be equilibrium values produced by the buffers. Gas–rock equilibration should be fairly rapid on the hot surface of Venus given that both gases are highly reactive even at room temperature. Thus, it is unlikely that HCl and HF are analogous to SO₂, which reacts slowly on geologic time scales (Fegley and Prinn 1989).

The buffers for HCl typically involve Cl-bearing phases such as halite and sodalite in combination with feldspar and/or feldspathoids. The best agreement between the observed and calculated HCl abundances was obtained for the reaction of HCl with wollastonite + sodalite, yielding halite + plagioclase (anorthite + albite) and water vapor (reaction 5 in Table II), and the reaction of HCl with nepheline, yielding corundum + albite + sodalite + water vapor (reaction 6 in Table II). Both HCl buffers involve reactants and products that are found in carbonatites and associated alkaline igneous rocks. Nepheline is abundant and widespread in such rocks (Deer et al. 1963, Bailey 1974, Hogarth 1989, Sorensen 1974, Dawson et al. 1994). Wollastonite and sodalite occur in some alkaline rocks and carbonatites, but they are not as widespread and not normally as abundant as nepheline. Wollastonite occurs in very large amounts in certain rare, hyper-alkaline rocks; for example, 26% by volume of an uritite consists of wollastonite (Le Bas 1977). Uritites are believed to be a differentiation product of ijolite magma, which crystallizes primarily to nepheline and mafic minerals. Interestingly, ijolite rocks with wollastonite are present as xenoliths in the natrocarbonatite–nephelinite volcano Oldoinyo Lengai (Dawson 1989, Dawson et al. 1994).

The buffers for HF typically involve feldspar and fluorophlogopite or feldspathoids and fluorarmphebolites. Two examples are reaction 8 (between HF + forsterite + microcline, yielding fluorophlogopite + enstatite + water vapor) and reaction 9 in Table II (between HF + nepheline + diopside + forsterite + enstatite yielding fluoridenite + water vapor). Both buffers reproduce the observed HF abundances (Fegley and Treiman 1992).

The HF buffers are generally compatible with the mineralogies of alkaline basalts and carbonatites, except that enstatite is not present in terrestrial carbonatites (Hogarth 1989). However, the augites of alkaline igneous rocks contain some enstatite component, which could be consumed in reaction 9 in Table II. But the major problem in finding suitable HF buffers is with the F-bearing
phases involved and generally not with the other minerals. In this respect, the pervasive occurrence of amphiboles in carbonatites is extremely interesting, because fluor amphiboles are involved in several potential HF buffers. We speculate that F–OH exchange reactions, such as that between richterite and fluor richterite (reaction 10 in Table II), could be involved in buffering HF on Venus. Although the equilibrium HF partial pressure for this reaction cannot be calculated because of a lack of thermodynamic data, analyses of amphiboles in terrestrial carbonatites show up to 3% F in richterites and magnesioarfvedsonites (Hogarth 1989). Where available, phase equilibria studies and thermodynamic data confirm the high stability of fluor amphiboles (Westrich 1981, Westrich and Navrotsky 1981, Gilbert et al. 1982, Valley et al. 1982, Graham and Navrotsky 1986).

Stability of Sulfates

Fegley (1988) and Fegley and Prinn (1989), following von Zahn et al. (1983), showed that the SO$_2$ abundance in Venus’ atmosphere is $\sim$100 times that necessary to stabilize anhydrite by reactions such as

$$\text{SO}_2 + \text{CaCO}_3 = \text{CaSO}_4 + \text{CO}.$$ (2)

Formation of anhydrite by reaction (2), though thermodynamically favored everywhere on Venus, is very slow on geologic time scales, so that the atmosphere cannot be buffered by this or similarly ineffective reactions with diopside (Fegley and Prinn 1989). As noted above, the CaO/SO$_2$ ratio of Venusian rock samples is inconsistent with complete conversion of calcic phases to anhydrite. The global average rate of anhydrite formation on Venus is calculated to be $\sim$1 $\mu$m per year. Over geologic time, weathering could produce large quantities of anhydrite, especially at lower, hotter elevations where reaction rates are relatively fast (e.g., reaction 2) should proceed three times faster at 740 K than at 700 K, Fegley et al. 1992). Therefore, calcite and anhydrite may coexist metastably (as primary igneous phases and/or as components of weathered basaltic rocks) everywhere on Venus, but this assemblage may be particularly important in the lowlands (Fegley 1990).

Summary

There is a continuing exchange of ideas on atmosphere–rock chemical equilibration on Venus, especially regarding important buffers, hydrospheric control of mineral stability, and reaction kinetics. An internally consistent argument has been presented for the stability or metastability (for geologically interesting periods) of calcite and wollastonite on Venus’ surface. This conclusion is more in accord with the available data than are the alternatives proposed thus far. All of the solid reactants needed by the important atmospheric buffers (calcite, wollastonite, olivine, diopside, sodalite, nepheline, K-feldspar, and richterite amphibole), with the exception of enstatite, involve common or known mineral assemblages in terrestrial carbonatites and closely related rocks (and pyroxene can provide the enstatite component). This does not prove that carbonatites supplied the necessary mineral assemblages to buffer the atmosphere, because other types of silica-undersaturated rocks, such as mafic feldspathoidal rocks (thought to be abundant on Venus, Kargel et al. 1993), can also supply these assemblages. However, on Earth the genetic and spatial association of carbonatites with mafic feldspathoidal rocks is very close; if the terrestrial analogy has any bearing on Venus, it can be predicted that if one of these rock types is present, the other probably is there, also. In any case, our knowledge of the geochemistry of Venus’ rocks and atmosphere is consistent with carbonatites as a major rock type.

The products of reactions (1) and (2) above, and the reactions in Table II involve salts (calcite, dolomite, magnesite, anhydrite, and halite) and silicate minerals (espeically albite, sodalite, fluorenenite, and fluor richterite) that are important components of carbonatites and/or associated silica-deficient silicate rocks. Anatexis of weathered crustal rocks could produce molten salt mixtures similar to carbonatites and silica-undersaturated alkaline rocks similar to phonolite. Hence, such lavas would not necessarily have to be generated directly in the mantle (though they could be).

High-Dielectric and Ferroelectric Phases in Carbonatites

We have examined the possibility that the distinct mineralogies of carbonatite and common silicate igneous rocks on Venus could be manifested in distinctive radar emissivities and reflectivities. The dielectric constants of calcite ($\varepsilon \sim 7$) and magnesite ($\varepsilon \sim 10$), two of the most abundant minerals in many terrestrial carbonatites, are in the general range of the dielectric constants of common silicate minerals, such as quartz ($\varepsilon \sim 7$), olivine ($\varepsilon \sim 7$), and pyroxene ($\varepsilon \sim 10$) (Garvin and Head 1985). The dielectric constants of these phases are not identical, so that pure calciomagnesian carbonatites, for instance, could have a slightly but distinctly different (lower or higher) radar reflectivity than adjacent silicate rocks, but the expected differences are small compared to Venus’ great range of radar reflectivities ($\sim$0.03–0.46, corresponding to $\varepsilon \sim 2$–27; Garvin and Head 1985). Certain other phases that are common and occasionally abundant in terrestrial (and maybe venusian) carbonatites and petrologically related types of silica-undersaturated alka-
line silicate rocks have extraordinary dielectric properties; these phases could contribute to the high radar reflectivities of some areas of Venus, particularly regions at high elevations but also some lowlands. The low radar emissivities, high reflectivities, and high dielectric constants of some regions (Pettengill et al. 1982, 1992; Garvin et al. 1985; Klose et al. 1992) may be due to the occurrence of perovskite and certain other carbonatite-associated oxides. Perovskite (ideal formula = CaTiO$_3$, general formula = ABO$_3$) and pyrochlore (ideal formula = 8[NaCaNb$_2$O$_8$F$_4$, general formula = $A_{16-x}B_{16}O_{48}(O, OH, F)_{8-x}$], where $x$ and $y$ denote vacant sites in the unit cell and $x \leq 13.25$ and $y \leq 3.8$, are common minerals in carbonatites (Hogarth 1989). Depending on the $A$ and $B$ ions, perovskite and pyrochlore may have high dielectric constants or may be ferroelectrics. Such phases may offer an explanation for the low emissivities observed in the highlands and some lowland plains.

Fegley et al. (1992) proposed that ideal perovskite (Ca-TiO$_3$), with a dielectric constant of 165–170 at radar frequencies (Von Hippel 1954), may account for the elevation dependence of radar emissivity. Recently, some old measurements of the dielectric constants of three natural calcium titanates have come to the authors’ attention. These constants are in the range of 1100–2200 at frequencies of 10 kHz (Timco 1977), thus allowing potentially interesting effects on the radar emissivity of venusian rocks even if perovskites are present at percent levels of abundance.

Fegley et al. (1992) calculated the gas–solid equilibria between perovskite and atmospheric CO$_2$, SO$_2$, HCl, and HF to determine the conditions under which perovskite could occur on Venus. They proposed that at the highest elevations (e.g., the summit of Maxwell Montes), perovskite is converted to fluorite + rutile at a rate that exceeds the production of fresh, perovskite-bearing rock. At slightly lower elevations (e.g., flanks of Maxwell) fluorite formation is thermodynamically unfavorable and the rate of perovskite destruction via attack by CO$_2$ and SO$_2$ is still very slow, so that perovskite can persist on a geological time scale. The temperatures are sufficiently high at the lowest elevations that perovskite tends to be destroyed rapidly by CO$_2$ and SO$_2$ and to be replaced by rutile, calcite, and anhydrite. The regions at intermediate elevations, where perovskite can persist metastably, tend to display low radar emissivity and high reflectivity. The regions at higher and lower elevations, where perovskite is readily destroyed, tend to display normal emissivity and radar reflectivity. This model provides a simple explanation for the observed elevation dependence of emissivity and radar reflectivity. Spatially variable differences in the elevation-dependent emissivity profiles on Venus (Klose et al. 1992) can be caused by variations in perovskite composition, hence, different upper and lower bounds to the perovskite stability field and variations in dielectric properties. Regions within the perovskite metastable zone, but which show normal emissivity and reflectivity, may simply not contain perovskite-bearing rocks.

Shepard et al. (1994) proposed an alternative model that the ferroelectric properties of perovskites and pyrochlores are responsible for the elevation dependence of emissivity and radar reflectivity on Venus. A ferroelectric is a material in which the electric dipoles become spontaneously aligned below a critical temperature known as the Curie temperature, $T_C$ (Kinger et al. 1976). As temperature increases to $T_C$, the dielectric constant of a ferroelectric undergoes a discontinuous increase of several orders of magnitude to values as high as $10^4$ or $10^5$; continued warming over tens of degrees causes a gradual drop in the dielectric constant. The relaxation in the dielectric constant occurs according to the Curie–Weiss equation (Shepard et al. 1994),

$$\varepsilon_S = C/(T - T_C) \quad \text{for } T > T_C,$$

where $\varepsilon_S$ is the dielectric constant of the ferroelectric mineral, $C$ is the Curie constant, and $T$ is absolute temperature. The relaxation in dielectric properties corresponds to changes in crystal structure (see the illustration for BaTiO$_3$, a perovskite, in Kinger et al. 1976). The dielectric and ferroelectric properties and $T_C$ of perovskites are sensitive to variations in composition.

The perovskite structure accommodates a wide range of compounds. The $A$ cation is generally Ca$^{2+}$ in natural perovskites; other possible $A$ cations are Ba$^{2+}$, Cd$^{2+}$, K$^+$, Na$^+$, REE$^{3+}$, Sr$^{2+}$, and Y$^{3+}$. The $B$ cation is generally Ti$^{4+}$ in natural perovskites, but other possible $B$ cations are Ce$^{3+}$, Cr$^{3+}$, Hf$^{4+}$, Nb$^{5+}$, Sn$^{4+}$, Ta$^{5+}$, and Zr$^{4+}$; charge balance determines which $A$–$B$ pairs are allowable. The most common substitutions in natural perovskites involve the replacement of Ca with REE or alkalies and the replacement of Ti with Nb. Cerium-rich perovskite (knopite), containing 2–3% Ce, La, and Y oxides, has been reported in alkaline basalts from Uganda and syenites from the Alnö region of Sweden, and niobian perovskite from the Kaiserstuhl, Germany, contains up to 26% Nb$_2$O$_5$ (Deer et al. 1963).

Pyrochlore minerals can have complex compositions with possible $A$ atoms being As, Ba, Bi, Ca, Cs, K, Mg, Mn, Na, Pb, REE, Sh, Sn, Sr, Th, U, and Y and possible $B$ atoms being Nb, Ta, Ti, and V. Hogarth (1989) tabulated analyses for several pyrochlores found in carbonatites; these are typically rich in Nb or Ta. The important $A$ atoms found in carbonatite pyrochlores include virtually all of those listed above except for As.

Table III lists some representative perovskites and pyrochlores and their $T_C$. Ideal pure perovskite, CaTiO$_3$,
TABLE III
Some Perovskite and Pyrochlore Phases
and Their Curie Temperatures

<table>
<thead>
<tr>
<th>Name</th>
<th>Ideal formula</th>
<th>Type</th>
<th>Curie temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perovskite</td>
<td>CaTiO₃</td>
<td>Perovskite</td>
<td>Not ferroelectric</td>
</tr>
<tr>
<td>Lead titanate</td>
<td>PbTiO₃</td>
<td>Perovskite</td>
<td>763</td>
</tr>
<tr>
<td>Potassium niobate</td>
<td>KNbO₃</td>
<td>Perovskite</td>
<td>708</td>
</tr>
<tr>
<td>Potassium–lithium niobate</td>
<td>K₃Li₂Nb₂O₉</td>
<td>Oxide</td>
<td>703</td>
</tr>
<tr>
<td>Lead–bismuth niobate</td>
<td>Pb₂Bi₂NbO₆</td>
<td>Pyrochlore</td>
<td>748</td>
</tr>
<tr>
<td>Lead–bismuth tantalate</td>
<td>Pb₂BiTaO₉</td>
<td>Pyrochlore</td>
<td>693</td>
</tr>
<tr>
<td>Lead–bismuth tungstate</td>
<td>Pb₂BiW₂O₁₈</td>
<td>Pyrochlore</td>
<td>673</td>
</tr>
<tr>
<td>Lead–bismuth molybdate</td>
<td>Pb₂BiMo₂O₉₁₈</td>
<td>Pyrochlore</td>
<td>773</td>
</tr>
</tbody>
</table>


is not a ferroelectric. Many other pure perovskites, especially Nb-rich perovskites, have high dielectric constants and are ferroelectrics (Lines and Glass 1977). Unfortunately, most data for ferroelectric properties concern industrial compounds rather than naturally occurring minerals, whose ferroelectric properties have not been investigated in much detail (as noted above and in Table III), natural CaTiO₃ is not a ferroelectric, thought it does have astonishingly high dielectric constants. However, some of the ferroelectric compounds listed in Table III are similar to natural minerals. Lueshite (NaNbO₃), is a pyrochlore known from carbonatites (Hogarth 1989), is similar to KNbO₃. Plumbo–pyrochlore (a Pb–Nb–Ce rich pyrochlore from the Oka carbonatite, Quebec; Hogarth 1989) resembles the lead–bismuth niobate listed in Table III, except that Ce appears to substitute for Bi. We suspect that many natural pyrochlores are ferroelectrics, though strictly pertinent data are not available.

This model requires traces (<1%) of ferroelectrics and can account for the lower and upper boundaries of the regions with low emissivity and high radar reflectivity. The upper elevation boundary is below Tc for the ferroelectric, while the lower elevation boundary is fixed by the Curie–Weiss equation and the composition of the ferroelectric. Observed variations in the upper and lower bounds of the low-emissivity regions (Klose et al. 1992) might be explained by chemical substitutions in the ferroelectrics, variations in the abundance of ferroelectrics, and variations in the amount of ferroelectric-bearing alkaline and carbonatitic rocks.

IV. CARBONATE MAGMAS

Carbonatites (rocks derived from carbonate-rich magmas) are uncommon on Earth, but they have been studied extensively because of their importance as ores and their information pertaining to mantle processes. Much of the physics and chemistry of carbonatite melts can be explained in terms of their structures. Carbonatite magmas are ionic liquids composed of discrete anions and cations bound only by electrostatic forces (Zarzycki 1962; Kleppa 1977, 1981). Polymerization and covalent bonding are unimportant in carbonate-rich melts; thus they lack many of the complexities of silicate melts.

**Thermophysical Inferences**

Thermophysical properties have been measured for many synthetic carbonate systems but for few natural carbonatite magmas (Janz et al. 1979, Norton and Pinkerton 1992). However, the simple structure of carbonate-rich melts allows reliable extrapolation of many properties from laboratory systems to natural magmas (Table IV, Treiman and Schell 1983, Treiman 1989). The enthalpies of fusion, ΔH fusion, for carbonate compounds are all similar (Table V), as are heat capacities of the melts (Janz et al. 1979). The lack of polymerized ions in carbonatite melts suggests that transport of heat, momentum, and ions is relatively rapid; this inference is borne out in the low viscosity, high thermal diffusivity, and large cation diffusivities of carbonatite melts (Table IV).

Carbonatite magma is very different than silicate magmas. Carbonatitites remain molten to temperatures below those of basaltic or komatitic magmas. Most terrestrial carbonatite magmas are inferred to have been molten below 1100 K, and in one case a solidification temperature of 763 K was measured (Barker 1989, Krafft and Keller 1990). Compare these values with the ~1350 and ~1600 K liquidus temperatures for basaltic and komatitic magmas (Table IV). The heat of fusion of carbonatite is about half that of basalt or komatite. Their low melting temperatures and low heats of fusion suggest that carbonatite magmas have little capacity to thermally erode silicate rocks (as komatiites can; Barnes et al. 1988); however, they can thermally erode channels in solid carbonatite (Dawson et al. 1990, Keller and Krafft 1990, Pinkerton et al. 1990), and they might mechanically erode channels in any type of rock (as water can). Carbonatite magmas are extremely fluid, comparable to water, and four orders of magnitude less viscous than basalt (Table IV). The thermal expansivity of carbonate magma is an order of magnitude greater than those of basalt or komatite (Table IV), suggesting that carbonatite magma bodies are susceptible to thermally driven convection (Treiman and Schell 1983).

**Thermochemical Inferences**

Thermophysical properties outlined above help us to understand how carbonate-rich magma should behave on Venus; thermochemical properties help us to understand
TABLE IV
Thermophysical Properties of Magmas near their Liquidus

<table>
<thead>
<tr>
<th></th>
<th>Carbonatitea</th>
<th>Carbonatib</th>
<th>Komatiitec</th>
<th>Basaltd</th>
<th>Rhyolited</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquidus temperature ($T_n$)</td>
<td>K</td>
<td>763</td>
<td>–1000</td>
<td>–1600</td>
<td>–1350</td>
</tr>
<tr>
<td>Viscosity ($\mu$)</td>
<td>Poise</td>
<td>0.03–0.5</td>
<td>0.05</td>
<td>0.01–1.0</td>
<td>500</td>
</tr>
<tr>
<td>Density ($\rho$)</td>
<td>g cm$^{-3}$</td>
<td>2.2</td>
<td>2.2</td>
<td>2.8</td>
<td>2.7</td>
</tr>
<tr>
<td>Thermal expansion ($\alpha$)</td>
<td>$10^{-4}$ K$^{-1}$</td>
<td>–</td>
<td>2.3</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>Heat of fusion ($\Delta H_{fu}$)</td>
<td>J g$^{-1}$</td>
<td>120$^c$</td>
<td>250</td>
<td>360</td>
<td>400</td>
</tr>
<tr>
<td>Heat capacity ($C_p$)</td>
<td>J g$^{-1}$ K$^{-1}$</td>
<td>2.3</td>
<td>2.0</td>
<td>0.73</td>
<td>1.2</td>
</tr>
<tr>
<td>Thermal diffusivity ($\kappa$)</td>
<td>cm$^2$ s$^{-1}$</td>
<td>–</td>
<td>0.004</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Thermal conductivity ($\kappa$)</td>
<td>J cm$^{-1}$ K$^{-1}$ s$^{-1}$</td>
<td>–</td>
<td>0.018</td>
<td>0.010</td>
<td>0.025</td>
</tr>
<tr>
<td>Cation diffusivity ($D$)</td>
<td>cm$^2$ s$^{-1}$</td>
<td>–</td>
<td>$5 \times 10^{-5}$</td>
<td>–</td>
<td>$5 \times 10^{-8}$</td>
</tr>
</tbody>
</table>


$^c$ Turner et al. (1986), Bottinig and Weil (1972).


$^e$ Norton et al. (1990) by DSC. Values for heat of fusion and heat of crystallization were significantly different. These differences may pertain to undercooling during crystallization of the lava.

how and why such magmas might form. Two immediate questions concern the melting temperature of carbonate-bearing rocks on Venus and the chemical interactions between carbonate magmas and the Venus atmosphere. (Note that Section III dealt with atmospheric interactions with solid rock under ambient surface conditions.) Some aspects of these questions can be answered with data in hand, but others require additional experimental and theoretical studies. Below, we will review the melting of calcite + anhydrite and the formation of low-temperature carbonatite magmas on Venus, and we will review aspects of possible magma–atmosphere chemical interactions.

Regular solution model applied to the system calcite–anhydrite. Fortunately, the thermochemical properties of carbonate melts are easily modeled because of their simple structure. Carbonate melts and other ionic liquids act in many respects as separate cation and anion solutions. This quasi-lattice or Temkin (1945) model is justifiable because of the enormous energy required to change (for instance) a cation surrounded by anions for an anion surrounded by anions (Blander 1964). Predictions based on the Temkin model are in good accord with experimental data on ionic liquids and are adequate to explain most available data on carbonate melts. The Temkin model of ionic liquids is consistent with ideal solution behavior in each ion solution and also with regular solution behavior, in which there is a heat of mixing but no excess entropy of mixing (Forland 1955). The regular solution model is phenomenologically accurate at the level of detail available for carbonate melts, it is familiar to the geological community (e.g., Ghiorsio et al. 1983), and it is the simplest case of the Margules parameter formulation of solution behavior.

Treiman (1994b) applied the regular solution model to a study of phase relations along the melting curve in various salt systems, including the system CaCO$_3$–CaSO$_4$. This system is relevant to Venus because its surface rocks may contain calcite (CaCO$_3$) and anhydrite (CaSO$_4$) as the dominant weathering products (Fegley and Prinn 1989, Fegley and Treiman 1992). The likely occurrence of these two phases together raises the possibility of interesting melting behavior, which was modeled by Treiman (1994b) with the regular solution model, ignoring the polymorphic transition in CaSO$_4$, and thermochemical parameters tabulated by Treiman (1989). In Fig. 9 we show the calculated calcite-saturated and anhydrite-saturated liquidus surfaces in the system CaCO$_3$–CaSO$_4$ and an experimentally determined liquidus for this same system (Fuerstenau et al. 1981). The calculated and ex-

TABLE V
Melting Properties of Potential Contributors to Carbonate-Rich Magmas: Molar Properties at 100 Bars Pressure for Pure Components

<table>
<thead>
<tr>
<th>Component</th>
<th>$T_m$ (K)</th>
<th>$\Delta H_{fu}$ (kJ/mol)</th>
<th>$\Delta S_{fu}$ (J/mol K)</th>
<th>$\Delta V_{fu}$ (cm$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$CO$_3$</td>
<td>1132</td>
<td>30.1</td>
<td>26.3</td>
<td>4.7</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>1714</td>
<td>28.2</td>
<td>23.5</td>
<td>4.8</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>1584</td>
<td>31.5 ± 1</td>
<td>19.7 ± 0.7</td>
<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>CaSO$_4$</td>
<td>1723</td>
<td>28</td>
<td>16.3</td>
<td></td>
</tr>
</tbody>
</table>

$^\text{Note.}$ $T_m$ is the fusion temperature at standard pressure. $\Delta H_{fu}$ is the molar enthalpy of fusion. $\Delta S_{fu}$ is the molar entropy of fusion. $\Delta V_{fu}$ is the change of molar volume during the melting reaction. Modified from Treiman (1989, 1994b).
Experimental liquidus curves indicate roughly similar eutectics, but the experimental anhydrite liquidus branch does not extrapolate to the melting point of pure anhydrite. We speculate that the experimental run may have included the growth of an unreported intermediate compound, such as Ca$_3$(SO$_4$)$_2$(CO$_3$), that melts incongruently to CaSO$_4$ + peritectic melt at about 1375 K.

The calculated eutectic temperature is 335 K below the melting point of pure calcite and 473 K below the melting point of pure anhydrite. When these data are applied to Venus, it is clear that calcite + anhydrite does not melt at normal Venus surface temperatures, 660–760 K (Seiff 1983). To melt calcite + anhydrite on Venus' surface would require temperatures at least 500 K above ambient, which could be caused by impact heating or basaltic volcanism (solidus temperatures near 1300–1400 K). However, additional chemical components, if present with calcite and anhydrite, would further reduce the melting point of the mixture.

**Minimum melt temperature.** The minimum melting temperature for carbonate–sulfate-rich melts on Venus defines the limit of carbonate–sulfate volcanism and the possible permanent presence of carbonate–sulfate melts on or in Venus. Little work has been done that is directly relevant to the formation of carbonatic magmas under venusian conditions; thus one relies on analogies with terrestrial carbonatite magmas and synthetic systems. The CaCO$_3$–CaSO$_4$ eutectic shown in Fig. 9 may represent a common venusian carbonate-rich magma of relatively simple composition and high melting temperature, but some carbonatites on Venus, as on Earth, probably are more complex chemically and would have lower melting points.

Experimental phase petrology shows that alkali cations and halogen ions are highly effective in reducing the melting points of carbonate–sulfate-rich mixtures (Mukimov et al. 1949; Rowe et al. 1965, 1967, 1972; Cooper et al. 1975; Jago and Gittins 1991) compared to carbonate-rich systems that lack these components (Fuerstenau et al. 1981, Wyllie 1989). For example, the minimum melting point in the system CaCO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ at 1 kbar is 938 K, compared with melting temperatures of 1584, 1132, and 1174 K for the pure end members (Cooper et al. 1975, Table V). The addition of NaCl to CaSO$_4$ produces a melting point of 998 K, 725 K below the melting point of pure anhydrite (Rowe et al. 1972). On Earth, carbonatite magmas with the lowest melting temperatures (natrocarbonatite), ~763 K, contain more Na and K than Ca, and they contain significant amounts of Ba, Sr, P (phosphate), S (sulfate), Cl, and F (Kraft and Keller 1989, Dawson et al. 1990, Keller and Kraft 1990, Peterson 1990).

Carbonate-rich melts with compositions and melting temperatures comparable to terrestrial natrocarbonatite may form under venusian conditions, because the chemical components of such melts are likely to be available in the mantle, crust, and atmosphere. Calcium carbonate and sulfate are likely to be present near the Venus surface as described above and by Fegley and Prinn (1989), and they could then have been drawn into the subsurface by tectonic processes or volcanic burial. Crustal silicates could provide Na and K (Barsukov 1992). Sulfur as SO$_2$ is abundant in Venus' atmosphere and is present as sulfate at 0.9–4.7% SO$_2$ in Venus' rocks (Barsukov 1992). Sodalite, halite, fluoropluogpite, and fluor amphibole may supply CI and F (Fegley et al. 1992). In sum, there is nothing in current knowledge of the chemical and mineralogic state of Venus' surface and crust that is inconsistent with the formation of high-temperature and low-temperature carbonate-rich melts comparable to the variety of carbonatites on Earth.

Contradicting Gregg and Greeley (1993), direct temperature measurements of active carbonatite flows (Kraft and Keller 1989) and phase equilibria of synthetic carbonate systems indicate that carbonatites would crystallize to thermally stable solids on Venus' surface (Treiman 1994a), although the low-temperature types melt at temperatures just barely warmer than the surface. Low-temperature types of carbonatite lava would erupt effusively on Venus as they do on Earth. The high-temperature varieties, such as calcicarbonatite carbonatitites and fairly pure calcite–anhydrite liquids, could erupt explosively because their CO$_2$ vapor pressures exceed the surface pressure of Venus. Depending on composition and elevation, the primary igneous minerals of carbonatites could be thermodynamically unstable and may weather (Section III), but the volcanic landforms created by carbonatite volcanism would remain stable.

**Magma–atmosphere equilibria; HF and HCl.** Carbonatites on Earth commonly contain abundant fluoride
and chloride phases, which are effective in lowering the melting points in carbonate-rich systems (Hogarth 1989, Jago and Gittens 1991). These components are normally leached either directly from the mantle (for direct mantle generation of carbonatites) or separate immiscibly (in solution with molten carbonates) from mantle-derived silicate magmas. On Venus there would be two other mechanisms whereby carbonate-rich melts could become enriched in F and Cl components. First, igneous and weathered rocks and soil on Venus may contain abundant halogen minerals, as noted above, and these may dissolve in carbonate-rich magmas. Second, the near-surface atmosphere of Venus contains ~5 ppb of HF and 500 ppb HCl (Pollack et al. 1993); one may inquire whether these amounts could significantly affect the compositions of ionic melts on the venusian surface if they were to equilibrate with the atmosphere (note that the treatment in Section III dealt with the equilibration of crystalline phases with the atmosphere). Treiman (1994b) modeled the chemical exchange of F between carbonate melt and atmospheric vapor according to the reactions

\[
\begin{align*}
F_2^{\text{(vapor)}} + CO_3^{2-}(\text{melt}) & \rightleftharpoons 2F^{-}(\text{melt}) + CO_2(\text{vapor}) + \frac{1}{2}O_2(\text{vapor}), \\
2HF + CO_2 & \rightleftharpoons F_2 + H_2O + CO, \text{ and} \\
2CO_2 & \rightleftharpoons 2CO + O_2.
\end{align*}
\]

Treiman found that the melt strongly concentrates F, which may reach an activity and molar anion concentration of ~0.0007. Gittins (1989) indicated that 5 wt.% F reduces the melting point of CaCO$_3$-Na$_2$CO$_3$ melts by 146 K. At a molar anion concentration of ~0.7%, the reduction in melting point should be ~10 K, a fairly small effect.

An equivalent model of magma–atmosphere exchange of HCl has not been calculated. However, the much higher atmospheric abundance of HCl (500 ppb) compared to HF (5 ppb) suggests that there could be fairly large effects on magma composition and melting temperature.

V. DISCUSSION

Rate of Solidification of Lava Flows

Komatsu et al. (1992) showed that ordinary basalt, under optimum conditions, could flow for thousands of kilometers, though it probably could not erode canali. However, they pointed out that canali could be more likely formed by a low-temperature lava, especially one with a low viscosity such as carbonatite. Contrary to statements by Gregg and Greeley (1993), all available data on natural carbonatite lavas indicate that they would solidify on Venus (Treiman 1994a), a point that Gregg and Greeley (1994) later accepted and modeled. Here we show that natrocarbonatite on Venus would solidify much more slowly than silicate lavas, thus enabling the lava to flow and remain highly fluid for the required distances. We model separately two stages in the solidification of a flow: first when the lava is at its liquidus and lacks appreciable solids, and finally when the lava is heavily crusted. We have not considered atmospheric convective cooling, which may be important on Venus (Gregg and Greeley 1994).

The initial formation of solids is modeled by the method of Komatsu et al. (1992), who equated the amount of heat lost due to thermal emissions from the surface of a molten eutectic flow with the amount of heat liberated by crystallization. For simplicity, this stage can be considered the initial development of a solid skin before it thickens sufficiently to reduce the surface temperature significantly below the eutectic. The radiant energy flux, $Q_r$, is

\[ Q_r = \varepsilon \sigma (T_e^4 - T_{e_0}^4), \quad (7) \]

where $\varepsilon \sim 0.9$ is the thermal emissivity, $\sigma = 5.67 \times 10^{-8}$ J sec$^{-1}$ m$^{-2}$ K$^{-4}$ is the Stefan-Boltzmann constant, $T_e$ is the eutectic temperature of the lava, and $T_{e_0}$ is the planet’s ambient surface temperature. Since the lava is assumed to have a eutectic composition, its temperature does not change; all radiative heat losses are balanced by the heat of crystallization. The initial rate of thickening of the lava skin (thickness, $h_{\text{skin}}$) is

\[ dh_{\text{skin}}/dt = Q_r/\rho \Delta H_f. \quad (8) \]

where $\rho$ is the density of the hot, eutectic, solid skin, and $\Delta H_f$ is the latent heat of fusion.

Results of this model are shown in Fig. 10 plotted against the lava’s eutectic temperature. The graph shows that venusian natrocarbonatite should initially solidify at a rate nearly two orders of magnitude more slowly than silicate flows. Among the lavas considered, only aqueous flows on icy satellites and Mars should initially solidify more slowly than natrocarbonatite on Venus. The high surface temperature on Venus causes a reduction in the initial rate of solidification of silicate flows compared with equivalent flows on Earth, but the effect is only 3% for komatiite and 7% for basalt.

After the formation of a thick, stable, chilled crust over the surface of a flow, the rate of heat loss is limited by thermal conduction through the crust, whose surface eventually cools nearly to the ambient planetary surface temperature. The rate of heat loss by conduction, $Q_c$, is

\[ Q_c \sim k(T_e - T_{e_0})/h_{\text{crust}}, \quad (9) \]
where \( k \) is the thermal conductivity of the solid crust of thickness \( h_{\text{crust}} \). For simplicity, \( k \) is taken as the thermal conductivity of the solid flow substance at a temperature corresponding to the geometric mean of \( T_c \) and \( T_s \). The thickness of crust increases with time, with the rate of thickening decreasing inversely with \( h_{\text{crust}} \) and exponentially with time:

\[
\frac{dh_{\text{crust}}}{dt} = \frac{Q_c}{\rho \Delta H_t} h_{\text{crust}}. \tag{10}
\]

The results are shown in Fig. 11—the crusts of most lavas thicken at similar rates (for a given value of \( h_{\text{crust}} \)).

However, natrocarbonatite on Venus solidifies more slowly by a factor of 15 than silicate flows during this stage of solidification. Gregg and Greeley (1994) arrived at qualitatively similar conclusions. High-temperature varieties of carbonatites, such as Ca–Mg-rich carbonatite, would solidify much more rapidly than natrocarbonatite but still more slowly than common silicate flows.

The rheological evolution of carbonate-rich lavas on Venus generally would be unlike the congealing of silicate lavas on Venus or Earth. Carbonate-rich melts do not polymerize as their composition evolves during cooling, and their viscosity is so low at all temperatures above the solidus that precipitated crystals commonly settle very readily (Treiman and Schedl 1983). Hence, venusian carbonatite flows should tend to remain highly fluid as they cool virtually to the point of complete solidification; this was shown by the 1988 eruptions of natrocarbonatite at Oldoinyo Lengai (Dawson et al. 1990). Carbonatite flows on Venus may behave somewhat like transient martian rivers and terrestrial arctic rivers during the autumn freeze-up—venusian carbonatite flows may gradually lose liquid as they flow but still remain highly fluid for a great distance. The rate of crystallization of such a flow is described by Fig. 10. Venusian carbonatite rivers may eventually partly fill their channels with sediment, thus causing avulsions or overbank floods of low-viscosity lava (analogous to ordinary crevasse splays of terrestrial rivers). Jams of crusted lava may cause overbank flows of blocky lava with high apparent viscosities (analogous to seasonal jams of river ice and consequent overbank iceflows (aufeis) in Earth’s cold regions). By contrast, silicate flows normally undergo rapid initial cooling and quickly develop chilled crusts, and the residual liquid undergoes rapid increases in viscosity due to polymerization and entrainment of suspended crystals. Hence, the effective viscosities of silicate flows normally increase rapidly after eruption, thus causing rapid downstream changes in rheologic behavior and hindering silicate flows from forming or even just flowing through long, shallow channels.

The distance that a channelized natrocarbonatite flow could travel on Venus is estimated under the condition that no solid crust forms. We take the flow depth as 24 m (the depth of the canale of Fig. 1) and the surface slope = 0.001. For a river-like channel bed (bed friction factor = 0.001) and a fully turbulent fluid (as modeled by Komatsu et al. 1992), the flow velocity is \( \sim 21 \) m sec\(^{-1}\). This is probably an upper limit to the average flow speed, because it assumes bank-full conditions, it does not account for the retarding effects of large-scale bed roughness (such as bars and dunes), and it does not consider the low flow speeds near the channel boundaries. Large deep rivers flowing on low gradients commonly have average flow speeds closer to 10 m sec\(^{-1}\); this lower speed is
probably a more accurate average speed for the canale flow (and would correspond to a Froude number ~0.7). The time required for the flow to solidify completely (by sedimentation) is approximated as the flow thickness divided by the solidification rate, ~8 days, during which time the flow could travel ~7000 km. In sum, natrocarbonatite could travel thousands of kilometers on Venus as a liquid-surfaced stream and still have liquid left to pool in a terminal basin, as commonly observed for canali.

Possible Duration of Canale Activity and the Implied Volumes of Lava

Regardless of the type of lava that was actually responsible for the formation of canali, a huge volume of lava was involved. Quantitative estimates of this volume depend on the discharge rate, which is fairly easy to estimate within a factor of several, and the duration of discharge, which is much more difficult to determine. The cross-sectional area of the canale shown in Fig. 1 is ~4 \times 10^4 m^2 (width 1900 m, depth ~24 m, flat floor, bank slopes ~6°). We assume a nominal average flow speed of 10 m sec^{-1} (from discussion above). Hence, bank-full discharge was ~4 \times 10^3 m^3 sec^{-1}. The dominant meander wavelength, \lambda, of terrestrial rivers depends on the bank-full discharge rate, \dot{Q}, according to the empirical relation (Dury 1964),

\[
\lambda = 30\dot{Q}^{1/2}.
\]  

The meander wavelength of the venusian canale of Fig. I and its theoretical discharge rate calculated above are plotted with empirical data for terrestrial rivers in Fig. 12. The range of uncertainty for the canale’s discharge rate was calculated with Eq. (5) of Komatsu et al. (1992) using plausible ranges of the values of the surface slope (\alpha = 0.0005 to 0.002) and bed friction coefficient (C_f = 0.001 to 0.03) that were used so as to yield minimum and maximum flow speeds of 3 to 29 m sec^{-1}. Within uncertainty, the datum for the canale is consistent with the empirical relationship for terrestrial rivers. Preliminary data for venusian lunar-type sinuous rilles plot slightly below and over an order of magnitude to the right of the datum for the canale (i.e., far off the empirical correlation line for terrestrial rivers).

The duration of canale activity is very difficult to pin down, but there are some clues. The evidence of channel migration and other signs of channel adjustment (Section II) may have required a long time to occur. We consider two cases.

(a) Analogy to terrestrial river dynamics. If bank erosion and downstream sediment transport processes dominated the sedimentologic regime of a canale then terrestrial river dynamics should offer a means to estimate the total duration of channel activity. The Rouge River (Que-

![Discharge at bank-full stage (m$^3$ s$^{-1}$)](image_url)

**FIG. 12.** Empirical relationship of the meander wavelengths and discharge rates of terrestrial rivers. The datum for the canale of Fig. I represents its observed meander wavelength and a calculated range of possible discharge rates (calculations described in text).
bec) has a recent history of gradual channel migration amounting to 1% of channel width per year over a period of 50 years (LaPointe and Carson 1986). The courses of highly sinuous river channels such as the Mississippi commonly relocate by one or more meander wavelengths once per one to several centuries (Schumm 1977). It is expected that the rate of channel migration of rivers is variable due to factors such as the frequency, duration, and magnitude of peak discharge, so that the quoted rates are probably typical but not average rates. If these rates apply to Venus at least roughly, then the extent of channel migration inferred for the canale of Fig. 1 suggests that this flow was active for at least 100 years. By contrast, several canali do not indicate channel migration or other signs of significant channel adjustment to flow regime, so that they may have been active for substantially less than about 100 years.

(b) Channel migration forced by crystal precipitation. The analogy to fluvial river dynamics might not be appropriate for the estimation of the duration of activity. The problem is that precipitation of crystals could greatly exceed the common rates of sediment input into terrestrial stream; hence, venusian canale could migrate more rapidly than terrestrial rivers. Indeed, the solidification and channel-filling rates of a liquid-surfaced natrocarbonatite flow on Venus (Fig. 10) suggest that a channel migration rate of a meander wavelength per year is possible. Hence, one year may be a characteristic period of activity for a sinuous canali.

For the sake of estimation, we take (a) 100 years and (b) 1 year as the period of activity of a typical canale. The discharge rate estimated above indicates a total volume of lava of (a) $1.3 \times 10^{15}$ or (b) $1.3 \times 10^{13}$ m$^3$. Much lava would have been spread over the volcanic flood plains or may have pooled beyond the terminal reach of the channel. These estimated volumes are sufficient for each canale of the size shown in Fig. 1 to spread a layer of volcanic deposits (a) 500 m thick over an area of 2.5 million km$^2$ or (b) 50 m thick over an area of 250,000 km$^2$ (for instance). These rough calculations imply that a large expanse of the lowlands may consist of volcanic deposits that are directly related to canale-forming eruptions (regardless of the lava composition). This conclusion is supported by geologic observations, which indicate a vast extent of plains associated with canali and their termini.

The discharged volumes of canale-forming lava given above can be compared to the amount of CO$_2$ and SO$_2$ contained in Venus' atmosphere. Komatsu et al. (1993) mapped the locations of about 40 canali on Venus (though some were not nearly as large as the one shown in Fig. 1). The range of estimated volume of lava discharged by the canale of Fig. 1 ($1.3 \times 10^{13}$ to $1.3 \times 10^{15}$ m$^3$) multiplied by 40 canali results in a total of $5 \times 10^{14}$ to $5 \times 10^{16}$ m$^3$ of lava. If, for simplicity, this lava consists wholly of molten CaCO$_3$, then the total amount of CO$_2$ contained in this total quantity of lava is equivalent to about 0.1–10% of the venusian atmospheric mass of CO$_2$. If the lavas also were sulfate-rich, for instance if they had roughly the composition of the calcite–anhydrite eutectic, then the amount of SO$_2$ contained in them may exceed the total mass of SO$_2$ at present in the atmosphere by a factor of 2.5 to 250. Hence, the atmosphere could still represent the main reservoir of CO$_2$ on Venus, but Venus' sulfur may be contained primarily beneath the atmosphere (in carbonate–sulfate-rich lavas) plus whatever S exists in weathered silicate rocks, the mantle, and core.

**Transient Melting of Crustal Salts, or a Ground-Carbonate Aquifer on Venus?**

Many aspects of venusian geology can be explained by carbonate–sulfate magmatism of crustal or mantle origin. There is strong theoretical argument and weaker observational data that venusian crustal rocks contain large amounts of salts. The possibility that salts might be abundant on Venus and may melt at shallow depths was first suggested by Sill (1984). Some landforms can be explained in terms of a shallow "ground-carbonate aquifer" or a shallow layer of rock that contains minerals that would melt with modest heating. How reasonable, from a thermophysical point of view, is this explanation? After all, a carbonate aquifer does not exist on Earth, despite this planet's vast sedimentary deposits of limestones, dolomites, and evaporites and a fairly high heat flow. The absence of a stable carbonate aquifer on Earth is explained by the fact that terrestrial sedimentary carbonates tend to metamorphose and decompose as they are heated below the melting point, thus liberating their CO$_2$ from the solid state. However, igneous carbonates of crustal derivation are not unknown on Earth. A melted sedimentary carbonate, now carbonate-rich dikes, was reported by Tiel and Cook (1971). Similarly, carbonate bodies in metamorphic terranes often show structures and field relations consistent with liquid-assisted flow (but are usually ascribed to solid-state deformation). In any case, igneous carbonates formed by anatexis of sedimentary rocks are rare on Earth. On Venus the situation may be different because its atmosphere contains a high partial pressure of CO$_2$ that tends to stabilize carbonates at temperatures within the melting range of carbonate-rich mixtures. This is partly illustrated in Fig. 13, which shows the calcite–wollastonite–quartz buffer; the venusian surface has a temperature below this buffer, meaning that calcite is stable (or metastable) in solid form on the surface. Given the addition of other components (e.g., other carbonates, anhydrite, and other salts) that would
lower the melting point of calcite, a liquid carbonate-rich phase could form and be stable with respect to decarbonation.

Figure 13 also gives the melting curves of carbonate-rich mixtures and two possible average venusian geotherms, which were calculated with two sets of assumptions— for the hotter geotherm it was assumed that (1) transport of heat is by thermal conduction, (2) crustal conductivity is that of nonporous basalt (Touloukian et al. 1975), (3) heat flow is the average surface heat flow on Earth (Fowler 1990). (4) heat flow emanates from deeper than 8 km, and (5) the surface temperature is 750 K (corresponding to the lowest 5th percentile of elevations, McGill et al. 1983). For the colder geotherm the first two assumptions above apply, as well as (3) heat flow is 70% of Earth’s average (accounting for a possible depletion of K). (4) 50% of Venus’ heat production (K, U, and Th) is uniformly concentrated in the upper 20 km, and (5) the surface temperature is 720 K (equivalent to the 95th percentile of elevations). Melting curves were plotted on the basis of known eutectic melting points at low pressures and the known pressure dependence of the melting points of carbonates and carbonate mixtures. (Due to a lack of strictly applicable data, except for MgCO3–CaCO3 (Irving and Wyllie 1975), the slopes of the pressure melting curves are for Na2CO3 and K2CO3; Koster van Groos and Wyllie 1966, and Klement and Cohen 1975.)

Figure 13 shows that the melting points of salt mixtures would be exceeded somewhere in the crust. Natrocarbonatite would melt at depths of only 400–1600 m. Hence, the existence of a large, shallow carbonate aquifer is possible so long as the salts include multiple chemical components, especially Na2CO3. Other salt mixtures lacking abundant alkalies have higher melting points, so that melting may be attained at much greater depths somewhere in the middle or lower crust, unless heating by igneous intrusions or other geologic activity produces a local or transient geotherm substantially hotter than the modeled geotherms.

**Energy Requirements for Impact Melting**

The crater in Fig. 8 is irregular and shallow, common for craters of this size, probably indicating atmospheric breakup of the impactor. The outflow is extensive, suggesting that a large amount of an impact melt of low viscosity was generated. Even though the impactor probably distributed its energy over a wide area (because of atmospheric breakup), and hence, imparted a relatively low energy density to the target rocks, extensive melting still occurred. One possibility is that a major crustal constituent with a low enthalpy of fusion and a low melting temperature allowed substantial partial melting by fairly modest heating. (Or the material may have been already liquefied below the surface.)

We expect that the carbonates and sulfates near ground zero would be completely destabilized by the impact shock heating and that vaporized CO2 and SO2 would be given off in the ejecta, but that carbonates and sulfates away from ground zero might melt but otherwise remain stable. Table VI shows that melting of salts on Venus consumes less energy than melting of silicates on either Earth or Venus. In fact, melting of nathrocarbonatite is more economical than melting of ice on Mars.

Chadwick and Schaber’s (1993) data on Venusian crater outflows are consistent with the hypothesis that salts contribute to impact melting. Those authors interpreted crater outflows as impact melt, but they did not suggest a specific type of melt. If it was composed of molten salts, then the melt abundance should relate to the abundance and melting point of salts in the target rocks. The fraction of craters with outflows decreases from 47% below an elevation of 2.3 km to 29% above it; this elevation roughly coincides with the emissivity “snowline” (Klose et al. 1992). Feagle et al. (1992) considered that perovskite is the major cause of low emissivity above the snowline, and that the replacement of perovskite by calcite and anhydrite accounts for the high emissivities below the snowline. As discussed in Section III, anhydrite is probably especially abundant at low elevations. Hence, carbonate–sulfate-rich weathered rocks can explain, to a first order, the distribution of crater outflows and emissivities on Venus.

Chadwick and Schaber (1993) found that the fraction of craters with outflows increases with crater diameter from 0% for craters smaller than 2 km to 100% for craters ~50
km in diameter, but then the fraction declines at larger diameters. This is similar to fluidized ejecta on Mars, whose craters smaller than 4 km and larger than 40 km generally have unfluidized ejecta, and craters of intermediate size have fluidized ejecta (Barlow and Bradley 1990); this fact often is attributed to the concentration of martian ground ice (though to cause fluidization) at depths of 800 to 4000 m (the depths excavated by craters of intermediate size). If this hypothesis is modified for the case of salts in Venus’ crust, then the data of Chadwick and Schaber (1993) suggest that the abundance of salts increases with depth to ~5 km and then decreases at greater depths, consistent with Chadwick’s and Schaber’s (1993) observation that oblique impacts tend to produce outflows more frequently than impacts at high incidence; the oblique impacts would tend to impart thermal energy to shallow levels, where salts are abundant, whereas impacts at high incidence would inject heat more deeply than 5 km (where salts may be absent).

Figure 13 shows that the model venusian geotherms exceed the temperature of the calcite–wollastonite–quartz buffer at depths of 3.5 to 8 km, below which calcite should decompose. Melting of any other salts that may persist below this depth would be more difficult in the absence of the freezing-point depression caused by calcite. Hence, the distribution of calcite in the upper crust may be an important control on the formation of crater outflows.

**CONCLUSIONS**

Fluvial-like venusian landforms can be explained by carbonate–sulfate volcanism (or, alternatively, by regular silicate lavas but exotic processes). Local present atmosphere–surface equilibrium suggests that mineral assemblages typical of terrestrial carbonatites exist on Venus’ surface. Carbonatite lavas would crystallize to thermally stable solids on Venus’ surface. The low-temperature varieties, such as natrocarbonatite, would erupt effusively; high-temperature varieties, such as calcite–anhydrite melts, could erupt explosively. Depending on composition and elevation, the primary igneous minerals of carbonatites could be thermodynamically unstable and may weather (e.g., calcite may slowly convert to anhydrite), but the volcanic landforms created by carbonatite volcanism would remain stable. The total quantity of CO₂ that may be contained in fluvial-type landforms on Venus and that would be required for the formation of canali is estimated to be equivalent to a small fraction of Venus’ atmospheric CO₂.

Carbonate–sulfate-rich magmas may form on Venus by small degrees of partial melting in a carbonated mantle and/or by anatexsis of weathered crust. The effectiveness of carbonate–sulfate magmas in forming the observed features is greatly increased if these magmas, like natrocarbonatites on Earth, contain large amounts of alkalies and halogens, which depress the melting point. Normal geothermal heat flow might induce melting of some carbonate–sulfate-rich mineral assemblages at shallow levels, allowing the possibility that an aquifer of molten salts exists beneath a frozen salt-rich permafrost hundreds to thousands of meters thick.

Further research is needed to assess better the possibility that extensive carbonate–sulfate volcanism has occurred on Venus. The possible stability of alkali and halogen components in carbonate–sulfate-rich assemblages

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**TABLE VI**

Energy Requirements for 15% Impact Melting on Venus, Earth, and Mars

<table>
<thead>
<tr>
<th>Planet and surface temperature (Tₑ)</th>
<th>Target rock → 15 wt.% impact melt + 85% residual rock</th>
<th>Tₑ of fusible substance (K)</th>
<th>Cₑ of target rock (kJ kg⁻¹ K⁻¹)</th>
<th>ΔH of melt (kJ kg⁻¹)</th>
<th>Energy per kg of melt (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Venus (730 K)</td>
<td>Natrocarbonatite melt, Basaltic residuum</td>
<td>763</td>
<td>1400</td>
<td>1.2 × 10³</td>
<td>4.3 × 10⁵</td>
</tr>
<tr>
<td>Venus (730 K)</td>
<td>CaCO₃–CaSO₄, melt, Basaltic residuum</td>
<td>1261</td>
<td>1500</td>
<td>2.5 × 10³</td>
<td>5.6 × 10⁶</td>
</tr>
<tr>
<td>Venus (730 K)</td>
<td>Andesitic melt, Basaltic residuum</td>
<td>1330</td>
<td>1500</td>
<td>3.5 × 10³</td>
<td>6.4 × 10⁶</td>
</tr>
<tr>
<td>Earth (290 K)</td>
<td>Andesitic melt, Basaltic residuum</td>
<td>1330</td>
<td>1300</td>
<td>3.5 × 10³</td>
<td>9.4 × 10⁶</td>
</tr>
<tr>
<td>Mars (200 K)</td>
<td>Liquid water, Basaltic residuum</td>
<td>273</td>
<td>700</td>
<td>3.3 × 10³</td>
<td>6.7 × 10⁵</td>
</tr>
</tbody>
</table>

*Note.* Natrocarbonatite lavas from Ol'doinyo Lengai, Tanzania, free of gas bubbles and phenocrysts: Kraft and Keller (1989), Dawson et al. (1990), Keller and Kraft (1990), Norton et al. (1990), Norton and Pinkerton (1992). Thermodynamic data adapted from Treiman and Schedl (1983), Treiman (1989), and Touloukian and Buyco (1970). Heat capacities of target rock are approximated as the heat capacity of enstatite at a temperature equal to the geometric mean of Tₑ and Tₑ; we note that the heat capacities of silicate minerals in basalt do not vary substantially with composition.
on Venus has not been sufficiently investigated, and little work has been done pertaining to phase stabilities in the upper crust beneath Venus' surface. The identities of ferroelectric and high-dielectric minerals on Venus are unknown, and their possible roles in carbonate or magmatic alkaline volcanism are unproven; this could be investigated in part by studies of the dielectric and ferroelectric properties of natural minerals and rocks. Additional chemical and mineralogic investigations of Venusian rocks sampled from carefully selected sites is most needed. The hypothesized lava flood plains and terminal deposits of canali would pose especially interesting regions for studies of canale origin and the roles of exotic lavas vs exotic processes in Venusian geologic history. Studies of rocks from high radar-reflectivity regions are necessary to address the hypothesized connections between Venus' radar reflectivity and dielectric properties and hypsometric control of mineral stability.

ACKNOWLEDGMENTS

The authors thank Vic Baker, John Chadwick, Goro Komatsu, Harry Pinkerton, Ken Tanaka, Doris Weir, and an anonymous reviewer for scientific and editorial reviews. JSK was supported by the NASA Venus Data Analysis Program (VDAP). BF was supported by Grants NAGW-2867 and NAGW-3446 from the NASA Planetary Atmospheres Program and VDAP.

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