Present-day volcanism on Venus as evidenced from weathering rates of olivine

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At least some of Venus’ lava flows are thought to be <2.5 million years old based on visible to near-infrared (VNIR) emissivity measured by the Venus Express spacecraft. However, the exact ages of these flows are poorly constrained because the rate at which olivine alters at Venus surface conditions, and how that alteration affects VNIR spectra, remains unknown. We obtained VNIR reflectance spectra of natural olivine that was altered and oxidized in the laboratory. We show that olivine becomes coated, within days, with alteration products, primarily hematite ($Fe_2O_3$). With increasing alteration, the VNIR 1000-nm absorption, characteristic of olivine, also weakens within days. Our results indicate that lava flows lacking VNIR features due to hematite are no more than several years old. Therefore, Venus is volcanically active now.

INTRODUCTION

The crust of Venus consists mostly of basaltic rock, which is in contact with its hot caustic atmosphere (1, 2). Chemical reactions between Venus’ basaltic crust and its atmosphere, i.e., weathering, modify the surface’s mineralogy and composition (3) and affect its visible to near-infrared (VNIR) spectral characteristics and radar backscatter (4, 5). Without liquid water, weathering, based on experimental and modeling work, is suggested to be geochemically slow and includes mainly oxidation reactions that produce coatings of hematite and/or magnetite on surfaces of Fe-bearing mineral grains (2, 3, 6, 7). However, the rates of oxidation on Venus, and how these weathering results affect VNIR reflectance spectra, are not well understood and are needed to constrain the ages of lava flows measured by the Venus Express mission.

The thick atmosphere of Venus prevents the acquisition of high spectral resolution data in the VNIR, which contain crucial sources of mineralogical inferences about planetary surfaces. Venus’ CO2-rich atmosphere is relatively transparent only in a few spectral windows in the NIR (at 1.01, 1.10, and 1.18 μm), which limits the characterization of its surface mineralogy (5, 7–11). Radar backscatter and emissivity of the surface can also be used to constrain mineralogy and rock physical properties by their surface dielectric and magnetic permeability properties (4). However, both radar and VNIR spectroscopic results cannot define the mineralogy of Venus’ crust alone, and one must also invoke constraints on specific mineral stability from experimental and geochemical modeling.

The rocks in Venus’ lowlands are in contact with an atmosphere dominated by CO2 and trace sulfur species at ~460°C and ~92 bars (metamorphic conditions on Earth) and, therefore, should be altered from their original basalt mineralogy. However, in the absence of liquid water, the alteration (or weathering) is predicted to be limited to oxidation and/or sulfurization along surfaces and cracks (2). Basalts on the Venus surface are predicted by thermodynamic modeling and experimental results to oxidize, producing mainly iron oxides [magnetite ($Fe_3O_4$) and/or hematite ($Fe_2O_3$)], pyroxene [(NaCa)(Mg,Fe,Al)(Al, Si)$_2$O$_6$], silica (SiO$_2$), and anhydrite (CaSO$_4$), with possibly minor iron disulfide (pyrite, FeS$_2$), aluminosilicates (e.g., andalusite, Al$_2$SiO$_3$), cordierite [(Mg,Fe)$_2$Al$_5$Si$_3$O$_{18}$], alkali feldspar (KAlSi$_3$O$_8$), enstatite (MgSiO$_3$), and forsterite (Mg$_2$SiO$_4$), depending on the chemistry of the original rock and of the assumptions of atmospheric composition (2, 5, 12–17).

These surface coatings of weathering minerals will affect the reflectance (and emissivity) of Venus’ surfaces in visible and near-infrared (NIR) wavelengths of light, including the NIR windows through Venus’ atmosphere. Earlier studies have used the NIR windows to constrain physical properties of the surface, including its mineralogy, chemistry, and the ages of lava flows (5, 7, 9–11). NIR emissivity variations at 1.02 μm (emissivity is effectively the difference between unity and reflectance) have been used to distinguish surface rich in Fe$^{3+}$-bearing silicates, with high emissivity (low reflectance), from those rich in hematite, with lower emissivity (high reflectance) (5); the NIR emissivity variations, in turn, can be used to constrain weathering (unweathered Fe$^{3+}$-bearing silicates versus oxidized/weathered products containing hematite). Thus, NIR emissivity can be used as an indicator of relative age of erupted material since young flows will be less weathered and should not have a signature of hematite. Smrekar et al. (7) suggested that some lava flows at large volcanoes were younger than 2.5 million years and possibly even younger than 250,000 years based on these flows having high emissivity; however, without experimental constraints on the rates of weathering/oxidation of iron and knowledge of how these affect NIR emissivity spectra, there is large uncertainty in the age of these flows.

To determine the rate at which olivine grains become coated with secondary minerals during weathering, characterize how the surface coatings affect VNIR spectra, and place bounds on the ages of lava flows on the basis of their measured NIR emissivity values, here we present VNIR reflectance spectra for olivine crystals (Mg,Fe)$_2$SiO$_4$, which are likely common in Venus surface basalts (1, 18), that have been oxidized in Earth’s atmosphere at 600° and 900°C for a range of durations (19). Oxidization of olivine produces hematite coatings (19) consistent with reaction products thought to be on Venus (2, 3, 6, 7); therefore, while our experimental results are under terrestrial atmospheric conditions, the results are applicable to the oxidation mineralogy of the surface of Venus.

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METHODS
We obtained VNIR reflectance spectra of samples of olivine that had been oxidized under Earth air in an earlier study (19): gem-quality crystals (~1 cm in size) from San Carlos, AZ and China. The crystals were purchased from mineral dealers and verified by appearance and composition to be consistent with the advertised sources. The crystals were oxidized in a box furnace, under air, at 600° and 900°C and were removed after durations of 0.2, 1, 5, 25, 125, and 625 hours (19). Samples to be oxidized at 900°C were placed directly on a plate in the furnace; samples to be oxidized at 600°C were placed in open-ended alumina crucibles. These temperatures were chosen for consistency with the established methods (20) for olivine oxidation; for comparison, the surface of Venus is ~460°C.

The oxidation state, or \( f_{\text{O}_2} \), in the experiments was that of Earth’s atmosphere: 0.24 bars or ~QFM+10 (21). In comparison, the \( f_{\text{O}_2} \) of the Venus surface atmosphere is predicted to be at or above the magnetite-hematite buffer, i.e., \( \geq \text{QFM}+5 \) (22, 23). The difference between Earth’s atmosphere and the Venus CO2-rich atmosphere (24) is a limitation on the applicability of our experiments. However, other recent experimental results show similar time scales of alteration as in our experiments, with oxide minerals forming within days without providing spectral analyses (25). Oxidation rates depend on temperature (in addition to the oxidation state); the rates should obviously be greater at 900°C than at 600°C, and we expect the latter to be of the same order as that for the Venus surface. The 900°C experiments were included because including these results provides a more advanced weathering reaction that can be observed with the VNIR measurements. Last, the effect of surface coatings on the VNIR spectra is directly applicable as the oxidation mineralogy is expected to be similar to that on the surface of Venus. Therefore, our results provide a direct constraint on the time scales of Venus weathering.

VNIR reflectance spectra of one unaltered olivine (China-10) and all oxidized olivine crystals were measured from 350 to 2500 nm with a Spectral Evolution oreXpress spectrometer with its benchtop reflectance probe. Raw measurements were normalized against the reflectance of a standard white panel. The magnetic properties of the samples were measured with a vibrating sample magnetometer, and their mineralogies were determined by Raman spectroscopy (19). The Raman spectrometer used a dual-laser (758 and 852 nm) excitation and fluorescence mitigation strategy involving successive heating of the laser.

RESULTS
Weathering experiments from Knafelc et al.
Figure 1 shows the progression of changes to the olivine crystals with increased oxidation duration. In the 900°C experiments, reddish-brown surface coatings with specular luster began to appear after only 12 min; the olivine was completely coated after 5 hours. With increasing oxidation time, the coating became darker red-brown in color, and the specular luster disappeared. In the 600°C experiments, the surface coating developed same as for the 900°C experiments, but progressed more slowly (Fig. 1) and never fully coated the olivine grains. Even after 1 month of simulated Venus weathering, green unreacted olivine was still visible through the coating. A thick section of an olivine crystal oxidized at 900°C for 625 hours was analyzed by Knafelc et al. (19) and showed three distinct morphologies of iron-oxide oxidative alteration formation: (i) surface coating; (ii) crack filling; and (iii) within the olivine crystal lattice. Recent experimental results of Venus rock–atmosphere interaction under more realistic atmospheric conditions (CO2-dominated, Ni-NiO buffer) confirm that the rates and alteration minerals in our study are representative of those at Venus surface conditions (25). Specifically, those experiments produced iron oxide coatings on olivine within 1 week (25), consistent with both the mineralogy and alteration time scales of our results.

Fig. 1. Images of olivine crystals before and after oxidation. (A) For the 900°C experiments, and (B) for the 600°C experiments. Images are arranged in the order of increasing time of alteration from left to right. Photo credit: Delia Enriquez-Draper, USRA. Results show a decrease in the green coloration of olivine and the formation of coating an increase in time of oxidation. The coating is initially metallic before becoming dull red with oxidation time.
Raman spectra of the altered samples were dominated by the scattering peaks of olivine even after 625 hours of oxidation (19). Raman signatures of the alteration products, magnetite and hematite, became stronger with alteration duration. Raman spectra also showed characteristic scattering peaks consistent with small proportions of enstatite and quartz in the most oxidized samples (those altered for 625 hours and 900°C); these phases are expected products of oxidation of iron in olivine. Some samples showed small Raman peaks consistent with clinohumite, (Mg, Fe₂)(SiO₄)(OH)₂, which was previously interpreted to be contamination from humidity (19) but is more likely to be present as intergrowths in the original olivine (26).

**VNIR results**

The minerals we interpret to be present in our VNIR reflectance spectra are the same as those identified in the Raman spectra. The reflectance spectra of the unaltered olivine are consistent with pure Fe-bearing olivine, with its characteristic broad absorption band centered at 1000 nm (27) and no absorptions from other phases (Fig. 2). However, oxidation at 900°C for only 12 min changed the VNIR spectra significantly, unlike Raman spectra, which were dominated by olivine features (Fig. 2A). With increasing oxidation duration, the olivine absorption around 1000 nm became weaker. Although the Raman spectra show that the crystal is still mostly olivine after oxidation, changes in the reflectance spectra suggest that the alteration process only occurred at the surface, as the penetration depth of Raman spectroscopy is deeper than that of reflectance spectroscopy. With yet longer alteration durations, reflectance spectra became almost flat, consistent with the development of a coating of magnetite on the olivine crystals. After 1 month of oxidation at 900°C, spectral features characteristic of hematite appeared: a shoulder near 700 nm and an absorption near 860 nm (28). This observation suggests that magnetite forms first during oxidation, followed by a conversion of magnetite to hematite with increasing alteration time scales. After 1 month of oxidation at 900°C, the VNIR spectra show no features characteristic of olivine (i.e., the broad 1000-nm absorption), even though the bulk sample remained predominantly olivine (19).

The spectra for the 600°C experiments show a similar but less severe flattening (Fig. 2B). The olivine absorption at 1000 nm weakened but never fully disappeared. This is consistent with the visually observed cloudiness of the olivine and the formation of magnetite/hematite coatings that did not fully enclose the olivine.

**DISCUSSION AND IMPLICATIONS FOR VENUS**

The Visible Infrared Thermal Imaging Spectrometer (VIRTIS) on Venus Express detected the Venus’ surface through three spectral windows at 1.01, 1.10, and 1.18 μm (8). The results here highlight an important issue for the detection of olivine (and other iron-bearing silicates) in this spectral region. For the 600°C experiments (Fig. 2A), the 1000-nm olivine band weakened after only 1 month of oxidation, which suggests time scales of several years for it to be completely obscured at Venus surface conditions. In the 900°C experiments, Fig. 2B shows that the 1000-nm reflectance band of olivine is entirely absent after 1 month; instead, these experiments show spectral features consistent with magnetite or hematite. The color of Venus’ surface rock and regolith at the Venera 9 and 10 landing sites (6) is consistent with that of red (pigmentary or nanophase) hematite. Therefore, NIR detection of igneous iron-bearing minerals at the Venus’ surface may be dominated by thin coatings of iron-oxide minerals complicating the measurement of primary igneous materials from orbit and challenging efforts to remotely resolve the bulk mineralogy of the Venus surface.

To place estimates on the ages of lava flows, previous studies have used the NIR windows through the Venus’ atmosphere to investigate variations in emissivity variations. High emissivity (or low reflectance) values are from Fe²⁺-bearing igneous minerals (dominantly olivine with pyroxene), whereas Fe³⁺-bearing alteration minerals (specifically hematite) have lower emissivity (or higher reflectance) (5). On the basis of this emissivity contrast, as well as from radar investigations (29), recent work (7, 9, 11) has suggested that some lava flows at large volcanoes on Venus are younger than 2.5 million years and possibly even younger than 250,000 years. The large uncertainty in the age estimate from (7) is due to a lack of constraints on alteration rates on Venus and how quickly that alteration affects the NIR reflectance and emission. If the inferences of (7) are correct, that unweathered Fe³⁺-bearing silicates are responsible for the high-NIR emissivities of some lava flows, our results suggest that these high-emissivity lava flows are not millions or even thousands of years old (7) but were emplaced at most a few years before detection. If so, then Venus is volcanically active today because our experimental results show that the emissivity/reflectance signature of olivine should be obscured by oxide coatings within months to years. This active
volcanism is consistent with episodic spikes of sulfur dioxide in the atmosphere measured by both the Pioneer Venus Orbiter (30) and the Venus Express (31), which could have been produced by the same eruption that formed the young lava flows described by (7).

REFERENCES AND NOTES

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