

PLANETARY SCIENCE

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

Justin Filiberto^{1*}, David Trang², Allan H. Treiman¹, Martha S. Gilmore³

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 (Fe₂O₃). 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 geologically 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 in only 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 (Fe₃O₄) and/or hematite (Fe₂O₃)],

pyroxene [(NaCa)(Mg,Fe,Al)(Al,Si)₂O₆], silica (SiO₂), and anhydrite (CaSO₄), with possibly minor iron disulfide (pyrite, FeS₂), aluminosilicates (e.g., andalusite, Al₂SiO₅), cordierite [(Mg,Fe)₂Al₄Si₅O₁₈], alkali feldspar (KAlSi₃O₈), enstatite (MgSiO₃), and forsterite (Mg₂SiO₄), 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 surfaces rich in Fe²⁺-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 Fe²⁺-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)₂SiO₄, 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). Oxidation 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.

¹Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd., Houston, TX 77058, USA.

²University of Hawai'i at Mānoa/Hawai'i Institute of Geophysics and Planetology, 1680 East-West Rd., Honolulu, HI 96822, USA. ³Department of Earth and Environmental Sciences, Wesleyan University, 265 Church Street, Middletown, CT 06457, USA.

*Corresponding author. Email: jfiliberto@lpi.usra.edu

Copyright © 2020
The Authors, some
rights reserved;
exclusive licensee
American Association
for the Advancement
of Science. No claim to
original U.S. Government
Works. Distributed
under a Creative
Commons Attribution
NonCommercial
License 4.0 (CC BY-NC).

Downloaded from <http://advances.sciencemag.org/> on February 11, 2020

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 fO_2 , in the experiments was that of Earth's atmosphere: 0.24 bars or ~QFM+10 (21). In comparison, the fO_2 of the Venus surface atmosphere is predicted to be at or above the magnetite-hematite buffer, i.e., \geq 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.

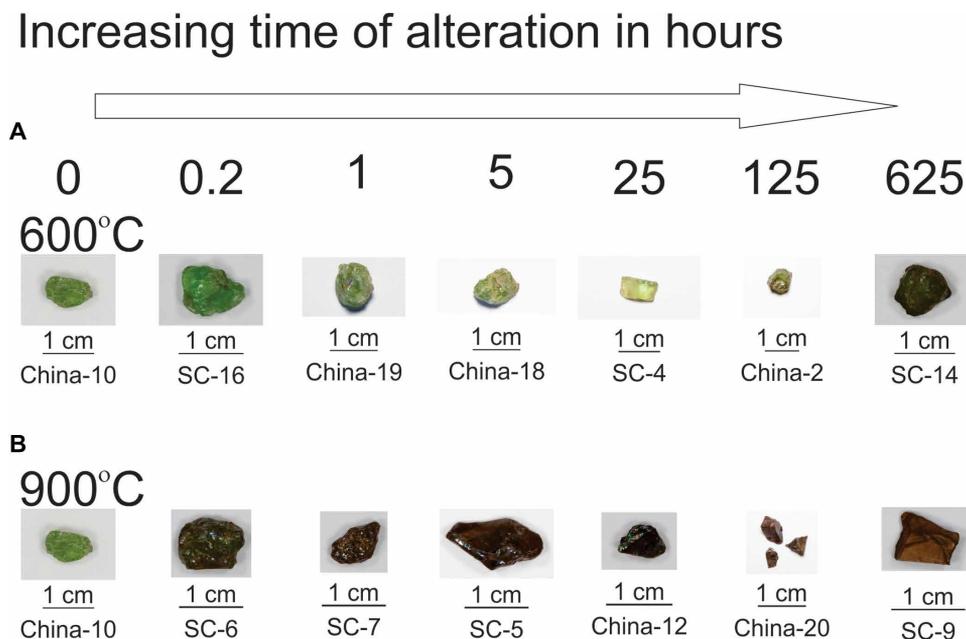


Fig. 1. Images of olivine crystals before and after oxidation. (A) For the 900°C experiments, and (B) for the 600°C experiments. Images are arranged in the order of increasing time of alteration from left to right. Photo credit: Delia Enriquez-Draper, USRA. Results show a decrease in the green coloration 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, $(\text{Mg, Fe})_9(\text{SiO}_4)_4(\text{OH})_2$, 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 Fe^{2+} -bearing igneous minerals (dominantly olivine with pyroxene), whereas Fe^{3+} -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 Fe^{2+} -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

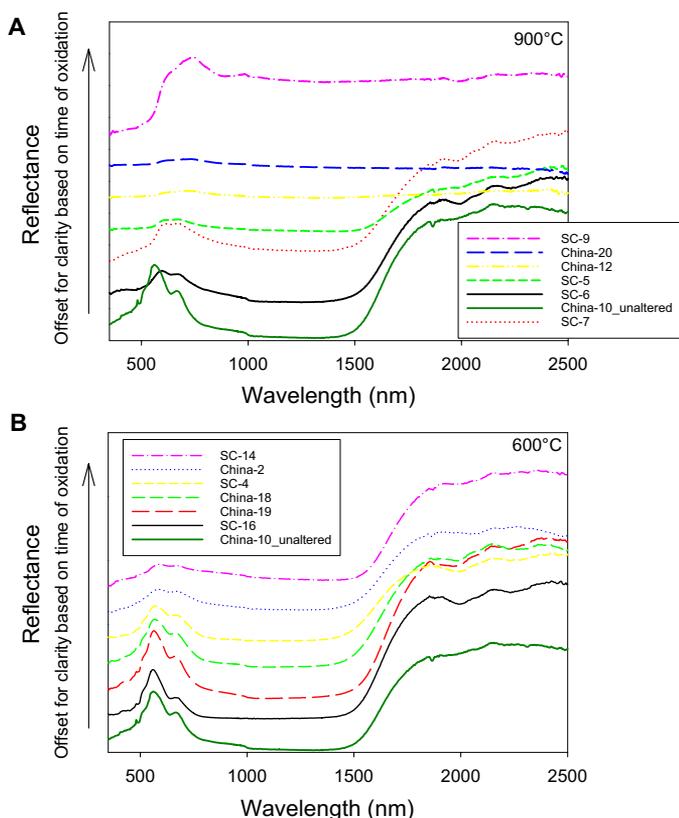


Fig. 2. VNIR reflectance for unoxidized and oxidized crystals of olivine. (A) Oxidation at 900°C and (B) oxidation at 600°C, offset for clarity based on increasing time of oxidation as indicated in Fig. 1. China-10 was also measured as the unaltered olivine crystal reference for both temperatures. Spectra show a decrease in olivine features with increasing time of oxidation by first becoming relatively featureless and then showing a hematite signature.

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

1. A. H. Treiman, in *Exploring Venus as a Terrestrial Planet*, L. W. Esposito, E. R. Stofan, T. E. Cravens, Eds. (Wiley, 2007), vol. 176, pp. 250, Geophysical Monograph Series.
2. M. Y. Zolotov, Gas-solid interactions on Venus and other solar system bodies. *Rev. Mineral. Geochem.* **84**, 351–392 (2018).
3. B. Fegley Jr., G. Klingelhöfer, R. A. Brackett, N. Izenberg, D. T. Kremser, K. Lodders, Basalt oxidation and the formation of hematite on the surface of Venus. *Icarus* **118**, 373–383 (1995).
4. J. B. Garvin, J. W. Head, G. H. Pettengill, S. H. Zisk, Venus global radar reflectivity and correlations with elevation. *J. Geophys. Res. Solid Earth* **90**, 6859–6871 (1985).
5. M. Gilmore, A. Treiman, J. Helbert, S. Smrekar, Venus surface composition constrained by observation and experiment. *Space Sci. Rev.* **212**, 1511–1540 (2017).
6. C. M. Pieters, J. W. Head, S. Pratt, W. Patterson, J. Garvin, V. L. Barsukov, A. T. Basilevsky, I. L. Khodakovsky, A. S. Selivanov, A. S. Panfilov, Y. M. Gektin, Y. M. Narayeva, The Color of the Surface of Venus. *Science* **234**, 1379–1383 (1986).
7. S. E. Smrekar, E. R. Stofan, N. Mueller, A. Treiman, L. Elkins-Tanton, J. Helbert, G. Piccioni, P. Drossart, Recent hotspot volcanism on Venus from VIRTIS emissivity data. *Science* **328**, 605–608 (2010).
8. P. Drossart, G. Piccioni, A. Adriani, F. Angrilli, G. Arnold, K. H. Baines, G. Bellucci, J. Benkhoff, B. Bézard, J. P. Bibring, A. Blanco, M. I. Blecka, R. W. Carlson, A. Coradini, A. di Lellis, T. Encrenaz, S. Erard, S. Fonti, V. Formisano, T. Fouchet, R. Garcia, R. Haus, J. Helbert, N. I. Ignatiev, P. G. J. Irwin, Y. Langevin, S. Lebonnois, M. A. Lopez-Valverde, D. Luz, L. Marinangeli, V. Orofino, A. V. Rodin, M. C. Roos-Serote, B. Saggin, A. Sanchez-Lavega, D. M. Stam, F. W. Taylor, D. Titov, G. Visconti, M. Zambelli, R. Hueso, C. C. C. Tsang, C. F. Wilson, T. Z. Afanasenko, Scientific goals for the observation of Venus by VIRTIS on ESA/Venus express mission. *Planet. Space Sci.* **55**, 1653–1672 (2007).
9. E. R. Stofan, S. E. Smrekar, N. Mueller, J. Helbert, Themis Regio, Venus: Evidence for recent (?) volcanism from VIRTIS data. *Icarus* **271**, 375–386 (2016).
10. D. Kappel, G. Arnold, R. Haus, Multi-spectrum retrieval of Venus IR surface emissivity maps from VIRTIS/VEX nightside measurements at Themis Regio. *Icarus* **265**, 42–62 (2016).
11. P. D'Incecco, N. Müller, J. Helbert, M. D'Amore, Idunn Mons on Venus: Location and extent of recently active lava flows. *Planet. Space Sci.* **136**, 25–33 (2017).
12. B. Fegley, A. H. Treiman, Chemistry of atmosphere-surface interactions on Venus and Mars, in *Venus and Mars: Atmospheres, ionospheres, and solar wind interactions; Proceedings of the Chapman Conference* (1992), Balatonfured, Hungary, 4 to 8 June 1990, pp. 7–71.
13. V. L. Barsukov, V. P. Volkov, I. L. Khodakovsky, The crust of Venus: Theoretical models of chemical and mineral composition. *J. Geophys. Res. Solid Earth* **87**, (1982).
14. K. B. Klose, J. A. Wood, A. Hashimoto, Mineral equilibria and the high radar reflectivity of Venus mountaintops. *J. Geophys. Res. Planets* **97**, 16353–16369 (1992).
15. V. Volkov, M. Y. Zolotov, I. Khodakovsky, in *Chemistry and Physics of Terrestrial Planets* (Springer, 1986), pp. 136–190.
16. Y. I. Sidorov, Mathematical simulation of complex natural systems. *Geochem. Int.* **44**, 94–107 (2006).
17. A. Treiman, S. Schwenzer, in *Venus Geochemistry: Progress, Prospects, and New Missions* (2009), Houston, Texas, 26 to 27 February 2009, vol. 1470, pp. 49–50.
18. J. Filiberto, Magmatic diversity on Venus: Constraints from terrestrial analog crystallization experiments. *Icarus* **231**, 131–136 (2014).
19. J. Knafelc, J. Filiberto, E. C. Ferré, J. A. Conder, L. Costello, J. R. Crandall, M. D. Dyar, S. A. Friedman, D. R. Hummer, S. P. Schwenzer, The effect of oxidation on the mineralogy and magnetic properties of olivine. *Am. Mineral.* **104**, 694–702 (2019).
20. D. L. Kohlstedt, C. Goetze, W. B. Durham, J. Vander Sande, New technique for decorating dislocations in olivine. *Science* **191**, 1045–1046 (1976).
21. C. McCammon, The paradox of mantle redox. *Science* **308**, 807–808 (2005).
22. B. Fegley Jr., M. Y. Zolotov, K. Lodders, The oxidation state of the lower atmosphere and surface of Venus. *Icarus* **125**, 416–439 (1997).
23. J. S. Lewis, F. A. Kreimendahl, Oxidation state of the atmosphere and crust of Venus from pioneer Venus results. *Icarus* **42**, 330–337 (1980).
24. F. P. Mills, L. W. Esposito, Y. L. Yung, in *Exploring Venus as a Terrestrial Planet*, L. W. Esposito, E. R. Stofan, T. E. Cravens, Eds. (American Geophysical Union, Washington, D.C., 2007), vol. Geophysical Monograph 176, pp. 73–100.
25. G. Berger, A. Cathala, S. Fabre, A. Y. Borisova, A. Pages, T. Aigouy, J. Esvan, P. Pinet, Experimental exploration of volcanic rocks-atmosphere interaction under Venus surface conditions. *Icarus* **329**, 8–23 (2019).
26. M. Kurosawa, H. Yurimoto, K. Matsumoto, S. Sueno, in *High-Pressure Research: Application to Earth and Planetary Sciences*, Y. Syono, M. H. Manghni, Eds. (American Geophysical Union, Washington, D.C., 1992), vol. 67, pp. 283–287.
27. R. G. Burns, *Mineralogical Applications of Crystal Field Theory* (Cambridge Univ. Press, ed. 2, 1993), pp. 551.
28. R. V. Morris, D. G. Agresti, H. V. Lauer Jr., J. A. Newcomb, T. D. Shelfer, A. V. Murali, Evidence for pigmentary hematite on Mars based on optical, magnetic, and Mossbauer studies of superparamagnetic (nanocrystalline) hematite. *J. Geophys. Res. Solid Earth* **94**, 2760–2778 (1989).
29. J. L. Whitten, B. A. Campbell, Recent volcanic resurfacing of Venusian craters. *Geology* **44**, 519–522 (2016).
30. L. W. Esposito, Sulfur dioxide: Episodic injection shows evidence for active Venus volcanism. *Science* **223**, 1072–1074 (1984).
31. E. Marcq, J.-L. Bertaux, F. Montmessin, D. Belyaev, Variations of sulphur dioxide at the cloud top of Venus's dynamic atmosphere. *Nat. Geosci.* **6**, 25–28 (2013).

Acknowledgments: We thank the USRA HQ for acquisition of the VNIR spectrometer. We would also like to thank D. Enriquez-Draper for help with photographing the samples, P. Byrne and an anonymous reviewer for comments that helped clarify the manuscript, and editor R. Klima for handling of this manuscript. **Funding:** A.H.T., J.F., and M.S.G. thank partial support from NASA SSW grant 80NSSC17K0766. **Author contributions:** J.F., D.T., A.H.T., and M.S.G. contributed to the writing, discussion, interpretation, and application of the results to Venus. **Competing interests:** All authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper. Additional data related to this paper may be requested from the authors. This is LPI contribution no. 2119. LPI is operated by USRA under a cooperative agreement with the Science Mission Directorate of the National Aeronautics and Space Administration.

Submitted 18 April 2019
Accepted 7 November 2019
Published 3 January 2020
10.1126/sciadv.aax7445

Citation: J. Filiberto, D. Trang, A. H. Treiman, M. S. Gilmore, Present-day volcanism on Venus as evidenced from weathering rates of olivine. *Sci. Adv.* **6**, eaax7445 (2020).

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

Justin Filiberto, David Trang, Allan H. Treiman and Martha S. Gilmore

Sci Adv **6** (1), eaax7445.
DOI: 10.1126/sciadv.aax7445

ARTICLE TOOLS <http://advances.sciencemag.org/content/6/1/eaax7445>

REFERENCES This article cites 23 articles, 6 of which you can access for free
<http://advances.sciencemag.org/content/6/1/eaax7445#BIBL>

PERMISSIONS <http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science Advances* is a registered trademark of AAAS.

Copyright © 2020 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).