VENUS ALTERATION: MODEL AND EXPERIMENTAL RESULTS. J. Filiberto[1], J. Semprich[2], K.S. Cutler[1,4], H. Teffeteller[3], R. Reid[3], M.C. McCanta[3], M. Rutherford[5], and A.H. Treiman[1]. Lunar and Planetary Institute, USRA, Houston, TX 77058. jfiliberto@lpi.usra.edu, [2]AstrobiologyOU, The Open University, Milton Keynes MK7 6AA, UK. [3]Department of Earth and Planetary Sciences, University of Tennessee at Knoxville, Knoxville, TN 37996. [4]Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK. [5]Dept. Earth, Environmental, & Planetary Sciences, Brown University, Providence, RI 02912.

Introduction: The surface of Venus is in contact with a hot (~470° C), high pressure (92 bars), and caustic (CO_2 with S) atmosphere, which should cause progressive alteration of the crust [1, 2]. Alteration should occur quickly, forming mainly rock coatings of iron-oxides and sulfates, since water is not stable on the surface to make clay minerals [1, 3]. These coatings could, in theory, be used as a way to age date different lava flows, since the amount of alteration should correlate with the age of the rock exposed to the atmosphere [4, 5]. However, the exact alteration mineralogy and rate are still not well constrained [5]. Further, how the alteration mineralogy affects orbital emissivity measurements of the Venus surface is similarly not well understood [6]. Here we combine recent geochemical modeling [7] and experimental [8-14] studies to show what should be the main alteration minerals, the alteration rate, and how these can be used to constrain the age of lava flows measured from orbit.

Modeling: [7] used the thermodynamic modeling code Perple_X [15] to calculate the equilibrium alteration mineralogy of the basaltic plains and mountain tops of Venus using relevant compositions (basalt, alkali basalt, and granite) and conditions (T, P, fO_2, fS_2, X_{H_2O}, and X_{CO_2}) to provide support that pyrite is causing the high radar backscatter observed at high elevations in the northern highlands. Here, we focus on the calculations for the basaltic plains (**Fig. 1**), which show that the mineralogy is dependent on bulk composition, oxygen fugacity, sulfur fugacity, and (not shown) X_{CO_2} of the atmosphere. The most applicable conditions (black box) show that the alteration mineralogy is dominated by magnetite, hematite, and anhydrite with possibly pyrite (at higher fS_2 and low fO_2).

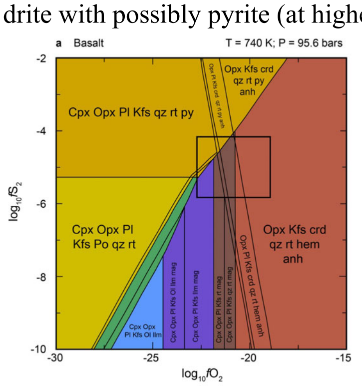

Fig. 1. From [7] Calculated phase equilibria for a basalt composition as a function of oxygen and sulfur fugacities and at temperature-pressure conditions relevant for planetary radius (740 K, 95.6 bar). The black box represents the most likely conditions.

Experimental: Experimentally it is difficult to replicate the exact conditions (combined 472K, 92 bars, CO_2 atmosphere, but water-free) of Venus for long duration. Therefore, here we summarize two different approaches: (1) long duration (up to 7 weeks) oxidation experiments at elevated temperatures and (2) shorter duration (1-2 weeks) experiments under more directly applicable conditions.

High temperature oxidation of basalt and glass produced iron oxide coatings within weeks depending on temperature (**Fig. 2**) [3, 10-12]. Pyroxene oxidation produced small iron oxide grains along cracks in the sample, as well as oxidation of Fe^{2+} to Fe^{3+} in the crystals. Unlike experiments on olivine and basalt glass, these experiments did not produce iron-oxides coating the sample [11, 16]. [9, 14] conducted experiments on basalt and alkali basaltic glasses at more applicable Venus surface conditions and a pure CO_2 atmosphere. Their results showed that the alteration phases iron oxide(s) and carbonates can form on the surfaces of basalts under Venus surface conditions. Finally, experiments under a sulfur-bearing CO_2 atmosphere [8, 13] produced similar results with oxidation of glasses and olivine forming iron oxides coatings. These experiments also contained sulfur and hence formed sulfates. Ongoing work suggests that sulfates form as quickly as iron-oxides (and possibly faster) coating the surface of rocks and minerals [13].

Implications for Mineralogy, Alteration Rate, and Lava Flow Age: Over the experimental range of pressure and oxygen fugacity conditions, the experiments produced similar mineralogy and rates of alteration: iron (and calcium) diffused through the sample to the surface on experimental time scales (one to seven weeks) producing iron-oxides **(Fig. 2)**. The iron oxides (first magnetite and then hematite) formed coatings on the olivine and basaltic glass depending on the time of alteration. The main difference between experimental results is the length of time and temperature of the experiment. This suggests that the driving force is not oxygen fugacity (above a certain threshold) and iron-oxidation, but instead is iron-diffusion through the sample, which has been previously suggested [17]. The mineralogy results are also consistent with the geochemical modeling result – that magnetite and hematite

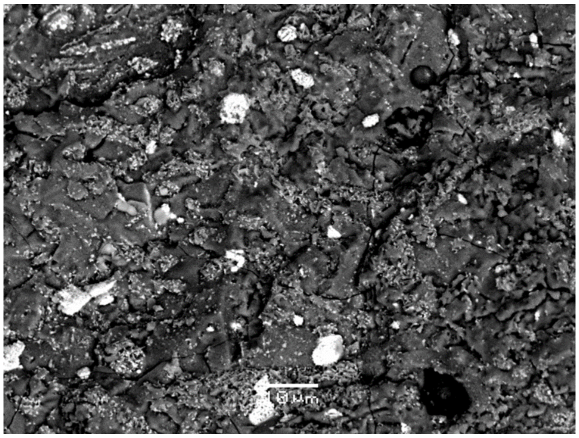

Fig. 2 Backscattered electron image of an experimentally oxidized and altered Venus analog basalt. The white specs throughout the image are experimentally produced the iron-oxide hematite. The hematite preferentially forms on glass, olivine, and the iron-rich rims of pyroxene. Image source: Cutler et al. (2020) in The Planetary Science Journal published under a creative license agreement.

should dominate the assemblage, depending on the fO_2. One caveat to this comparison is that the geochemical modeling approach assumes equilibrium conditions and that the entire bulk rock is reacting, while the experiments show that this is not the case.

Combining the experimental results and modeling calculations suggests that fresh basalt on Venus' surface should react quickly with the atmosphere, and produce mainly iron-oxides and sulfates. Red hematite (pigmentary or nanophase) coating the surface of rocks is consistent with the color of surface rocks and regolith on Venus at the Venera 9 and 10 landing sites [18]; however pigmentary hematite at 470° C may be more brown than red [19]. Further, orbital emissivity measurements of lava flows at Idunn Mons range from >0.9 to <0.8, which is consistent with a change from fresh basalt to altered hematite coated basalt [5, 10, 11]. Suggestions based on laboratory derived alteration rates are consistent with recent (a few but no more than ten thousand years old) lava flows [9-11]. These estimates are based on the rate of iron-oxide formation, which may be hindered if sulfates form and coat the surface of basalt faster than iron can diffuse [6]. However, anhydrite ($CaSO_4$) can have an emissivity as low as 0.1 [20], and should affect orbital measurements similar to hematite. Therefore, the alteration rates for hematite formation should be considered a lower bound and calculated lava flow unit ages based on those should be considered a maximum, but more combined experimental and spectroscopy studies with S-added are needed to fully constrain these rates.

Implications for Future Measurements: The results here show that the surface of Venus should be covered in sulfate and iron-oxide (mainly hematite) coatings, which would preclude VNIR detections of old bedrock or regolith from orbit. To further complicate this, Venus' thick CO_2-rich atmosphere prevents VNIR spectroscopy of the surface except for a few spectral windows near 1 µm [21]. However, the combined results show that any bedrock with VNIR properties of unaltered rock (not hematite + sulfates) must be young (years to about ten thousand years old depending on the bulk chemistry and the exact reaction rate). Therefore, orbital measurements from DAVINCI+ or VERITAS [22, 23] could produce age maps of basaltic lava flows similar to what has been proposed for Idunn Mons [5, 10, 11]. For a future lander, if rocks can be broken or drilled *in situ:* (1) the interior should be largely free of alteration to get a bulk composition and (2) the weathering or alteration rind could be measured and used as a potential geochronometer (with further detailed experimental calibrations).

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