EXPERIMENTAL INVESTIGATION OF BASALT AND PYROXENE OXIDATION: IMPLICATIONS FOR SPECTROSCOPIC ANALYSIS OF THE SURFACE OF VENUS.

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Introduction: The surface of Venus should be extensively altered by interactions with its CO_2-CO-SO_2 atmosphere, which is at ~95.6 bars and ~470°C at the surface [1,2]. These gas-solid interactions should include oxidation and sulphurisation, which produce thin coatings of magnetite, hematite, and/or sulphates on the surfaces of minerals and rocks [3]. Previous studies have examined the effect of high-temperature oxidation of ferromagnesian silicate minerals on visible to near-infrared (VNIR) spectrum [e.g. 4], but these experiments have used various elevated temperatures with short duration runs. Hence, here we look to isolate oxidation effects on diagnostic pyroxene absorption bands at a stable elevated temperature for longer durations. The subsequent changes in the spectrum enables constraints for estimates of pyroxene and basalt weathering rates to be determined.

Pyroxenes, ferromagnesian silicate minerals, are abundant in terrestrial basalts, and thus should be a major constituent of Venus basalts [5,6]. In VNIR, pyroxenes exhibit distinctive absorption bands near the 1 and 2 µm wavelengths; both arise from Fe_{2+} crystal field (CF) transitions [7]. One of these absorption bands may be visible from space as Venus' surface is visible through three spectral "windows" at 1.01, 1.10 and 1.18 µm, which were recognised and used by Venus Express' Virtual Infrared Thermal Imaging Spectrometer (VIRTIS) [8]. Using VIRTIS and Venus Express data on light emitted by Venus' surface in these bands, [9] identified 'hotspot' regions with anomalously high emissivity (or low reflectance). These 'hotspots' were suggested to be fresh, unweathered basalt flows, implying that the flows are young, perhaps less than 250,000 years old. Our previous work [10] indicates that these flows may be only a few years old, but that result is based only on the oxidation of olivine and not other basaltic minerals. This study extends [10] by investigating weathering rates of pyroxene and a terrestrial basalt analog, discerning the effects of oxidation on VNIR spectra of pyroxene and basalt, and testing implications for volcanism on Venus.

Sample, Experimental and Analytical Details:

Samples. These experiments involved diopside (D), augite (A), and pyroxenite (P) samples, which were bought from Ward's Science. In addition, we obtained a basalt (B) from Sverrefjell volcano in Spitsbergen (Svalbard, Norway) [11]. We verified the chemical composition of these samples by Electron MicroProbe Analysis (EMPA).

Experimental. This study follows the approach from [10] for the oxidation of olivine. First, we cut all of the samples to approximately 5 mm thickness. Then we placed the unmounted and unpolished samples of D, A, P, and B in an Thermo Lindberg/Blue M box furnace at NASA Johnson Space Centre (JSC), under terrestrial atmospheric conditions at 600°C, and were removed after being exposed for 1, 2, 4 and 7 weeks. The furnace gas had the oxygen fugacity (fO_2) of Earth's atmosphere, ~$10^{-0.24}$ bar [12], compared with that of Venus' atmosphere of ~$10^{-21.0}$ bars [13]. Despite differences in our experimental conditions to Venus' atmospheric conditions, only the effect of temperature is explored here as it is the main factor causing key spectral changes [14].

Analytical. Chemical analyses of the unoxidised samples were obtained by EMPA using the Cameca SX 100 instrument at JSC. The analyses used an electron accelerating potential of 15 kV, a focused beam for all mineral analyses but a defocused beam for the basalt glass. Beam currents were between 1 and 20 nA, depending on the sample. The instrument was calibrated for Na, Mg, Al, Si, K, Ca, Ti, Fe, Cr and Mn, using natural and synthetic mineral standards. Any analyses with sums totalling <99.5% or >100.99% were discarded.

VNIR reflectance spectra of unoxidised and oxidised samples were acquired using a Spectral Evolution OreXpress Spectrometer with a Benchtop Reflectance Probe. Reflectances were measured on sawn surfaces, at 0° phase angle, between 0.35 to 2.5 nm wavelengths. Reflectances were calibrated against the manufacturer's provided white panel.

The reacted surface of each sample was then examined by Scanning Electron Microscopy (SEM).
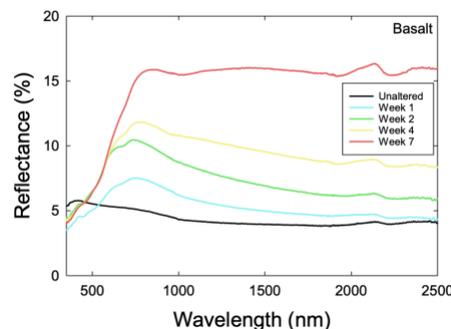

Fig. 1: Reflectance spectra for alkali basalt samples after oxidation at 600°C.

The back-scattered electron (BSE) images were obtained using the JEOL JSM-5910LV at JSC with a 15-kV accelerating voltage and working distances of 18-23 mm.

Results: VNIR spectra were acquired for all samples, but only the results for basalt glass (B) are highlighted here (**Fig. 1**). B is an alkali basalt with 44.7 wt% SiO_2, 5.0 wt% Na_2O and 1.9 wt% K_2O. This composition is similar to that obtained by the Venera 13 probe at its landing site [15]. The alkali basalt is vesicular, and contains: glass, euhedral-subhedral olivine phenocrysts (average $Fo_{84.3}$ cores and $Fo_{83.6}$ rims), clinopyroxene ($Wo_{50}En_{35}Fs_{15}$), plagioclase (An_{49}), and euhedral to subhedral spinels (from Cr-magnetite to Fe-chromite).

The unoxidised alkali basalt have very low reflectances, $< 6\%$, across the range measured (Fig. 1). Superimposed on this generally dark spectrum are absorption bands at 1005 and 2210 nm, both of which arise from the abundant high calcium pyroxene (augite) [16] in the basalt matrix. Both bands are caused by Fe_{2+} M2 site CF transitions [17, 18].

In the oxidised basalt, one of the main features is the 1005 nm augite band that weakens after two weeks (**Fig. 1**). Other changes to wavelength and band depth for both absorption bands are being investigated further. The diagnostic VNIR characteristics of hematite increase substantially during the 7 weeks of reaction (**Fig. 1**). The fine-grained (pigmentary) hematite has an intense absorption edge centred around 700 nm [19]; shorter wavelengths of light are strongly absorbed, and longer wavelengths reflected (hence its red colour). This absorption edge is evident even for B weathered for only a week (**Fig. 1**) and increases in strength with duration of weathering. BSE images of the weathered surfaces demonstrate the process behind this change in VNIR spectrum. Surfaces of weathered basalt are decorated with abundant micron-sized grains of hematite (**Fig. 2**). The development of these hematite grains is the result of migration of iron ions to the surface [20]. These grains reflect light (giving the characteristic hematite spectrum of **Fig. 1**), and obscure the underlying basaltic minerals from view. BSE images also illustrate how the VNIR spectra is highly sensitive to even small changes in the amount of hematite present on sample surfaces [21](**Fig. 2**). With longer periods of oxidation, the
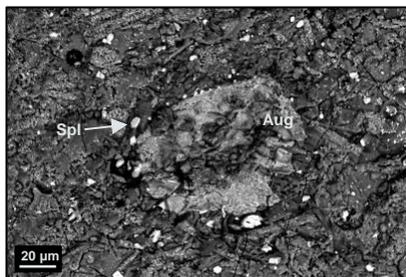

Fig. 2: BSE image of alkali basalt oxidised after 7 weeks. There is an abundance of hematite grains present on the surface shown by small white specks. Aug= augite; spl= spinel.

amount of hematite on the surface increases. The hematite is most abundant on the surfaces of minerals with higher Fe contents –the olivine phenocrysts, the ferroan rims of augite phenocrysts, and on the glass.

Discussion: The timescale of volcanism on Venus [9] can now be revised by incorporating the experimental oxidation rates presented here and in [10]. [10] showed that olivine oxidation occurs over weeks at 900°C and a year at 600°C. The results here show that oxidation of pyroxene is an order of magnitude slower than olivine [10] and can be constrained to approximately tens of years. However, the results for basalt here show that a thin layer of hematite would form within months of contact with the atmosphere, which would obscure the diagnostic VNIR bands of olivine and pyroxene. This implies that lava flows in [9] with high emissivity (or low reflectance) are substantially younger than previously estimated, and are consistent with recent estimates based on olivine oxidation [10] to be a few years old or less. Subsequently, this implies that emissivity in the 1.0 µm region might be used from orbit to estimate the ages of basalt lava flows.

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