ASSESSMENT OF THE EFFECT OF BULK COMPOSITION ON BASALT WEATHERING ON VENUS'

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Introduction: The basaltic surface of Venus is exposed to an average temperature of ~470°C and ~90 bars of pressure in a CO₂-rich (~96%) atmosphere, with significant (~150 ppmv) SO₂. In this caustic, oxidizing environment (oxygen fugacity (fO₂) near magnetite-hematite buffer), basalts on Venus' surface are likely to have been altered extensively [1]. Recent experiments show that basalt in a pure CO₂ atmosphere alters to produce a rind similar to that expected on Venus, and that such rinds would be detectable in NIR emissivity after reaction in ~240 to ~12,000 years [2]. In contrast, similar alteration experiments at higher temperatures (600°C and 900°C) on olivine and basalt glass in Earth air suggest that emissivity reducing coatings of Feoxides may form in months to a few years [3,4].

However, neither of these studies considered the effects of Venus' atmospheric SO₂. Several studies in both experimental and natural settings have demonstrated that, under similar oxygen fugacities, SO₂-enriched gas rapidly alters natural and synthetic basaltic glasses, producing surficial Ca- and Na-sulfate species and iron oxides [5-9]. Here, we report on the effect of bulk-rock starting compositions on the mineralogy of alteration products and their abundances, produced experimentally by reacting synthetic tholeiitic and natural alkali basalt glasses in a dry CO₂-SO₂ gas atmosphere at Venus surface conditions.

Methods:

Experimental. Experiments were run on 1) a synthetic tholeiite glass with a composition similar to that of Venus' plains basalts (from Venera 14 and VEGA 2 XRF analyses) [10] and 2) a natural alkaline basalt from Sverrefjell volcano, Norway, which has a composition similar to that of the Venera 13 basalt. Experiments were designed to approximate Venus' surface pressure (90 bars), temperature (700°C & 470°C), and atmosphere composition. They were run for 14 and 22 days in cold-seal pressure vessels in the lab of M. Rutherford at Brown University. A magnetite-hematite buffer was used to approximate Venus' surface oxygen fugacity. Powdered pyrite was added as a source of SO₂ gas [11].

Analytical. At the conclusion of the runs, the surfaces of the samples were characterized using backscatter electron (BSE) images using the Phenom Pro scanning electron microscope (SEM) at the University of Tennessee. Specifically, each sample surface was imaged in a transect of 25 individual

frames, with a field of view for each frame of $\sim 50 \ \mu m$. Phases (and phase aggregates) in each image were then characterized using energy dispersive X-ray spectroscopy (EDS) to determine their mineralogies. Mineral abundances were estimated visually by comparing them with a chart of modal abundance [12]. Finally, the 25 estimates were averaged to produce overall abundance percentages of the alteration phases present on each sample surface. For comparison, these steps were repeated using identical samples from 2-week runs in pure CO_2 [2].

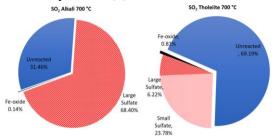


Figure 1. Graphic showing estimated abundances of alteration phases observed on alkali (left) and tholeiite (right) samples reacted for 2-weeks at 700 $^{\circ}$ C in a CO₂ and SO₂ gas mixture under 90 bars pressure.

Results: On the alkaline basalt sample, the surface is covered by 68.5% reaction products at 700° C (Fig. 1). Nearly all of the reaction product is Na₂SO₄ (metathenardite, hereafter thenardite) in grains of (~1 μ m to > 30 μ m in diameter. Reaction products are less dense on the sample's microphenocrysts of olivine, pyroxene, and plagioclase (Fig. 2A). Iron oxides are rare, 0.1% of the surface, in grains of < 1 μ m.

On alteration at 470°C, the surface of the alkali basalt (Fig. 3) is partially coated with thenardite in subhedral masses ~1–5 μm in diameter and possibly as nearly uniform sized and evenly dispersed phases < 1 μm in diameter (Fig. 2C). However, there are several regions on the surface with distinct grain boundaries (e.g., Fig. 2C, white arrows) showing no obvious evidence of reaction. Fe-oxides are rare (0.02%), as randomly spaced grains of ~1 μm .

The tholeiite sample reacted at 700°C is covered with a nearly-continuous frost-like coating of grains smaller than 1 μ m, possibly anhydrite, (Fig. 1), with larger subhedral masses of anhydrite (~1–10 μ m in diameter). Rare grains of Fe-oxide appear either as

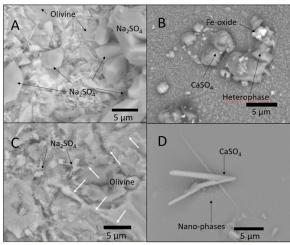


Figure 2. SEM microphotographs of the surfaces of samples from this study. A) 700°C, alkali composition with thenardite and olivine shown. B) 700°C, tholeiite showing anhydrite and iron-oxide in a heterophase patch andnanophases covering most of the surface. C) 470°C, alkali showing thenardite grains, olivine with a sharp grain boundary, and likely sulfate nanoscale phases. D) 470°C, tholeiite with anhydrite and barely visable nanophases.

isolated grains $< 1 \mu m$, as aggregates of such grains, or with anhydrite grains in clusters (Fig. 2B).

After reaction at 470°C, the surface of the tholeiite (Fig. 3) is coated by a frosting of nanometer-sized anhydrite grains, with scattered larger acicular crystals ~1–10 μ m long (Fig 2D). Fe-oxides are randomly distributed on the surface as single grains $\leq 1 \mu$ m, or as aggregate spheroid masses ~1–3 μ m in diameter.

For comparison, the surfaces of alkali and tholeiite glasses reacted for two weeks in pure, dry CO₂ at 700°C had abundances of 0.2% and 0.7%, respectively, of Feoxide and siderite (FeCO₃) aggregates [2]. Additionally, Fe-oxide+siderite was observed on both samples from the 2-week, 470°C, CO₂-only run (Fig. 4).

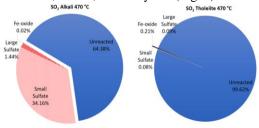


Figure 3. Graphic showing estimated abundances of alteration phases observed on alkali (left) and tholeiite (right) samples reacted for 3-weeks at 470 $^{\circ}$ C in a CO₂ and SO₂ gas mixture under 90 bars pressure.

Implications: The formation of sulfate mineral reaction products is consistent with prior thermodynamic and experimental work [1,5-9]. However, the mechanisms and rates of alteration and production of anhydrite have informed most of our assumptions regarding reactions between Venus' basaltic materials and SO₂-bearing atmosphere. Although anhydrite was observed on the surfaces of tholeitic samples from both experimental runs, the effect of a CO₂-SO₂ gas on the reaction rate relative to a pure CO₂ atmosphere is unclear—the very low (0.4%)

abundances of total reaction products found in the lower temperature tholeiitic sample from this study are lower than those in both the 700°C (0.7%) and 470°C (2.1%) runs in pure CO₂. This may be explained by the crystallization of siderite, which is likely stable at the lower temperature, but is not stable at temperatures greater than ~470°C [13]. The abundances and larger grain sizes of thenardite observed here, however, suggest that reaction rates on Venus' surface may be substantially faster on Na-rich alkali (plume) basalts than on tholeiitic (plains) basalts.

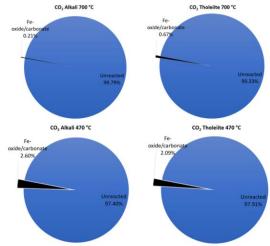


Figure 4. Graphic showing estimated abundances of alteration phases observed on alkali (left) and tholeiite (right) samples reacted for 2-weeks at 700°C and 470°C in pure CO₂ under 90 bars pressure.

Future directions: More experimental runs at longer durations are needed to constrain the effect of time on these reactions and to disambiguate the results observed on the tholeitic composition in this study. Additionally, confirmation of the compositions of nanoand microscale reaction products and determination of alteration surface thickness and potential reaction front depths using higher resolution instruments (e.g., transmission electron microscopy) are being pursued. Finally, these measurements will be used to calculate reaction rate as a function of bulk composition to better constrain the ages of Venus' surface basalts.

References: [1] Zolotov (2018) Rev Min Geochem 84, 351-392. [2] Teffeteller et al. (2021) 52nd LPSC, this issue [3] Filiberto et al. (2020) Sci Adv 6, eaax7445 [4] Cutler et al. (2020) Plan Sci Jour 1, 21 [5] McCanta et al. (2014) Am Min 99, 291-302. [6] Berger et al. (2019) Icarus 329, 8-23. [7] Palm et al. (2018) Rev Min Geochem 84, 257-283. [8] Renggli, and King (2018) Rev Min Geochem 84, 229-255. [9] Renggli et al. (2019) CMP 174, 1-19. [10] Filiberto (2014) Icarus 231, 131-136. [11] Lv et al. (2015) Proc Combust Inst 35, 3637-3644. [12] Terry and Chilingar (1955) J Sed Pet 25, 229-214. [13] Koziol (2004) Am Min 89, 294-300.