

THE STABILITY OF CALCIUM SILICATES AND CALCIUM CARBONATE ON THE SURFACE OF VENUS. B. G. Radoman-Shaw¹, R. P. Harvey¹, G. C. C. Costa², N. S. Jacobson², A. Avishai³, and L. M. Nakley²,
¹Department of Earth, Environmental, and Planetary Science, Case Western Reserve University, 10900 Euclid Avenue Cleveland, OH 44106 (bgs21@case.edu). ²NASA Glenn Research Center, 21000 Brookpark Road Cleveland, OH 44135. ³Swagelok Center for Surface Analysis of Materials, Case Western Reserve University, 10900 Euclid Avenue Cleveland, OH 44106.

Introduction: Crust – atmosphere interactions are thought to play an important role in the Venus greenhouse climate [1]. Limited *in situ* analysis of the surface of Venus and minimal determination of major and minor constituents in the lower atmosphere provide inadequate insight into possible dominant solid-gas reactions that can occur. Based on assumptions using available data and geochemical modeling of surface temperature and pressure, Ca-bearing minerals are often suggested as key phases possibly reactive on the surface [1,2,3,4].

Prior experimental modeling provides conflicting hypotheses as to the importance and chemical stability of calcium-bearing mineral phases on the surface of Venus [5,6,7]. There is also debate over the influence minor atmospheric components have over these phases, such as SO₂. For this study, we exposed a matrix of material including calcium silicates and calcium carbonate for 42 days to Venus surface conditions using the Glenn Extreme Environment Rig (GEER) at NASA Glenn Research Center. From this exposure, we can experimentally suggest which Ca-bearing phases are more or less likely to be stable on the surface, and which are more reactive with the atmosphere.

Samples: For the 42-day experiment we exposed a total of 6 calcium-bearing phases. These included a pyroxenite (containing both augite and diopside), labradorite, calcite, and diopside from the CWRU student mineral collection, enstatite from Alfa Aesar chemical company and wollastonite from the National Museum of Natural History in Washington, D. C.. The sample chips weighed on average 40 mg and were roughly 1 square cm in size. Two opposing faces of each sample were polished to create a common surface texture for pre- and post-exposure electron microscopy. These samples were then attached to custom 316 stainless steel mounts using gold wire. We verified the mineralogy and crystallinity of each sample through powder x-ray diffraction (Figure 1).

Methods: The Glenn Extreme Environment Rig (GEER) at the NASA Glenn Research Center in Cleveland, OH, provides unparalleled high fidelity simulation of Venus atmospheric pressure, temperature and chemistry. The temperature and pressure for this experiment were kept at 460°C and 92 bar (1334 psia) for

Sample Name	Sample	Dominant Phase(s) (XRD)
CWRU-Lbd-R4dd-R7jj	Labradorite	Anorthite Na ₄₈ Ca ₅₂ (Si _{2.5} Al _{1.5})O ₈
NMNH-8243802-Wol-R1v	Wollastonite	Wollastonite CaSiO ₃
CWRU-ADK-Pyx-R5ee	Pyroxenite	Diopside CaMgSi ₂ O ₈ Augite Ca(Mg,Fe)Si ₂ O ₆
CWRU-Dio-R1	Diopside	Diopside CaMgSi ₂ O ₈
CWRU-Cal-R2b	Calcite	Calcite CaCO ₃
AA-Ent-R7bb	Enstatite	Enstatite Si(Mg _{0.781} Co _{0.132} Mn _{0.087})O ₃

Figure 1: Samples selected for the 42-day exposure experiment and identified phases with XRD.

42 days, thereby keeping the simulated atmosphere above the supercritical point for CO₂ and within accepted near-surface temperature and pressure conditions for Venus.

The gas fill for the experiment, in order of abundance, included CO₂, N₂, SO₂, OCS, H₂O, CO, H₂S, HCl, and HF. SO₂ concentration was monitored during the experiment. The concentration dropped below the desired level of 180 ppm twice and was subsequently boosted both times in order to maintain the desired levels.

Results: We analyzed exposed and representative unexposed sample chips with secondary electron (SE) imagery along with XEDS chemical analysis to see if any alteration occurred. For labradorite, pyroxenite, diopside and enstatite the alteration was very minimal (on the nm level). Wollastonite and calcite showed strong reactivity, as described below.

Wollastonite: Among the silicates, this sample experienced the most surface alteration and deposition of secondary mineralogy. The altered texture is botryoidal in some instances and in certain areas almost appears faceted. On the edges of the sample this material is clumped together. On the surface however, the material looks more separate, like an immiscible fluid beading up on the surface (Figure 2b). This material is silica absent and sulfide rich, and is most likely a sulfate.

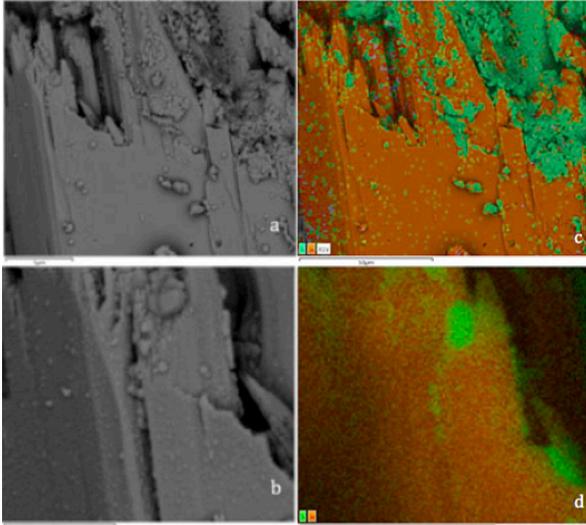


Figure 2: Images 2a and 2b are SE images of the reacted NMNH-8243801-Wol-R1v specimen. XEDS map 2c corresponds to the electron image 2a and 2b corresponds to the XEDS map 2d. Sulfur is green and silicon is in orange in both maps.

Due to the small grain-size of the material, its exact composition is unclear but it is most consistent with calcium sulfate (anhydrite).

Calcite: Sample CWRU-Cal-R2b (Figure 1) reacted to form a “vermiform” texture of semi-faceted material connected in a disjointed way (Figure 3). The surface texture is varied, with the vermiform material above smaller pseudo-faceted material and some almost acicular textured phases (Figure 3c). Although the size of these textured materials is too small to confirm their composition, XEDS shows strong sulfur and oxygen peaks suggesting anhydrite (Figure 3d).

Discussion: The most common secondary minerals formed in our experiments are sulfur-bearing compounds, suggesting that although sulfur-bearing gases are relatively minor atmospheric components, they play an exceptionally active role in crust-atmosphere interactions. Geochemical modeling using the program FactSage [8] suggests both calcite and wollastonite are unstable under Venus surface conditions; the former reacting to form anhydrite, and the latter reacting to form anhydrite, calcite, and quartz. Neither quartz nor calcite were identified on the wollastonite but the anhydrite was seen on the calcite (Figure 3). The most stable phases were the enstatite, clinopyroxenes and feldspar. If these phases are present on the surface of Venus, they apparently are most likely slow to react and are involved only in longer-term reactions. The lack of observed secondary carbonate material in this study suggests that mineral sinks that could sequester

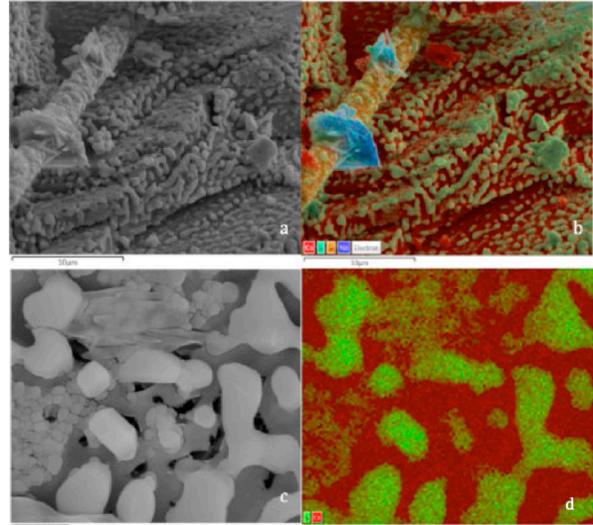


Figure 3: The two electron backscatter images are of the reacted CWRU-Cal-R2b sample and image 3a and 3c correspond to the XEDS maps 3b and 3d respectively. The elements shown in both maps are calcium, sulfur, silicon, and sodium corresponding to red, green, orange and blue respectively.

CO₂ within the crust of Venus may be absent, resulting in the observed high abundance of CO₂ in the atmosphere.

Further Work: We are currently exploring higher-resolution analytical techniques to better identify the stoichiometry of our submicron secondary phases. We are also examining other phases from the 42-day experiment (including glasses) to identify additional reactions occurring through the secondary minerals that form. A second, longer exposure with better control of gas chemistry is scheduled to begin late January 2017.

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