

DECOMPOSITION OF CALCITE AFTER 30 DAYS OF VENUS CONDITIONS IN GEER. X. R. Lopez, M. S. Gilmore, A. R. Santos, Department of Earth & Environmental Sciences, Wesleyan University, Middletown CT (xlopez@wesleyan.edu).

Introduction: Rock weathering interactions on planetary surfaces record mineralogy and current and past climates. The mineralogy of Venus has not yet been directly measured, but can be constrained through thermodynamic modeling and experiment. The NASA Glenn Extreme Environments Rig (GEER) offers a new opportunity to perform experiments on materials under Venus surface conditions of $\sim 460^\circ\text{C}$ and ~ 93.5 bars of pressure, with the most realistic simulated atmosphere to date of 96.5% CO_2 , 3.5% N_2 , 180 ppm SO_2 , 51 ppm COS, 30 ppm H_2O , 12 ppm CO, 2 ppm H_2S , 0.5 ppm HCl, 2.5 ppb HF derived from in situ and orbital measurements of the Venus atmosphere [1]. Here we report changes in calcite (CaCO_3) exposed to these conditions in GEER for 30 days.

Calcite is predicted to be thermodynamically unstable at the Venus surface where it is predicted to react with SO_2 to produce anhydrite (CaSO_4) [e.g., 2]. Experiments examining the stability of calcite under SO_2 and SO_2/CO_2 gas mixtures at temperatures of $600\text{--}850^\circ\text{C}$ have shown that anhydrite forms a continuous layer of $\sim 20\text{ }\mu\text{m}$ thickness in <14 days [3]; experiments under SO_2 , 460°C , ~ 5 bars yielded an anhydrite crust up to ~ 1 micron in thickness in 4-5 days [4]. Calcite was reported to show a $0.25\text{ }\mu\text{m}$ rim in a 42-day test in GEER [5]. While these experiments support the thermodynamic predictions of calcite instability, it is also important to understand the rate at which calcite reacts with atmospheric SO_2 , and the texture of the reaction products, as it has been proposed by [6] that carbonation is an intermediate step in alteration of basaltic glass on the Venus surface.

SEM Analysis: Each mineral that entered the GEER chamber has a control/duplicate that will be used as the “unaltered” sample for comparison. The unaltered sample will simply be referred to as “*calcite*” while the altered sample will be referred to as “*G_calcite*”. Using the SEM (Scanning Electron Microscope) at Wesleyan University, the calcite specimens are analyzed with backscatter electrons (BSE) and secondary electron (SE) detectors to look for secondary mineral growth and changes in texture, and energy dispersive X-ray spectroscopy (EDS) to look for qualitative chemical changes. The two specimens were not carbon coated so to avoid excess charging they were analyzed in low vacuum mode when available (~ 80 Pa). The surface of both samples and a cross section of *G_calcite* was analyzed.

Results: Surface Analysis: EDS analyses of the two specimens show that *G_calcite* experienced sulfurization (Fig. 1).

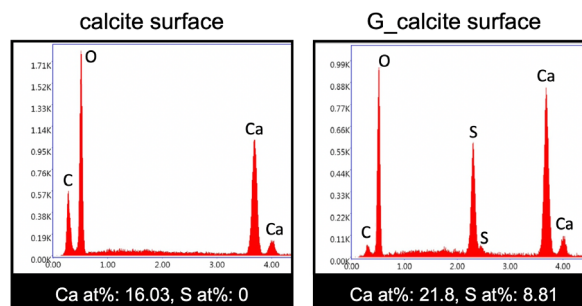


Figure 1. Qualitative EDS analysis of representative areas of the surfaces of calcite before GEER (left) and *G-Calcite* after GEER (right). Atomic percent (at%) of calcium and sulfur are provided. The sample acquired S after exposure to Venus conditions in GEER.

SE analyses of the surface reveal two textures: 1) a granular texture consisting of subhedral crystals on the order of a few microns across and 2) a smoother texture with scattered crystals (Fig. 2 & 3). The granular texture was not present in the unweathered calcite sample (not shown) and typically comprises $>75\%$ of the surface of the sample after the 30-day GEER test. EDS analysis of the two textures (Fig. 3) show that the granular texture consistently has a higher sulfur peak compared to the smooth texture, and the smooth texture has more S than the unaltered sample. The granular material also contains Ca.

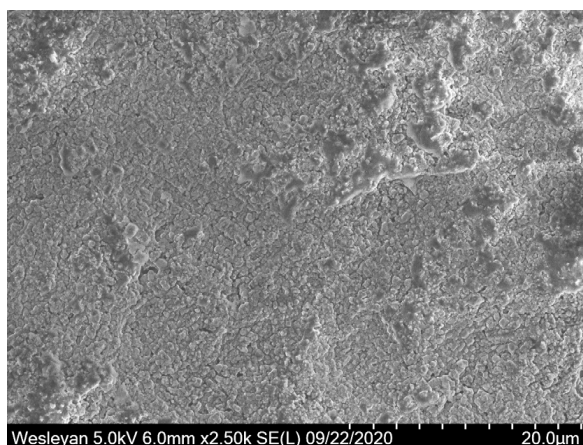


Figure 2. SE image of *G_calcite*'s surface. The granular texture (brighter) comprises most of the image. Small

darker areas are charging effects. This texture was not present on the unmodified calcite.

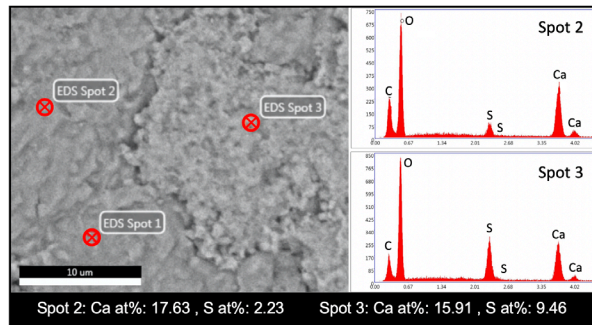


Figure 3. EDS analysis of the surface texture. Spot 2 is on the smooth texture while Spot 3 is on the granular texture which contains more sulfur.

Cross Section Analysis: A cross section of G_calcite was analyzed to understand the extent of mineral alteration. The top and left edges of the sample have an apparent rim of sulfur-rich material with the granular texture, of thickness that varies between 3-5 microns (Fig. 4). EDS analyses of these points from the rim to the interior show that the sulfur is present below the rim but the signal drops off sharply after a depth into the sample of 20 μm (Fig. 5). In contrast, the right edge of the cross section of G_calcite does not have a discrete rim on the exterior of the sample, rather the granular texture appears to form a layer that extends semicontinuously in the crystal perpendicular to the surface. The extent of sulfur penetration on the right edge exceeds ~400 μm into the specimen (Fig. 5).

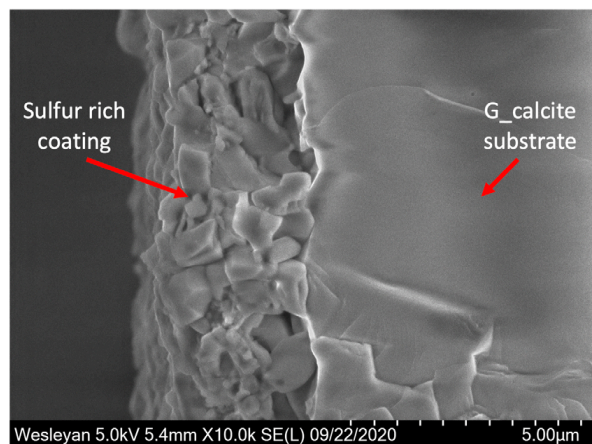


Figure 4. SE image of the left edge of the cross section of G_calcite. The textured sulfur rich material is ~3.5 microns thick.

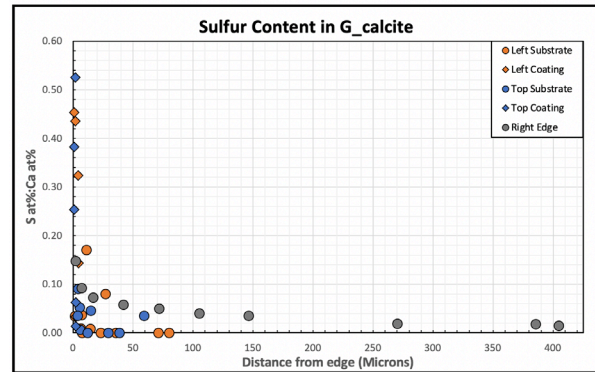


Figure 5. Ratio of atomic % S to atomic % Ca as a function of distance from multiple edges of the cross section of G_calcite.

Discussion: All surfaces of G_calcite acquired S, that is correlated to a coating of variable thickness comprised of subhedral crystals. This coating is an order of magnitude thicker than S-rich rims on calcite in a previous 42-day GEER test [5]. We assume that these materials changed to anhydrite (CaSO_4) as seen in previous experiments [5]. However, the atomic ratio of calcium to sulfur is half of what is expected for anhydrite, perhaps indicating that this reaction has not gone to completion in 30 days. It is also consistent with a combination of carbonation and sulfurization reactions that may produce both anhydrite and carbonate at the surface as proposed by [6].

Cross sections of the exposed sample show that the penetration of S into the sample varies at different edges. Edges with a visible rim of granular materials have higher values of S:Ca which drop to zero within 50 microns of the surface. Rimless surfaces have lower values of S:Ca at the edge, and the values drop more slowly approaching zero >400 μm into the sample. We hypothesize that the formation of the surface rim limited the diffusion of S into the interior. The differences between the surfaces with or without a rim may be due to crystallographic control or preferred zones of weakness which would facilitate diffusion into the interior. The attitude of the granular texture on the right side of the crystal suggests that it is forming along a crack in the crystal that facilitated the formation of weathering products into the sample interior.

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References: [1] Kransnopolsky and Lefèvre (2013) CCTP, 231. [2] Zolotov M.Y. (2018) Rev. Min. Geochem. 84, 351, and references therein. [3] Fegley B. & Prinn R.G. (1989) Nature 337, 55. [4] Aveline D.C. et al. (2011) LPSC 42, #2165. [5] Radoman-Shaw B. (2019), CWRU, Ph.D. Dissertation. [6] Dyar M.D. et al. (2021) Icarus, in press.