

STABILITY OF ACTINOLITE ON VENUS. A. R. Santos¹, K. E. Vander Kaaden², A. R. Graham¹, J. A. Lewis³, R. V. Morris³, V. M. Tu², G. Moore², F. M. McCubbin³, K. Phillips⁴, C. J. Doehne¹, J. E. Rymut¹, ¹NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH 44135 (alison.r.santos@nasa.gov), ²Jacobs, NASA Johnson Space Center, Houston, TX. ³ARES, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, ⁴HX5 Sierra, LLC, 21000 Brookpark Rd., Cleveland, OH 44135.

Introduction: Venus currently has a hostile surface environment with temperatures of ~460 °C, pressures near 92 bars, and an atmosphere composed of supercritical CO₂ hosting a myriad of other potentially reactive gases (e.g., SO₂, HCl, HF) [summarized in 1]. However, it has been proposed that its surface may not have always been so harsh [e.g., 2]. Models suggest there may have been billions of years of clement conditions allowing an Earth-like environment with liquid water oceans [2, 3]. If such conditions existed, it is possible Venus formed a similar array of hydrous or aqueous minerals as seen on other planets with liquid surface water (e.g., Mars, Earth) [4]. Based on thermodynamic modeling, many of these phases would not be stable under the current atmospheric conditions on Venus, dehydrating due to the high temperatures and low concentration of H₂O in the atmosphere [5]. However, the rate of decomposition of these phases may allow them to remain present on the surface over geologic time [4]. For example, experiments on the reaction rate of tremolite (Ca₂Mg₅Si₈O₂₂(OH)₂) show a 50% decomposition time of 2.7 Gyr for micrometer sized grains in unreactive atmospheres (i.e., without SO₂) at 740 K, and a 50% decomposition time of 70 Gyr for crystals several millimeters to centimeters in size [6]. If hydrous minerals can remain on the surface of Venus over geologic time, it has implications for our detection of evidence of these past environments, and also for the overall water budget of the planet. If after surficial dehydration the planet was able to still store water in its crust, possible processes such as subduction or metamorphism could still have operated using stored water long after liquid surface water evaporated.

Several previous studies have focused on experimental investigations of mineral stability on Venus [summarized in 7]. In particular, the works of [4, 6] studied the decomposition rate of tremolite under conditions relevant to Venus. As their focus was on decomposition of the mineral due to lack of water in the atmosphere, their experiments were undertaken using only CO₂ or N₂ gas at atmospheric pressure [4, 6]. Recent experiments have examined reactivity of other minerals with the Venusian atmosphere using more complex gas compositions at similar pressures to those seen on Venus [8, 9]. These studies show reaction of silicate minerals with atmospheric components on relatively short timescales (i.e., on the order of days). The

reported reactions of silicate materials in both studies produced iron oxides, Ca sulfates, and Na sulfates [8, 9]. These ions are present in many amphiboles, and Ca was proposed by Johnson and Fegley [6] to potentially have an important role in the decomposition mechanism for tremolite, with the Ca-O bond being the first to break during decomposition. The potential involvement of Ca in both processes raises the question of whether or not the reaction to form a secondary mineral phase will influence the rate of amphibole breakdown (e.g., discussion in [10] for tremolite). Additionally, reaction of Ca with atmospheric gases may result in a different secondary mineral assemblage than simple amphibole decomposition, which will need to be recognized when searching for evidence of past hydrated minerals on the Venusian surface [10].

In order to understand the effect of this reaction on the overall preservation potential of amphibole on the surface of Venus, we are conducting experiments in both reactive and non-reactive atmospheres using the mineral actinolite (Ca₂(Mg,Fe)₅Si₈O₂₂(OH)₂), an amphibole with similar crystal structure to tremolite that contains both Ca and Fe.

Methods: Our starting materials consist of a natural actinolite sample from an unknown locality. In order to facilitate reactions in the timeframe of our experiments, the sample was powdered using a mortar and pestle under ethanol.

Experimental Methods. Two experiments are being performed to determine the impact of SO₂ on actinolite decomposition. One experiment follows similar methods to [4] in order to provide a more direct comparison between the actinolite and tremolite behaviors. This experiment uses a DelTech 1-atmosphere gas mixing furnace at NASA's Johnson Space Center (JSC). Experimental parameters include: a pure CO₂ gas stream, 900 °C, held for a duration of 15 days. The second experiment will be conducted using the Miniature Glenn Extreme Environments Rig (MiniGEER) facility at NASA Glenn Research Center (GRC) (Figure 1). This facility consists of a 2.33 L working volume 304 stainless steel pressure vessel connected to a pre-mixed gas source. Experimental parameters include: an initial gas composition of 96.5% CO₂, 3.5% N₂, and 180 ppm SO₂, representing a simplified Venusian atmosphere containing reactive gas species, 460 °C temperature and 92 bars pressure, with an accumulated duration of 15 days. In an experiment at similar

pressure and temperature conditions with a more complex atmosphere, biotite grains within a granite sample were observed to begin forming secondary minerals after eleven days [11]. This suggests that fifteen days using a powdered sample is a reasonable duration to expect reactions. After each experiment, sample powders will be removed and stored in a desiccator while awaiting analysis.

Analytical Methods. Unexposed and exposed sample powders will be analyzed using the same techniques. Mineralogy will be determined using powder X-ray diffraction with a Rigaku MiniFlex 600 benchtop X-ray diffractometer fitted with a cobalt X-ray source ($\text{CoK}\alpha_1$ $\lambda=1.79801$ Å). The patterns will be collected in reflection mode from 4 to 80 $^{\circ}2\theta$ with a step size of 0.02 $^{\circ}$ for 10 seconds per step. Data analysis will be completed using HighScore software. High resolution images of grain morphology and grain surface features as well as qualitative chemical mapping will be performed using a JEOL 7600F field emission-scanning electron microscope (FE-SEM) with a silicon drift detector for energy dispersive spectroscopy. An Al-metal SEM stub will be covered with double sided carbon tape and a small scoop of the sample material will be placed in the center. Each stub will then be carbon coated with ~32 nm of carbon to avoid charging effects. The oxidation state of Fe in the samples will be determined using Mössbauer (MB) spectroscopy. Mössbauer spectra will be obtained in backscatter measurement geometry, at room temperature, and on powder samples using ESPI, Inc. spectrometers, similar to those employed by the Mars Exploration Rovers [12]. The measurements will be made directly on the powders, preserving them uncontaminated for study at later times. The computer programs MERView and MERFit will be used, respectively, to velocity calibrate and least-squares fit the spectra [13, 14]. Areas and widths of doublet peaks (Lorentzian line shapes) are constrained equal during the fitting procedures. The values of the center shift are reported with respect to metallic foil at room temperature. Subspectral areas include a correction factor (the f-factor) to account for differences in the recoil-free fractions of Fe^{2+} and Fe^{3+} [$f(\text{Fe}^{3+})/f(\text{Fe}^{2+}) = 1.21$ independent of mineralogical composition]. MB parameters (center shift CS, quadrupole splitting, QS, full width at half-maximum intensity, and subspectral area) are based on various independent fits described in more detail by Morris et al. [15].

Expected Results: The results of the 1 atmosphere, CO_2 experiment will be compared to the findings of [4, 6] on tremolite based on the similarity in techniques and mineral types. This experiment serves as the baseline for comparison by defining actinolite decomposition over our experimental time range. The

high pressure, SO_2 -bearing experiment serves to expose the sample to a reactive gas at Venus-like temperatures and pressures so that the competing reactions of decomposition and secondary mineral formation can be compared and to determine how the rate of decomposition (i.e., water loss) is affected. Based on previous experimental work, it is expected that the Ca in the actinolite will react to form a Ca-sulfur-bearing species, while the Fe in actinolite may produce an Fe-oxide [e.g., 8, 9].



Figure 1: The miniGEER experimental setup located at NASA GRC. Image courtesy of Bridget Caswell/NASA GRC.

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