

PHLOGOPITE DECOMPOSITION, WATER, AND VENUS. N. M. Johnson^{1,2} and B. Fegley, Jr.³, ¹NASA's Goddard Space Flight Center, Astrochemistry Branch, Greenbelt, MD 20771, njohnson@lepvax.gsfc.nasa.gov, ²NAS/NRC Resident Research Associate, ³Planetary Chemistry Laboratory, Department of Earth and Planetary Sciences, Washington University, St. Louis, MO 63130, bfegley@levee.wustl.edu.

Introduction: Venus is a hot and dry planet with a surface temperature of 660 to 740 K and 30 parts per million by volume (ppmv) water vapor in its lower atmosphere [1]. In contrast Earth has an average surface temperature of 288 K and 1-4% water vapor in its troposphere. The hot and dry conditions on Venus led many to speculate that hydrous minerals on the surface of Venus would not be there today even though they might have formed in a potentially wetter past. Thermodynamic calculations predict that many hydrous minerals are unstable under current Venusian conditions (e.g., [2]). Thermodynamics predicts whether a particular mineral is stable or not, but we need experimental data on the decomposition rate of hydrous minerals to determine if they survive on Venus today.

Previously, we determined the decomposition rate of the amphibole tremolite, and found that it could exist for billions of years at current surface conditions [3,4]. Here, we present our initial results on the decomposition of phlogopite mica, another common hydrous mineral on Earth.

Background: Phlogopite ($\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) is an important member of the mica group. As a sheet silicate, many substitutions are possible and indeed, most, if not all, phlogopite samples contain some iron and/or fluorine. Typically, phlogopite is found in metamorphosed Mg-rich carbonates and ultra-basic rocks. When phlogopite decomposes, it loses water and leaves behind anhydrous silicates. Mueller [5] suggested that phlogopite may exist on Venus but later calculations showed it is thermodynamically unstable on Venus today (e.g., [2]).

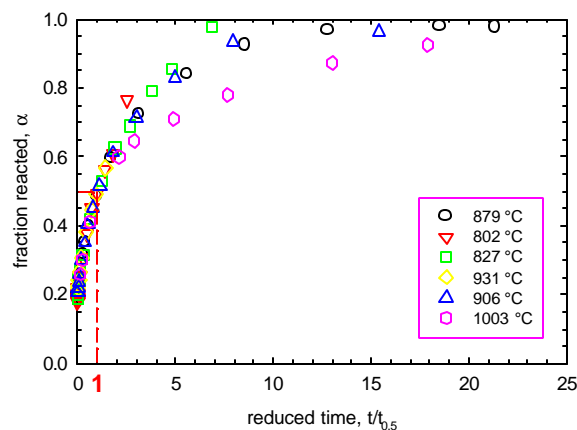


Figure 1. Fraction of mass loss versus reduced time. Reduced time is time normalized to 50% decomposition time.

Experiments: We studied thermal decomposition of natural phlogopite (Quebec, Canada) by isothermally heating powder samples (53–106 μm grains) in dry flowing CO_2 ($\sim 3 \text{ cm min}^{-1}$) at ambient pressure. These samples contain both iron and fluorine. We selected samples that had the lowest amount of iron. Experiments were run at temperatures from 1075 to 1475 Kelvin and ranged in duration from days to a little over four years. Ideally, experiments were run until no further appreciable mass change was observed.

The extent of reaction was determined by measuring the mass loss (all mass loss was attributed to volatile loss). Typical mass loss curves are shown in Figs. 1 and 2 as reduced time plots where the fraction of mass loss is plotted versus time normalized to the time required for 50% of total mass loss (i.e., $t/t_{0.5}$). Figure 2 is an enlarged version of the lower left hand part of Fig 1. Samples were examined by electron microprobe and by X-ray diffraction (XRD).

Kinetics: The decomposition rate was determined by fitting the data to a kinetic model via linear least squares regressions. We used a first-order reaction kinetic model, $f(\alpha) = -\ln(1-\alpha)$, where α is the fraction of total mass lost. This model is often used to describe the decomposition of fine powders [6]. We then calculated the rate constant for each temperature studied, k (hr^{-1}), via the relationship $k = f(\alpha)/t$, where t is in hours.

The Arrhenius plot in Figure 3 shows the linear relationship between the log of the reaction rate constants and inverse temperature. Analysis of the data gives the rate equation

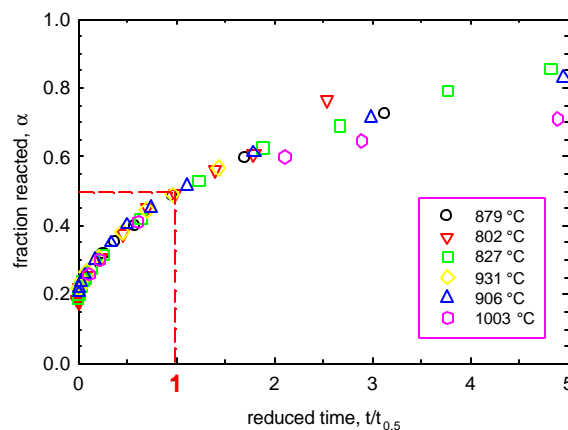


Figure 2. An enlargement of the lower left hand part of Fig 1. Points at different temperatures fall onto the same curve.

$$\log_{10}k \text{ (hr}^{-1}\text{)} = 15.63(\pm 0.68) - 21,631(\pm 425)/T$$

where T is in Kelvin. The corresponding activation energy is $414 \pm 8 \text{ kJ mol}^{-1}$ (one sigma error).

Discussion: The reduced time plot in Figure 2 shows that samples decompose by the same mechanism (i.e., set of reactions) until they lose 50% of the total mass loss. The rate equation above was derived using data up to this 50% mass loss. This was done because analyses of the microprobe results suggest that water loss was complete by this point. (The F abundance is about half that of OH in these samples). The scatter in the reduced time plot after 50% decomposition suggests that the mechanism changes after water loss is complete.

Phlogopite stability and fluorine: Using the rate equation given above, we calculated that a sample of our phlogopite powder could survive on Venus' surface under current conditions for at least ~3Ga. This is not wholly unreasonable as tremolite survival times were also quite long (see [3,4]). Note that even though these samples were heated for very long periods of time, the phlogopite XRD patterns still remained. This is consistent with literature results summarized in [2]. Fluorine stabilizes amphiboles [7,8] and may do so for phlogopite. The implication is that we might be able to detect this 'hydrous' remnant signature if phlogopite formed on Venus in the past.

Mineral detection: Several spacecraft have been sent to Venus, yet none have taken direct mineralogical observations of the surface. We only have elemental surface abundances for Mg and heavier elements measured by X-ray fluorescence in three similar terrains [9,10]. The mineralogical information that we have about Venus' surface is derived through thermodynamic models, deductions based on the XRF elemental analyses and orbital radar. In order to obtain a clearer picture of Venus' history, we need to know the surface mineralogy. This can be done using X-ray diffraction and/or IR reflectance spectroscopy on landers, penetrators, rovers and/or automated balloons (aerobots). Suggested sites include the tesserae, the highland plateaus, and crater ejecta blankets.

Summary: Fluorine substitution for OH in phlogopite makes F-bearing phlogopite both thermodynamically and kinetically more stable. The extrapolation of our kinetic data predicts phlogopite survival for billions of years at Venus' current surface temperatures. This result strengthens our previous conclusions [3,4,5] that if hydrous minerals ever formed on Venus during a wetter past, they could still be there today.

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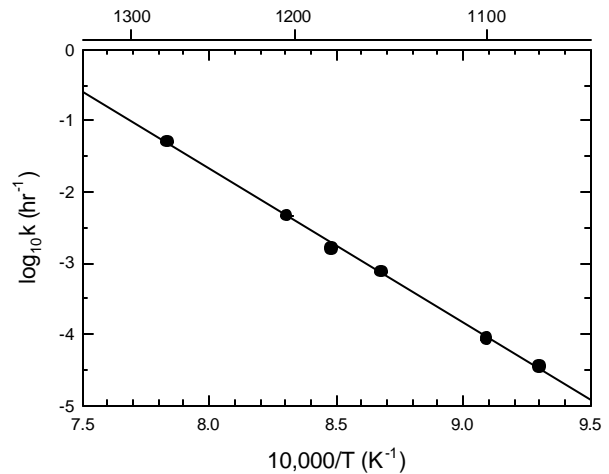


Figure 3. Arrhenius plot of the rate constants (hr^{-1}). Error bars are smaller than the symbols. (continue to Fig. 4)

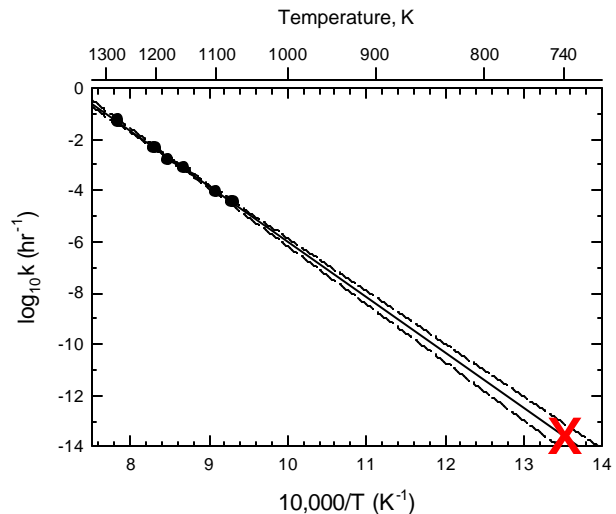


Figure 4. Regression extended to Venus' surface temperature. Dashed lines show 95% confidence prediction interval.