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Longevity of fluorine-bearing tremolite on Venus

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Abstract

There is a general belief that hydrous minerals cannot exist on Venus under current surface conditions. This view was challenged when Johnson and Fegley (2000, Icarus 146, 301–306) showed that tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$), a hydrous mineral, is stable against thermal decomposition at current Venus surface temperatures, e.g., 50% decomposition in 4 Ga at 740 K. To further explore hydrous mineral thermal stability on Venus, we experimentally determined the thermal decomposition kinetics of fluorine-bearing tremolite. Fluor-tremolite is thermodynamically more stable than OH-tremolite and should decompose more slowly. However how much slower was unknown. We measured the decomposition rate of fluorine-bearing tremolite and show that its decomposition is several times to greater than ten times slower than that of OH-tremolite. We also show that F-bearing tremolite is depleted in fluorine after decomposition and that fluorine is lost as a volatile species such as HF gas. If tremolite ever formed on Venus, it would probably also contain fluorine. The exceptional stability of F-bearing tremolite strengthens our conclusions that if hydrous minerals ever formed on Venus, they could still be there today.
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1. Introduction

Over the last 40 years, the planetary community has debated whether or not hydrous minerals could exist on the surface of Venus. There is indirect evidence from Venus' atmospheric deuterium/hydrogen ratio that there once was more water on Venus in the past (Donahue et al., 1997), yet it was generally dismissed that any hydrous minerals formed during this wetter period could have survived into the present day. The high surface temperatures (660–740 K) and the dry atmosphere ($\sim$ 30 parts per million by volume water vapor) (Lodders and Fegley, 1998), and predictions of equilibrium thermodynamic calculations (Zolotov et al., 1997) both suggest that hydrous minerals are unstable at Venus surface conditions. Although hydrous mineral decomposition is predicted by thermodynamic calculations, the decomposition rates of hydrous minerals are generally unknown. Johnson and Fegley (2000) addressed this lack of kinetic data by studying the decomposition rate of tremolite, an amphibole, and determined that tremolite could exist for billions of years at current Venus surface conditions. They
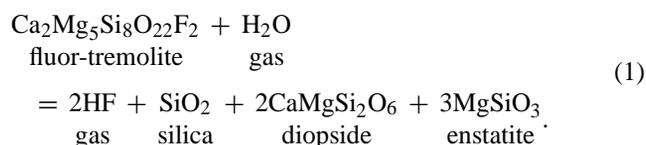
concluded that if hydrous minerals formed in a wetter Venusian past, then some hydrous minerals would still exist and retain their water. Consequently, if landers detect hydrous minerals, we will have solid proof that Venus had more water in the past. The existence of such minerals, particularly on the surface, also has the potential to regulate abundances of atmospheric gases such as HF via gas-solid reactions (Fegley and Treiman, 1992).

Hydrogen fluoride (HF) gas was discovered in Venus' atmosphere by Connes et al. (1967) and determined to exist in trace amounts above and below the clouds at approximately 5 parts per billion by volume (Connes et al., 1967; Bézard et al., 1990). By comparison, the average abundance of HF in Earth's troposphere is significantly smaller at 27 ± 14 parts per trillion by volume (Sen et al., 1995). Thermochemical equilibrium models predict that Venus and Earth contain similar inventories of fluorine (Fegley and Lewis, 1980) and calculations suggest that there is still a considerable amount of fluorine within the Venusian surface (Fegley and Treiman, 1992). On Earth, the sources for tropospheric HF are volcanic emissions and influxes of HF from the stratosphere due to photolysis of anthropogenic chlorofluorocarbons. The residence time of HF in Earth's troposphere is very short, approximately 5.5 days (calcula-

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tions following Warneck, 1988), because HF is soluble and is removed by precipitation. The sources for fluorine in Venus' atmosphere also include volcanic eruptions but fluorine (as HF) in Venus' atmosphere is most likely a direct result of Venus' high surface temperature. The residence time of HF in Venus' atmosphere is probably longer because of the lack of precipitation. The combination of similar abundances of HF above and below the clouds, high surface temperature, and high reactivity of HF suggest that this gas is in chemical equilibrium with the surface minerals. In other words, fluorine is 'cooked out' of the surface rocks. Lewis (1968) and Mueller (1968) suggested this type of gas-solid regulation of the HF abundance. Fegley and Treiman (1992) reviewed several mineral assemblages that could regulate the HF abundance in Venus' atmosphere. One possible system involves fluor-amphiboles such as fluor-tremolite. Reaction (1) is believed to regulate fluor-tremolite stability in felsic rocks (i.e., granitic rocks) on Venus.

$$\begin{aligned} Ca_2Mg_5Si_8O_{22}F_2 &+ H_2O \\ \text{fluor-tremolite} &\quad \text{gas} \\ = 2HF &+ SiO_2 + 2CaMgSi_2O_6 + 3MgSiO_3 \\ \text{gas} &\quad \text{silica} \quad \text{diopside} \quad \text{enstatite} \end{aligned} \tag{1}$$

The diopside and enstatite are present as two pyroxenes, both of which are a solid solution of one in the other.

Fluorine is found in many types of rocks and in different concentrations. One of the controls of the fluorine abundance in rocks is the presence of minerals that can host fluorine. Fluoride and hydroxyl ions are isoelectronic and isomorphous so that one can substitute for the other within mineral structures (Shannon and Prewitt, 1969; Ribbe and Gibbs, 1971). Not surprisingly, hydrous minerals such as amphiboles and micas are prime candidates for fluorine substitution (Fleischer and Robinson, 1963; Troll and Gilbert, 1972; Shawe, 1976). In fact, it is difficult to find tremolite samples that do not contain fluorine (see compilation of analyses by Deer et al., 1997 and Leake, 1968). The relative ease of fluorine accommodation within the amphibole structure, coupled with the high probability of finding fluorine within the surface rocks of Venus, suggests that hydrous mineral formation on Venus would incorporate some amount of fluorine within the mineral structures.
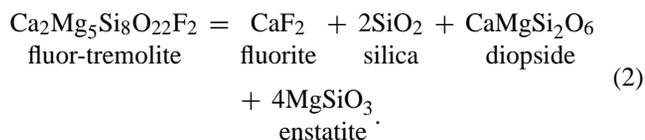
Generally, pure OH end-member amphiboles are thermodynamically less stable than their F-bearing counterparts because F substitution for OH increases amphibole stability (e.g., Gilbert et al., 1982). Thermodynamically, OH-tremolite is one of the least stable amphiboles at Venus surface conditions and is predicted to decompose (Zolotov et al., 1997). However, Johnson and Fegley (2000) showed that hydroxyl tremolite is kinetically robust at current Venus surface temperatures. The greater thermodynamic stability in tremolite generated by F substitution suggests that F-bearing tremolite will decompose even more slowly than hydroxyl tremolite but just how much slower is unknown. The present study is a natural extension of the previous experimental

work and here we determine the rate of F-bearing tremolite decomposition and discuss the implications that it holds for Venus.

2. Experimental

The tremolite used in this study originated from Campolungo in the Ticino Alps of Switzerland and was generously supplied by Dr. P. Brack of the Institut für Mineralogie und Petrographie at ETH in Zürich, Switzerland. Tremolite grains were hand picked, ground into powder (< 1–150 μm size particles), and agitated in HCl to remove carbonate contamination. Talc was detected in the resulting powder at approximately four mole percent. This talc component was not wholly unexpected because talc occurs as a pseudomorph after tremolite in this region (Mercolli, 1980) and the grains are visually indistinguishable. The talc was not removed because of the fine grain size. Any effects caused by the contamination are accounted for in both the experiments and data analyses and do not change the conclusions. Electron microprobe results show that the tremolite used in these experiments is fluorine-bearing and contains 1.41 wt% F. The chemical formula for Campolungo tremolite is $K_{0.01}(Ca_{1.93}Na_{0.11})(Mg_{4.99}Fe_{0.01})(Si_{7.92}Al_{0.11})O_{22}(OH_{1.40}F_{0.60})$ and the corresponding formula for talc is $(Ca_{0.01}Na_{0.17})(Mg_{5.79}Fe_{0.00})(Si_{7.89}Al_{0.22})O_{20}(OH_{3.36}F_{0.66})$ based on 24O. Table 1 lists the chemical compositions for ideal hydroxyl tremolite, our Campolungo tremolite, a decomposed tremolite sample, and a published analysis of tremolite from the Campolungo vicinity.

Fluorine bearing tremolite can be represented as a solid solution of hydroxyl tremolite ($Ca_2Mg_5Si_8O_{22}(OH)_2$) and fluor-tremolite ($Ca_2Mg_5Si_8O_{22}F_2$). Ideal hydroxyl tremolite contains 2.22 wt% H_2O and ideal F-tremolite contains 4.65 wt% F. Assuming stoichiometric endmember compositions and using our fluorine microprobe analysis, the tremolite powder used in these experiments contains 30 mol% F-tremolite in solid solution with 70 mol% OH-tremolite. Pure F-tremolite is predicted to decompose via reaction (2) (Deer et al., 1997).

$$\begin{aligned} Ca_2Mg_5Si_8O_{22}F_2 &= CaF_2 + 2SiO_2 + CaMgSi_2O_6 \\ \text{fluor-tremolite} &\quad \text{fluorite} \quad \text{silica} \quad \text{diopside} \\ &+ 4MgSiO_3 \\ &\quad \text{enstatite} \end{aligned} \tag{2}$$

Our X-ray diffraction (XRD) results show that the decomposition products of the Campolungo tremolite are a mixture of a solid solution of two pyroxenes and a high temperature silica phase. We did not detect, via XRD or electron microprobe (see Table 1), fluorite or any other F-bearing mineral in the decomposed samples. We propose that the fluorine escapes from fluor-tremolite as a volatile species such as HF, SiF_4, or F_2 during thermal decomposition. Fluorine loss from F-bearing minerals is observed during the kiln firing

Table 1
Tremolite chemical analyses

Oxides	Stoichiometric tremolite $Ca_2Mg_5Si_8O_{22}(OH)_2$	Campolungo tremolite		Decomposed tremolite[c] ($\pm 1\sigma$)
		Mercolli, 1980[a]	This work[b] ($\pm 1\sigma$)	
SiO_2	59.20	58.46	58.55(0.25)	59.85(0.79)
TiO_2		–	b.d.l.	b.d.l.
Al_2O_3		0.45	0.69(0.07)	0.63(0.18)
Cr_2O_3		–	b.d.l.	b.d.l.
FeO		0.20	0.10(0.03)	0.12(0.04)
MnO		–	b.d.l.	b.d.l.
MgO	24.80	24.71	24.77(0.14)	25.13(0.36)
CaO	13.80	13.12	13.32(0.07)	13.89(0.65)
Na_2O		0.12	0.41(0.03)	0.48(0.19)
K_2O		0.03	0.04(0.01)	0.05(0.03)
H_2O	2.20	1.80	1.55[d]	–
F		0.82	1.41(0.09)	b.d.l.[e]
Total	100.00	99.71	100.84	100.15

Notes: b.d.l.: analyzed-below detection limits $1\sigma \geqslant$ measured value < 0.10 wt%.

[a] Published microprobe analysis of tremolite from Campolungo (Tessin) region.

[b] Microprobe analysis of tremolite used in this study (12 spots). Total not corrected for oxygen equivalence with fluorine.

[c] Decomposed tremolite[b] (12 spots), (1273 K, 220 hr).

[d] H_2O calculated using ideal tremolite composition formula.

[e] Fluorine content < 0.01 wt%.

of bricks and other refractory ware and is an environmental problem for the ceramics industry.

We heated the samples in instrument grade CO_2 (99.99%) because Venus' atmosphere contains 96.5% CO_2 (Lodders and Fegley, 1998). The high temperature furnaces are airtight and allow constant gas flow over the samples (~ 3 cm per minute). This continuous gas flow allows volatiles released by the sample to be removed in order to prevent any pressure build up immediately around the sample. Before and after heating, the sample and its reaction vessel (alumina combustion boat) were weighed on an analytical balance (accuracy of ± 1 μm). Each sample was heated and weighed until no further appreciable mass loss was observed. About seventy experiments, ranging in duration from one hour to five months, were done at temperatures of 1178–1254 K. We ran these experiments at temperatures higher than those at Venus' surface so that decomposition would occur in reasonable timescales.

We confirmed tremolite decomposition by electron microprobe analyses, mid-infrared spectroscopy, and XRD. For the microprobe analyses, we used the Washington University JEOL-733 electron microprobe (1–10 μm beam diameter, 15 kV accelerating voltage, 20 nA beam current) and calibrated the probe with an internal tremolite standard. We used synthetic fluor-phlogopite for microprobe fluorine calibration (sample source McCauley et al., 1973). Mid-infrared spectra were taken of thin films compressed in a diamond anvil cell using a Fourier transform infrared Bomen DA3.02 spectrometer with an HgCdTe detector. For XRD patterns, we used a Rigaku vertical powder diffractometer with CuKα radiation and the diffraction angle was calibrated using a silicon powder standard (NIST 640b). Backscatter electron images of decomposed tremolite samples show that the reacted
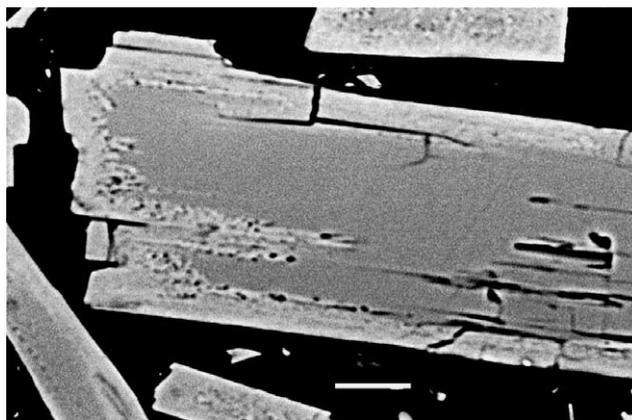

Fig. 1. A backscatter electron image of a typical F-bearing tremolite powder grain that was heated at 1228 K for approximately 50 hours. The scale bar is 10 μm. The decomposed areas are lighter in hue, depleted in fluorine, and porous. The dark and smooth regions are similar, if not identical, to non-heated F-bearing tremolite. Decomposition progression into the unreacted material is very similar to that of F-poor tremolite (see Fig. 2 in Johnson and Fegley, 2000).

regions are porous and the resulting phases are indistinguishable (Fig. 1). These regions are similar to the reacted powder morphology observed for F-poor tremolite decomposition (Johnson and Fegley, 2000).

3. Kinetic results

We determined the thermal decomposition rate by measuring the mass loss of each sample over time. When tremolite decomposes, it loses mass by releasing water and fluorine. This volatile loss was verified by mid-IR spectroscopy
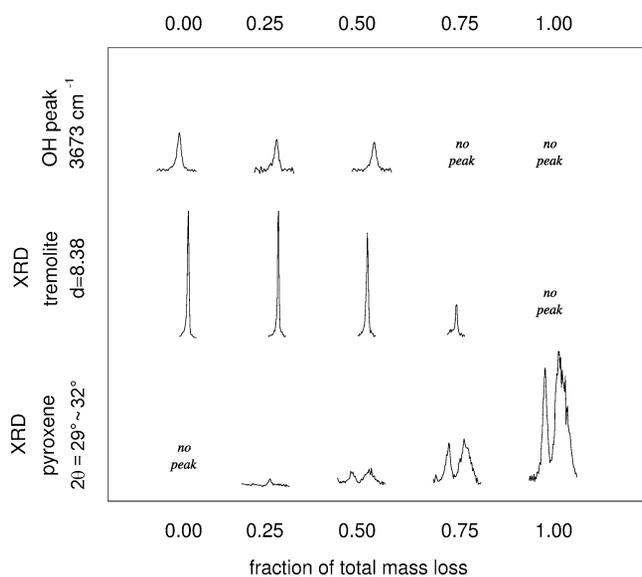
Fig. 2. This plot shows decomposition progression with peaks from mid-IR spectroscopy and X-ray diffraction.

and electron microscopy. Figure 2 shows the decrease of the tremolite hydroxyl peak with decomposition and fluorine loss is noted in Table 1. The extent of reaction is presented as a fraction of mass loss (α) and is calculated using

$$\alpha = \left(\frac{\Delta m}{m_i} \cdot \frac{1}{\delta_{\max}} \right), \tag{3}$$

where Δm is the mass change, m_i is the initial mass, $\delta_{\max}$ is the maximum possible fractional mass loss. Using the volatile content of tremolite and the talc component determined by electron microprobe analysis, we calculated the maximum fractional mass loss to be 0.0307. The observed maximum fractional mass loss of 0.026681 was determined by measuring the mass loss of three completely devolatilized samples heated at ~ 1273 K. Devolatilization was considered complete when the mass change was less than two parts per million. Electron microprobe analyses of these samples showed that there was no fluorine in the decomposed tremolite. The smaller observed mass loss compared to the calculated mass loss suggests that some, but not all, of the fluorine deposited onto the reaction vessel during heating. During the remainder of this paper, we use the observed maximum mass loss to determine α because the observed value indicates complete decomposition or devolatilization of the sample. Table 2 lists the mass loss and the mass loss fraction (α) of our experiments. Three typical mass loss curves are shown in Fig. 3 to illustrate the increasing time required for decomposition at lower temperatures. The shapes of these curves are similar to those observed for decomposition of fluorine-free tremolite (Johnson and Fegley, 2000, 2003).

Figure 4 shows the mass loss fraction plotted versus time normalized to the time required for 50% of total mass loss (i.e., $t/t_{0.5}$). This type of plot (e.g., see Brown et al., 1980) shows that F-bearing tremolite decomposition follows the same kinetic behavior and obeys the same mechanism (al-
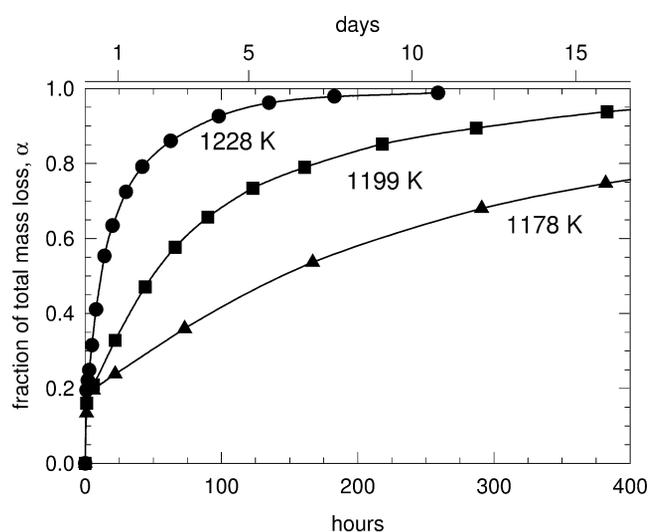

Fig. 3. Three typical weight loss curves for F-bearing tremolite decomposition. This plot shows that samples heated at lower temperatures take longer to decompose. The extent of reaction, α, is calculated from the mass loss (see text for details) and is plotted here as a function of time. When the observed weight loss is half of the complete mass loss, α is 0.5. The observed weight loss reaches its maximum and the extent of reaction is one when the sample has completely decomposed.
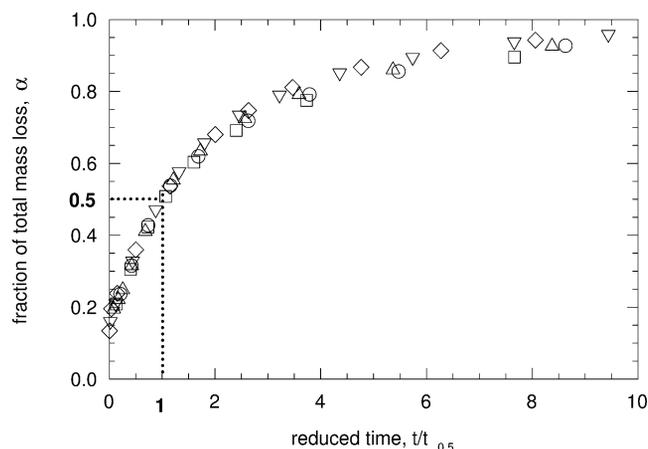

Fig. 4. Reduced time plot that shows the fraction of total mass loss, α, of the samples with reduced time. Reduced time is time normalized to 50% decomposition time ($t_{\mathrm{reduced}} = t/t_{0.5}$). Each symbol indicates a different temperature: [○] 1254 K, [□] 1241 K, [△] 1228 K, [▽] 1199 K, [◇] 1178 K.

though at a different rate) at all of the temperatures studied. Figure 4 also shows that complete decomposition takes several to ten times longer than the time required for 50% of total mass loss.

The first order rate model is often used to describe the decomposition rate behavior of powder grains (e.g., Brown et al., 1980; Galwey and Brown, 1999) and best describes our data for tremolite powder decomposition (Johnson and Fegley, 2003). The first order rate model is represented by the equation, $kt = -\ln(1 - \alpha)$, where k is the rate constant (hr^{-1}), t is time (hr), α is the fraction of total mass lost. The first order rate equation is a version of the Avrami–Erofe'ev

Table 2
Fluorine-bearing, Campolungo tremolite powder decomposition data

Exp	Time (hr)	Mass loss (mg)	Mass loss fraction[*] (α)	Exp	Time (hr)	Mass loss (mg)	Mass loss fraction[*] (α)
Temperature: 1254 K, initial mass: 100.692 mg				Temperature: 1199 K, initial mass: 102.396 mg			
e106	1.0	0.635	0.236	e104	1.0	0.438	0.160
e106b	2.0	0.847	0.315	e104b	6.0	0.573	0.210
e106c	3.5	1.148	0.427	e104c	22.0	0.897	0.328
e106d	5.5	1.444	0.537	e104d	44.0	1.286	0.471
e106e	8.0	1.663	0.619	e104e	66.0	1.575	0.576
e106f	12.5	1.929	0.718	e104f	90.0	1.795	0.657
e106g	18.0	2.126	0.791	e104g	123.0	2.006	0.734
e106h	26.0	2.298	0.855	e104h	161.0	2.158	0.790
e106i	41.0	2.490	0.927	e104i	218.0	2.327	0.852
e106j	68.0	2.625	0.977	e104j	287.0	2.444	0.895
e106k	96.0	2.651	0.987	e104k	383.0	2.563	0.938
				e104l	472.0	2.619	0.959
Temperature: 1241 K; initial mass: 101.330 mg							
e105j	1.0	0.564	0.209	Temperature: 1178 K, initial mass: 101.515 mg			
e105k	3.0	0.825	0.305	e107	1.0	0.364	0.134
e105l	5.5	1.143	0.423	e107b	6.0	0.530	0.196
e105m	8.0	1.373	0.508	e107c	22.0	0.646	0.239
e105n	12.0	1.631	0.603	e107d	73.0	0.974	0.360
e105o	18.0	1.869	0.691	e107e	167.0	1.453	0.536
e105p	28.0	2.096	0.775	e107f	291.0	1.842	0.680
e105q	57.5	2.421	0.896	e107g	382.0	2.023	0.747
e105r	94.0	2.612	0.966	e107h	503.0	2.196	0.811
e105s	121.0	2.657	0.983	e107i	691.0	2.349	0.867
e105t	283.0	2.717	1.005	e107j	910.0	2.474	0.913
e105u	449.0	2.731	1.010	e107k	1169.0	2.552	0.942
e105v	1267.0	2.746	1.016	e107l	1672.0	2.615	0.965
e105w	3303.0	2.766	1.023	e107m	3690.0	2.684	0.991
Temperature: 1228 K, initial mass: 100.128 mg							
e102	1.0	0.520	0.195				
e102b	2.0	0.591	0.221				
e102c	3.0	0.664	0.249				
e102d	5.0	0.842	0.315				
e102e	8.0	1.097	0.411				
e102f	14.2	1.478	0.553				
e102g	20.2	1.694	0.634				
e102h	30.0	1.935	0.724				
e102i	42.0	2.114	0.791				
e102j	62.8	2.298	0.860				
e102k	98.0	2.474	0.926				
e102l	135.0	2.570	0.962				
e102m	183.0	2.615	0.979				
e102n	259.0	2.640	0.988				

[*] Calculated using a maximum fractional mass loss of 0.026681, see text (3 samples, $1\sigma = 5.3 \times 10^{-5}$).

models that describe nucleation and growth kinetic behavior. The selection of this model is discussed in detail in Johnson and Fegley (2003). We use α values from 0.1 to 0.8 to determine the rate constants. We excluded values less than 0.1 because of the talc component and values greater than 0.8 because of a possible transition to a different reaction mechanism (e.g., Brown et al., 1980). Table 3 lists the mean rate constant for each temperature.

The Arrhenius plot in Fig. 5 shows the linear relationship between the log of the reaction rate constants and inverse temperature. The Arrhenius equation is $k = A \exp(E_a/RT)$, where A is the pre-exponential factor, T is the temperature in Kelvin, R is the gas constant, E_a is the activation energy

(kJ mol^{-1}), and k is the rate constant (hr^{-1}). Analysis of the data gives the rate equation

$$\log_{10} k = 20.35\ (\pm 0.05) - 26{,}879\ (\pm 1{,}229)/T, \qquad (4)$$

where T is in Kelvin with a corresponding activation energy of 515 ± 24 kJ mol^{-1}.

4. Discussion

4.1. Tremolite stability and fluorine

Amphiboles occur in a variety of pressure, temperature regimes and are found in both igneous and metamorphic

Table 3
Rate data used to calculate the rate equation and activation energy

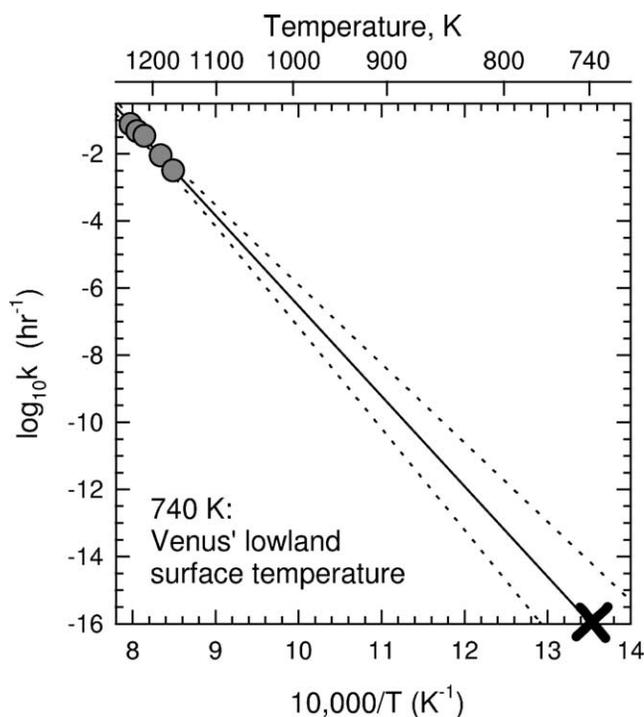| Temperature (K)	Rate constant, k (hr^{-1}) $\times 10^{-3} \pm 1\sigma$
1254	76 ± 5
1241	47 ± 4
1228	34 ± 2
1199	9 ± 0.4
1178	3 ± 0.1

Fig. 5. Reaction rate constants versus $10,000/T$ shown in an Arrhenius plot. Table 3 lists the rate constants and the rate equation is given in Eq. (4). The solid line shows the linear regression of the tremolite powder decomposition and the dashed lines indicate the 95% confidence prediction interval of the regression.
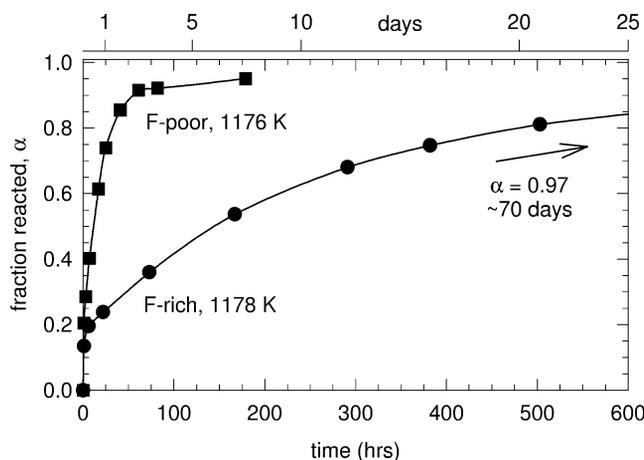

Fig. 6. Decomposition curves of two different tremolite samples, F-rich and F-poor, heated at approximately the same temperature. The F-poor tremolite data is from decomposition experiments used in Johnson and Fegley (2000, 2003).

rocks. We reviewed possible locations for tremolite formation and its paragenesis on Venus in Johnson and Fegley (2000). With the exception of fluorine, F-rich tremolite is expected to form under similar conditions as OH-tremolite. Hydroxyl-tremolite and fluor-tremolite have the same crystalline structure except the hydroxyls are replaced by fluorine. As mentioned earlier, the substitution of fluorine for OH increases amphibole thermodynamic stability (e.g., Troll and Gilbert, 1972; Gilbert et al., 1982; Grigoriev and Isküll, 1937; Graham and Navrotsky, 1986). Even a small amount of fluorine (0.5 wt% F) increases the thermal stability of tremolite (Jenkins and Clare, 1990). It stands to reason that the thermal stability of intermediate compositions of (OH, F)-tremolite increase with increasing amounts of fluorine. The stabilizing influence of fluorine in the tremolite structure is shown in Fig. 2. This figure illustrates that the tremolite structure remains even though the hydroxyls have

been removed by the time α reaches 0.75. At this stage of reaction, fluorine is still present in the unreacted portions of the sample but is decreased or absent in the reacted regions. This apparent bimodal loss of volatiles suggests that there might be two different mechanisms (or rates) involved in the decomposition of fluor-tremolite: one for OH loss and the other for fluorine. However, we do not observe two different kinetic steps. We use Eq. (4) to describe the entire decomposition.

The tremolite used by Johnson and Fegley (2000, 2003) contains less than 0.1 wt% F and the fluorine-bearing tremolite used in this study contains 1.41 wt% F. Decomposition of the F-bearing tremolite takes much more time than decomposition of the F-poor sample. Figure 6 shows the decomposition curves for two different tremolite samples, F-rich and F-poor, heated at approximately the same temperature. The fluorine-bearing tremolite takes about ten times longer to decompose than the fluorine-poor tremolite. All things being equal between these two samples except for fluorine content also suggests that fluorine substitution increases the kinetic stability of tremolite. Table 4 lists times for 50% decomposition of F-bearing tremolite powder (this study) and the results for F-poor tremolite from Johnson and Fegley (2003). It is apparent that decomposition slows dramatically with decreasing temperature. However, the key point is the large difference in decomposition times between F-rich and F-poor tremolite heated at the same temperature. The values for the F-rich tremolite should be considered upper limits because of the impact of fluorine deposition onto the reaction vessel. The fifty percent decomposition times for both tremolites are plotted in Fig. 7. This graph illustrates that while it takes a long time for fluorine-poor tremolite to decompose at Venus lowland temperatures, a time increase of several orders of magnitude is needed for fluorine-rich tremolite to decompose at the same temperature. Additionally, decomposition is even slower in the Venusian highlands where the temperatures are cooler.

Table 4
Time for 50% decomposition (tremolite powder)

T (K)	F-poor[a]	F-rich[b]
1200	11 hr	78 hr
1100	28 days	352 days
1000	11 yr	270 yr
900	5000 yr	260,000 yr
800	10 Ma	1400 Ma

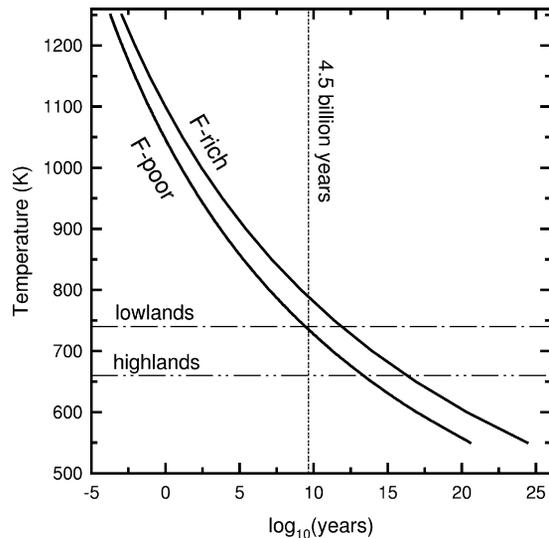[a] Calculated from Eq. (6) (Johnson and Fegley, 2003).
[b] Calculated from Eq. (4), this study.

Fig. 7. A plot of the fifty percent decomposition times calculated from rate equations derived for F-poor and F-rich tremolite decomposition. The rate equation for F-rich tremolite is Eq. (4) in this paper. The rate equation for F-poor tremolite is Eq. (6) of Johnson and Fegley (2003). The vertical line (Solar System age) is given for timescale.

These results strengthen our previous conclusion in Johnson and Fegley (2000) that if hydrous minerals, such as tremolite, formed in a wetter past, they could survive on Venus at current surface temperatures to the present day. This statement assumes that there were no temperature fluctuations or catastrophic geologic activities since the possible formation of hydrous minerals. It is reasonable to assume there were temperature differences in Venus' past and climate models suggest that surface temperatures on Venus could have previously been higher (e.g., Hashimoto and Abe, 2001; Bullock and Grinspoon, 2001; Solomon et al., 1999). Phillips et al. (2001) modeled the evolution of the Venus' interior with climate and also propose possible surface temperature variation behaviors. The range of different temperature fluctuations and their durations are as many and varied as there are models (e.g., temperature fluctuations can vary from 60 to greater than 200 degrees higher than the current temperature on Venus). As for catastrophic activity, Venus may have undergone rapid and global resurfacing about 500 Ma ago (Schaber et al., 1992) or resurfacing may have occurred more frequently on small-scales (i.e., regional) during the recent past (Phillips et al., 1992). This

leads to another question, "Could resurfacing destroy all possibilities of finding hydrous minerals on Venus' surface?" The answer depends on variables such as the temperature, the depth of the overlying layer, the temperature gradient and its duration, the composition of the magma, the water vapor pressure of the gas during magma deposition, and the location of hydrous minerals. These variables only begin the list of data needed in order to answer the above question.

4.2. Mineral detection

Several spacecraft have been sent to Venus over the past forty years yet we have no direct mineralogical information about Venus' surface. We only have elemental surface abundances for Mg and heavier elements measured by X-ray fluorescence in three similar terrains (Surkov et al., 1984, 1986). Theoretical models of atmosphere-surface equilibria, elemental analyses at three landing sites, and the radar emissivity of the surface give us a rough idea of the surface mineralogy (e.g., Pettengill et al., 1982; Barsukov, 1992; Fegley and Treiman, 1992). However, the lack of direct mineralogical observations limits our ability to make sound conclusions about the role of atmosphere-surface interactions on Venus and to what degree these reactions control the atmosphere and surface compositions. If we are to gain a clearer picture of Venus' history, we need to know the surface mineralogy. This can be done using instruments such as XRD and/or IR reflectance spectroscopy (Blake et al., 1994; Rossman, 1988). Such equipment could be delivered to the surface via landers, penetrators, and/or automated balloons. It is important to sample from a variety of sites because measuring from one location would be of limited value. The highlands and lowlands could be very different mineralogically. If the tesserae are metamorphic (Nikolaeva et al., 1992), these areas will host a suite of minerals very different than those found in the lowlands that are considered to be primarily basaltic (Grimm and Hess, 1997). Hydrous minerals are found in both basaltic and metamorphic areas but with cooler temperatures in the highlands and some tesserae, it is better to sample in these locations because of potentially greater hydrous mineral preservation. If hydroxyls are preferentially lost at higher temperatures compared to fluorine, then we might expect OH-rich tremolite to be abundant at higher elevations with F-rich tremolite dominating at lower elevations. Other sampling sites include crater ejecta blankets because they could contain hydrous minerals excavated from rocks formed prior to resurfacing. Zolotov et al. (1997) and Johnson and Fegley (2000) also discuss these potential sites and additional sampling techniques.

5. Summary

The presence of HF in Venus' atmosphere, the relatively high concentration of HF and the estimated fluorine inventory on Venus suggests that fluorine is present in the sur-

face rocks. Fluorine substitution for OH in tremolite makes F-bearing tremolite both thermodynamically and kinetically more stable. These experiments and data analysis show that the decomposition rate of F-bearing tremolite is considerably slower than that of OH-tremolite (refer to Table 4) and that only a small amount of fluorine extends the lifetime of tremolite by billions of years at Venus' surface temperatures. The exceptional stability of F-bearing tremolite strengthens our previous conclusions in Johnson and Fegley (2000, 2003) that if hydrous minerals ever formed on Venus, they could still be there today.

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