REACTIVITY OF CALCIUM-BEARING MINERALS UNDER SIMULATED VENUS CONDITIONS

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Introduction

- SO_2 is reactive with several common elements e.g. calcium [1-4]
- Knowledge on chemical reactions has implications for the past and current state of Venus
  - Venus may have had liquid water on its surface [5], thus hydrous silicates may have formed at that time [6].
  - The Venus Emissivity Mapper (on VERITAS and EnVision) will be used to determine bulk composition of the surface by observing transition metal content [8-9]
    - Calcium diffuses through basalt to react with CO_2 and SO_2, changing the bulk composition and decreasing the emissivity from orbit [8]
    - Experiments investigating kinetics will be informative for future emissivity data
- **Goal**:
  - Constrain reaction rate between several calcium minerals and SO_2
  - Determine the effect, if any, crystal lattices may have on these rates

Methods

- Sample
  - Calcium bearing minerals. Each mineral was created under different formation processes and exhibit different crystal structures that will affect their interaction with SO_2
- Experiment
  - Thermogravimetric Analysis (Figure 1)
  - Tested Gas:
    - CO_2
    - CO_2/1.5% SO_2: SO_2 abundance similar to molecular number density as on Venus [2]
  - Tested Temperatures:
    - 460°C: average lowland temperature on Venus [1]
    - 700°C: to increase reaction rate
  - Temperature and mass of sample are collected in real-time
- Analysis
  - XPS
  - Milled using FIB
  - SEM/EDS

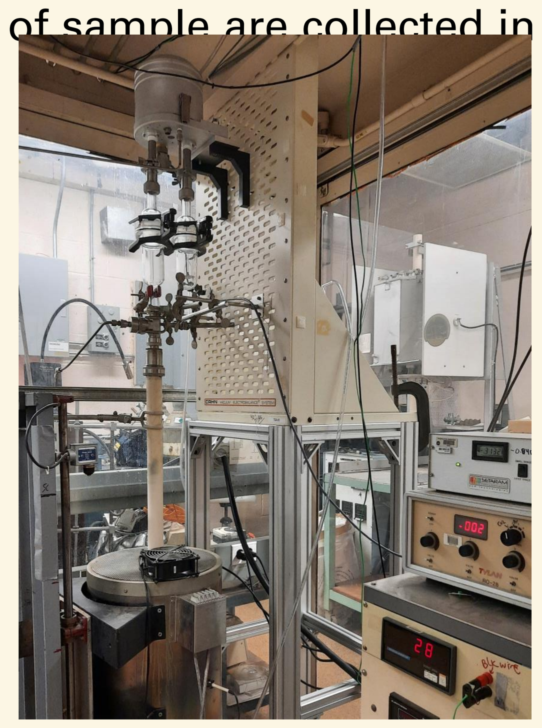


Figure 1: Experimental Apparatus used in these experiments.

Results

Mineral	Chemistry	Temp	Gas	Time
Calcite	$CaCO_3$	460°C	CO_2/SO_2	6 days
Calcite	$CaCO_3$	700°C	CO_2	5 days
Calcite	$CaCO_3$	700°C	CO_2/SO_2	5 days
Wollastonite	$CaSiO_3$	460°C	CO_2/SO_2	6 days
Anorthite	$CaAl_2Si_2O_8$	460°C	CO_2/SO_2	6 days
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$	460°C	CO_2/SO_2	6 days

Table 1: Summary of all experiments completed so far

Mineral	Location	S/Ca ratio
Calcite	Surface	1.05
	sputtered 1 min (100Å)	0.77
	sputtered 5 min (500Å)	0.51
Wollastonite	Surface	0.72
	sputtered 1 min (100Å)	0.23
	sputtered 2 min (200 Å)	0.14
Anorthite	Surface	0.95
	sputtered 1 min (100Å)	0.03
Tremolite	Surface (black)	1.24
	sputtered 1 min (100Å) (black)	0.33
	sputtered 2 min (200 Å) (black)	0.29
	Surface (white)	0.72

Table 2: XPS analysis of samples that were exposed to 460°C in CO_2-1.5% SO_2 for 6 days. Some samples, such as anorthite, had very little sulfur after sputtering indicating little reactivity

Figure 6: Tremolite before (left) and after (right) an experiment. Afterwards, tremolite exhibited dark and light patches on its surface. Dark patches have elevated abundances of sodium and sulfur

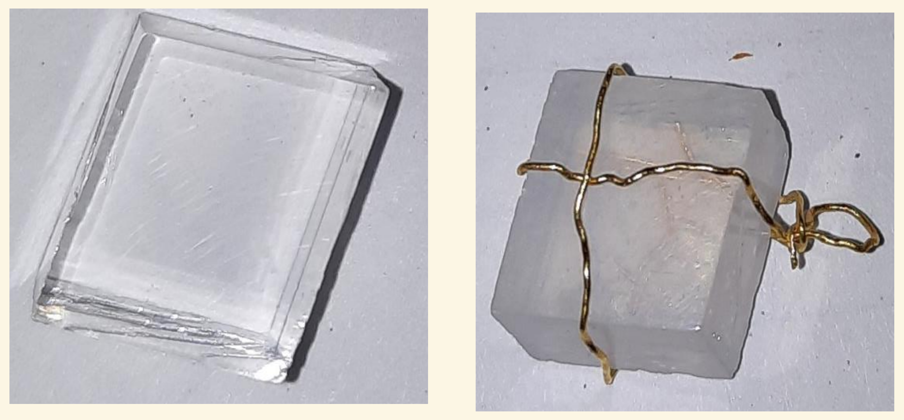


Figure 2: Calcite before (left) and after (right) it was heated to 700°C in CO_2-1.5% SO_2 for 5 days

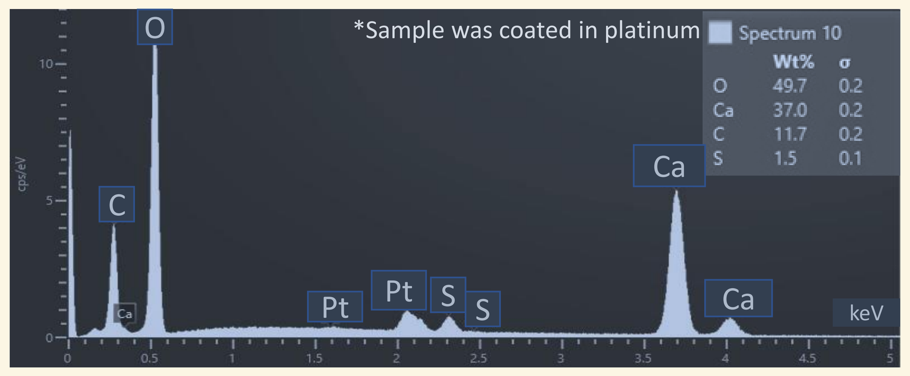


Figure 5: Calcite was heated to 460°C in CO_2-1.5% SO_2 for 6 days. The sample was milled via FIB, and EDS was used to determine the elemental composition at the surface. Sulfur is present on the surface

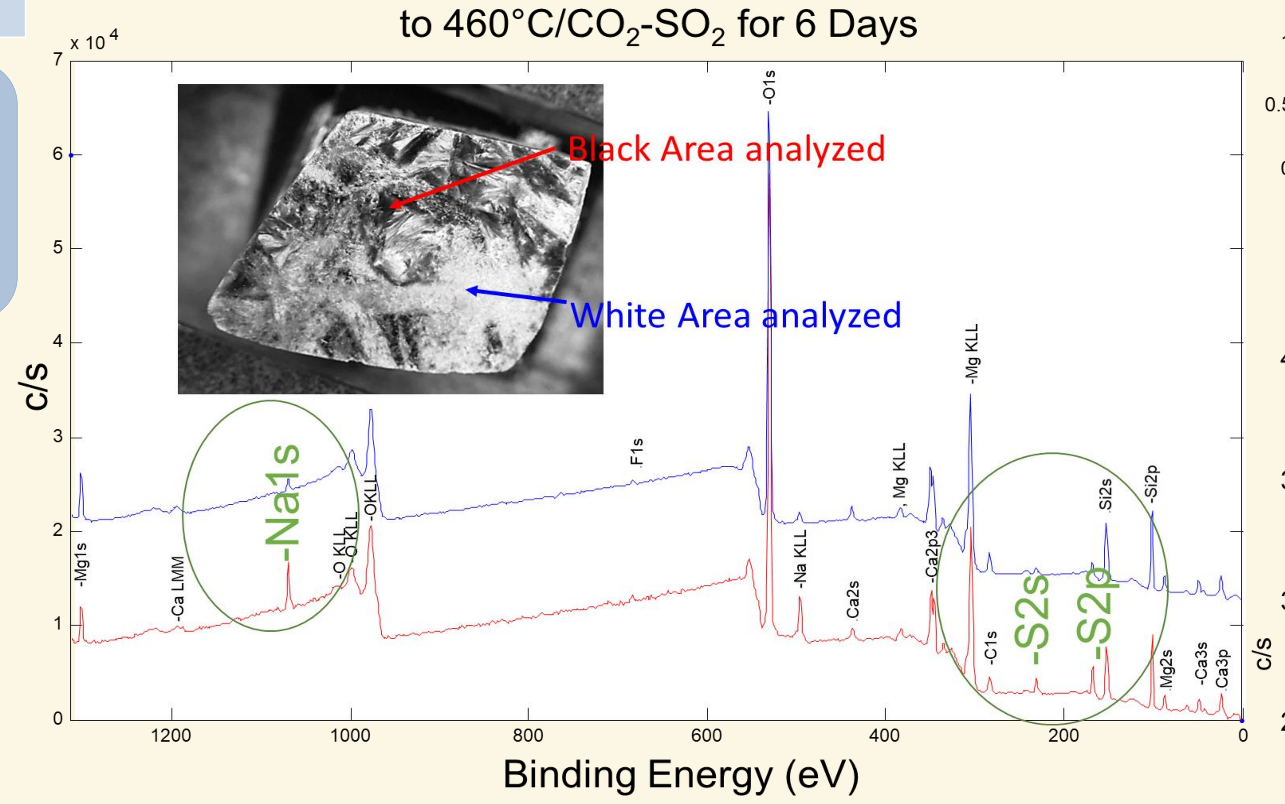


Figure 7: XPS spectra of a light colored and dark colored patch on tremolite. The dark patch had elevated abundances of sodium and sulfur

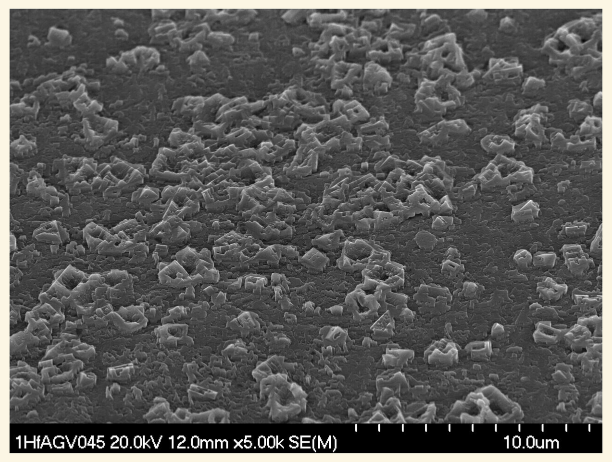
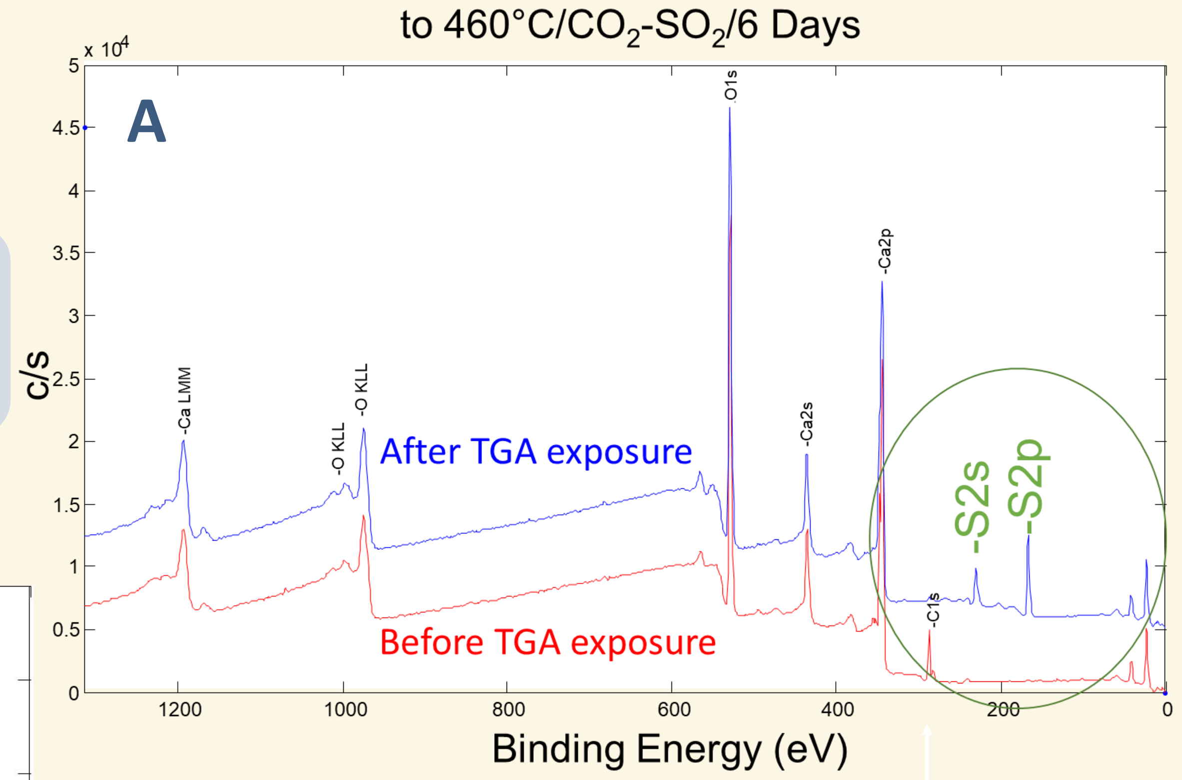
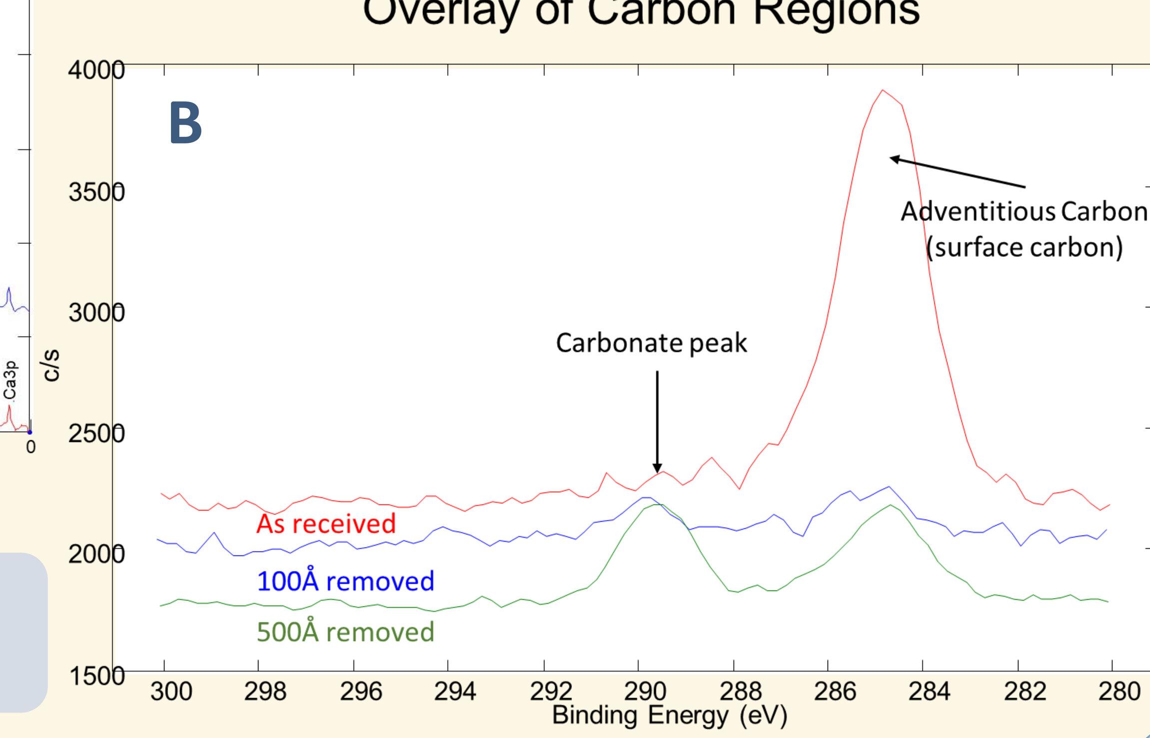


Figure 3: The surface of calcite after it was heated to 700°C in CO_2-1.5% SO_2 for 5 days. Mineral growth is observed on the surface

Figure 4: XPS spectra of calcite before and after a 460°C, CO_2-1.5% SO_2 for 6 days. Sulfate, but not carbonate, is present on the surface of the sample (A). Carbonate is detected at depth (B).





Conclusions

- All samples formed sulfate on the surface
- Calcite is reactive with SO_2 and will produce $CaSO_4$ at the surface, but the reaction is slower at 460°C compared to 700°C
- According to XPS results, wollastonite, anorthite, and tremolite are less reactive to SO_2 than calcite (460°C in CO_2-1.5% SO_2 for 6 days):
  - Calcite: 15.1 at% of sulfur at the surface
  - Wollastonite: 6.1 at% of sulfur at the surface
  - Tremolite: darker regions had 4.1 at% of sulfur at the surface while the white areas had 2.6 at%
  - Anorthite: 5.9% of sulfur at the surface
- Longer experiments will be completed in the future
- This information combined with the dimensions of the sample and the known change in mass will be used to constrain the reaction rate

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