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Effect of sulfuric acid exposure on common mineral dust particles

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Mendoza, Miguel D., "Effect of sulfuric acid exposure on common mineral dust particles" (2014).

Celebrating Scholarship & Creativity Day. 16.

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Effect of Sulfuric Acid Exposure on Common Mineral Dust Particles

Abstract:

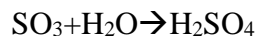
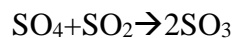
Mineral dust has a large effect on cloud formation and ultimately the climate. Several studies have shown the addition of acid to these mineral dust particles decreases their ability to nucleate ice. This study explores what chemistry occurs between common components of mineral dust particles and sulfuric acid. Hematite (Fe_2O_3), calcite (CaCO_3), and quartz (SiO_2) were exposed to sulfuric acid, and then analyzed using a combination of Attenuated Total Reflectance-FTIR, Diffuse Reflectance-FTIR Spectroscopy, X-Ray Diffraction, and Inductively Coupled Plasma Atomic Emission Spectroscopy to identify functional groups, mineral species, and aqueous phase elements. Quartz did not react with sulfuric acid. Calcite and hematite react readily with sulfuric acid to produce bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and rhomboclase (H_3O^+ $\text{Fe}(\text{SO}_4)_2 \cdot (\text{H}_2\text{O})_3$) respectively. Knowing how sulfuric acid affects these common mineral dust particles helps us understand how they age in the atmosphere and the effect on climate from this aging. Future experiments will explore other mineral dust components and eventually relate what chemical changes affected ice nucleation abilities.

Introduction:

Atmospheric aerosols are minute particles that are suspended in the atmosphere. When these particles reach sufficient size they start to scatter and absorb sunlight. The scattering and absorbing sunlight can affect the climate of the planet as a whole in two main ways: the direct and the indirect effect. The direct effect includes the physical scattering of sunlight directly back into space. As the indirect effect, aerosol particles can change the size of cloud particles altering their ability to absorb and reflect light. Cloud formation occurs when sufficient humidity and

temperature levels are reached; at this point ice forms on the particle, multiple particles then form the basis for clouds (Wayne, 1985). Further, cloud lifetime tends to be extended due to nucleation on these aerosol surrogates as opposed to natural cloud formation (Lohmann, 2006).

Many aerosol particles spend significant time in the atmosphere and often undergo physical changes from various other chemical species. These changes, called atmospheric aging, become extremely prevalent over continental polluted regions where the byproducts of many human processes release sulfur and nitrate species into the atmosphere. This aging significantly influences the ability of some aerosol particles to properly nucleate ice on their surface, greatly impeding cloud formation (Sullivan, 2010). One of the larger contributors to aging, sulfuric acid species, are investigated here. Multiple pathways have been proposed for the sulfur reactions in the atmosphere, Hecklen proposed a pathway of some significant importance (Hecklen, 1976):



Although the SO_4 intermediate and electronic states are under some amount of scrutiny, it's generally accepted that a majority of sulfur species in the atmosphere are in the sulfuric acid form (Hecklen, 1976; Wayne, 1985).

Sulfuric acid was chosen primarily because sulfuric acid species are among some of the highest pollutants in the atmosphere with the vast majority of sulfur species being products of fossil fuel usage and production. The various mineral dusts were chosen for a couple of reasons: mineral dust is one of the greatest heterogeneous ice nucleators in the atmosphere, clay minerals

(such as hematite) are the greatest proportion of mineral dust particles, and quartz and calcite make up another 20 percent together. Many papers have already cited that sulfuric acid exposure permanently reduces the ability of these mineral dust particles to nucleate ice (Chernoff et. al., 2010; Cziczo et. al., 2009, Niedermeier et. al., 2010; Sullivan et. al., 2010). The intention of this paper is to figure out why ice nucleation is lost.

Experimental:

For every experiment compounds were used as provided by Sigma-Aldrich including hematite, calcite, quartz, and sulfuric acid. All powdered items were used as received while sulfuric acid was diluted to a 1 Molar solution as documented by Moran (Moran, 1988). Multiple characterization techniques were used to analyze products of reactions including Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), X-Ray Diffraction (XRD), and Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). The ATR-FTIR system was from Thermo Scientific/Nicolet model iS 50 while the XRD used was a model TTRAX III from Rigaku.

Results:

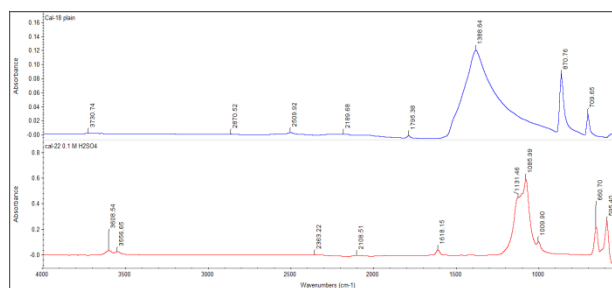


Figure 1: ATR data for calcite before (top) and after (below) exposure to 1 Molar sulfuric acid

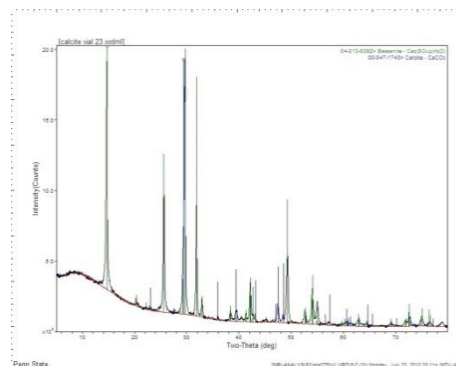


Figure 2: XRD data before and after exposure to 1 Molar sulfuric acid. Green vertical lines indicate bassanite peaks while blue lines indicate pure calcite peaks

Figure 1 shows ATR-FTIR data for calcite before and after exposure to 1 Molar sulfuric acid. The most important peak is the mid-range peak at roughly 1600 cm^{-1} . This peak and the absence of another in the $1800\text{-}1900\text{ cm}^{-1}$ region indicate the presence of bassanite as opposed to the dihydrate calcium sulfate species gypsum. The data also shows there is almost a complete change in composition from the calcite to bassanite because there is complete lack of the previous peaks seen in the pure calcite sample in the bottom spectra after exposure. This same conclusion is seen in the XRD data. There's nearly a complete loss of calcite peaks after exposure while the bassanite peaks shown in green are almost completely identical to the bassanite standard.

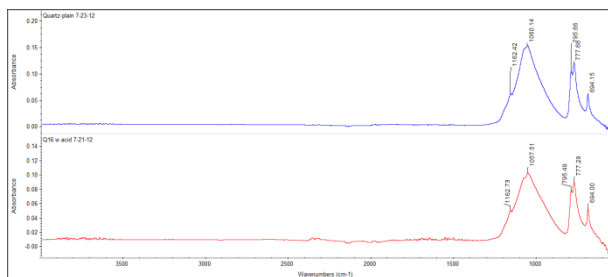


Figure 3: ATR data for quartz before (top) and after (below) exposure to 1 Molar sulfuric acid

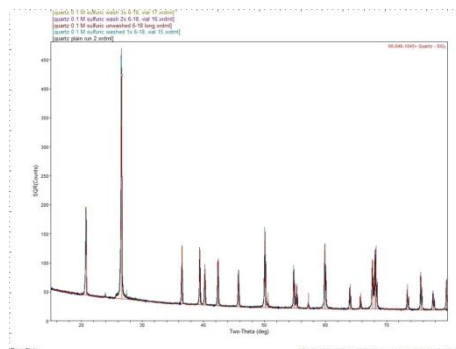


Figure 4: XRD data before and after exposure to 1 Molar sulfuric acid. Purple vertical lines indicate quartz standard peaks while the varying spectra lines indicate quartz after exposure to sulfuric acid

Figure 3 and Figure 4 show quartz data before and after exposure to sulfuric acid. In figure 3, no change has occurred between the two spectra indicating that sulfuric acid has no effect on quartz. Figure 4 shows the XRD data for the quartz samples and confirms the previous findings seen in the ATR data. Multiple samples align perfectly with the pure quartz used in the reaction as well as the quartz peaks from the XRD standard. Therefore, sulfuric acid exposure has no chemical effect on the quartz samples.

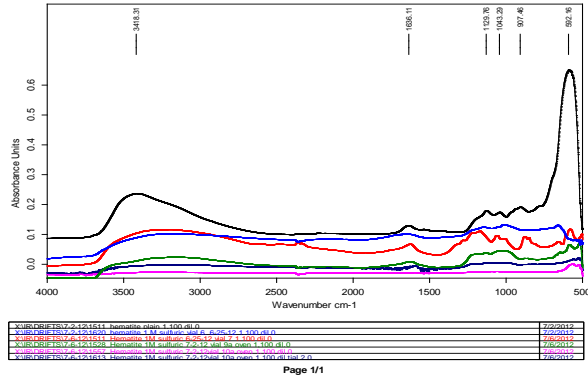


Figure 5: DRIFTS data for hematite before (black line) and after (all other spectra) exposure to 1 Molar sulfuric acid.

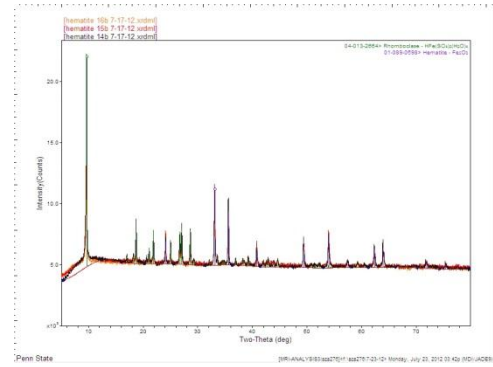


Figure 6: XRD data before and after exposure to 1 Molar sulfuric acid. Green vertical lines indicate hematite standard peaks while the varying spectra lines indicate hematite after exposure to 1 Molar sulfuric acid

Figure 5 shows the DRIFTS data collected for the hematite samples. The black spectral line shows hematite without exposure to sulfuric acid. All the other colored lines show varying samples of hematite after exposure to 1 Molar sulfuric acid. Although the data does show consistent spectra, it's hard to see what functional groups may be formed after exposure. It is evident that some change has occurred because of the loss in some of the larger pure hematite peaks. Figure 6 shows the XRD data for the hematite samples and confirms the fact that the sulfuric acid exposure has changed the chemical composition of the mineral dust sample. The green vertical bars indicate rhomboclase standards while the blue vertical bars indicate hematite standard peaks. Again, there's consistent data as multiple samples of hematite provide similar spectra. The spectrum also shows that there is some presence of hematite left over in the sample combined with rhomboclase after exposure to sulfuric acid.

Discussion:

After exposure to sulfuric acid we found that there was some chemical change that occurred in two of the three mineral dusts I studied. Quartz showed absolutely no change after exposure to sulfuric acid even at varying concentrations of sulfuric acid. With no change seen after exposure, it's fair to conclude that the ice nucleation abilities of quartz before and after long distance atmospheric aging should be relatively similar. The effects of exposure on calcite and hematite showed more interesting results. In the case of calcite, after exposure to sulfuric acid bassanite was formed. This hemi-hydrated compound was a very accurate match after analyzing via ATR-FTIR. When XRD was used to analyze the product residual calcite was seen to be present as shown in Figure 2. This same effect was seen in the case of hematite. Although the DRIFTS data does not appear to be very helpful in determining what product was present, it does tell us that some change has occurred compared to the black pure hematite spectra. This change is confirmed in the XRD spectra for hematite. After comparison to known standards, hematite formed rhomboclase while some residual hematite was still present as well. The results of hematite are similar to that of calcite. For both hematite and calcite, a hydrated compound was formed and there was residual starting material left over. The presence of residual starting materials raises a few questions. Although the FTIR data for both hematite and calcite show changes, in the case of calcite there does not seem to be any residual calcite leftover after exposure as seen in the ATR spectra. This observation was not repeated in the XRD spectra. In both cases, residual starting material was seen in both spectras implying an incomplete transformation. One possible explanation could be that only the surface of the mineral dust particles was modified after exposure to sulfuric acid. When analyzing the bulk matrix using ATR, the samples were analyzed after exposure without any modification. When it came time to

analyze the data using XRD, a mortar and pestle was needed to produce a fine powder necessary for analyzing. It's possible that the bassanite/rhomboclase "shell" was broken open in this process exposing the inner calcite/hematite. This same conclusion was drawn in an article by Reitz in 2011. Reitz et. al. found that the ice nucleation abilities were permanently modified by exposure to sulfuric acid, but due to chemical modification of the surface and not just a sulfuric acid coating (Reitz, 2011).

Although this study has been helpful in understanding what chemical changes can occur in the atmosphere, it does not tell the whole story. More mineral dust and aerosols need to be studied in order to have a better understanding of sulfuric acid aging in the atmosphere. Besides more mineral dusts, we know that sulfuric acid is not the only pollutant in the atmosphere. More work is needed on compounds such as nitric acid and various ammonia species to understand the full extent of aging on the mineral dust compounds. Finally, now that we have determined some sort of chemical modification does indeed occur after exposure to sulfuric acid we need to study these changes in more atmospherically relevant conditions. First, analysis in the gaseous phase will be more helpful in observing the reaction capabilities of the various reactants. Next, more atmospherically relevant temperatures and relative humidities are important to understand whether the hydrated complexes we found are indeed the product. Overall, there is much more work needed to better understanding what actually occurs in our atmosphere.

Conclusion:

In the end, data proved to be quite interesting. Quartz was unaffected by sulfuric acid exposure while calcite and hematite showed fundamental changes to bassanite and rhombochase respectively. The discrepancies between the ATR spectra and the XRD spectra may be explained by the differences in the ways the samples were analyzed. In the case of XRD, a fine powder created via mortar and pestle is believed to have exposed the inner pure mineral dust powder. Although this is only a guess, more data is needed to understand why there is residual mineral dust left over. Further studying is also needed in areas of atmospherically relevant conditions such as relative humidities, temperature, and gaseous phase molecules. Overall, much more work is needed to better understand the effects of long distance aerosol aging in the atmosphere.

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