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Solubility and freezing effects of Fe^{2+} and Mg^{2+} in H_2SO_4 solutions representative of upper tropospheric and lower stratospheric sulfate particles

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[1] Chemical elements characteristic of earth minerals and meteorites are present within background tropospheric and stratospheric sulfate aerosol particles. However, it is unknown if these elements are present predominantly as solids, including possible sulfates, carbonates, and oxides, or rather as soluble aqueous metal ions or complexes. Further, it is unclear how these impurities could affect particle freezing. To address these questions, we have determined the total equilibrium metal solubility ($[\text{Fe}^{2+}]_T$ and $[\text{Mg}^{2+}]_T$) in 20–90 wt % sulfuric acid solutions over the temperature range 200–300 K. We have measured solubilities using samples of MgSO_4 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and a mixture of metal sulfates representative of some meteorite samples. Because Fe^{2+} oxidation by O_2 was found to be negligible over a 28 day period when air was bubbled through the solutions, we conclude that aqueous Fe^{2+} may be present at high concentrations in atmospheric sulfuric acid particles. We estimate that soluble Fe^{2+} and Mg^{2+} compose ~ 0.01 – 0.28 wt % of the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}/\{\text{Fe}^{2+}, \text{Mg}^{2+}\}$ solutions at temperatures and acid compositions representative of the atmosphere. Compared to composition measurements done by mass spectrometry of atmospheric particles showing ~ 0.75 wt % Fe and 0.20 wt % Mg, we conclude it is plausible that solid Fe^{2+} and Mg^{2+} minerals often occur inside atmospheric sulfuric acid particles. Bulk freezing experiments were also carried out on H_2SO_4 solutions containing amounts of dissolved metal determined by the low-temperature solubility studies. It was found that 57.6 wt % H_2SO_4 containing soluble meteoritic metal and 60 wt % H_2SO_4 containing either soluble Fe or soluble meteoritic metal froze ~ 12 – 20 K higher than solutions containing no soluble metal. Soluble metal ions in sulfuric acid solution may therefore provide a mechanism for sulfuric acid tetrahydrate formation in the lower stratosphere. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; **KEYWORDS:** polar stratospheric cloud formation, phase transformations, stratospheric aerosol, metal solubility, sulfuric acid, meteoritic metals

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1. Introduction

[2] Sulfate aerosol particles are ubiquitous in the upper troposphere and the lower stratosphere and are known to

impact the Earth's atmosphere in several ways. These particles can affect the Earth's radiation balance directly by scattering solar radiation or indirectly by serving as cloud condensation nuclei [DeMott and Rogers, 1990]. Sulfate aerosol particles are also important for chemistry in the Earth's atmosphere. In the lower stratosphere, polar stratospheric clouds (PSCs) form on background sulfate aerosols and convert inert chlorine species into active chlorine species that destroy ozone in the Antarctic [Solomon, 1988]. Direct reactions of chlorine on sulfate aerosols have also been implicated in global ozone loss [Solomon *et al.*, 1997].

[3] While most studies of the chemistry and climate impact of sulfate aerosol particles have assumed pure

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H₂SO₄/H₂O compositions, new data reveal that there is many trace species present in the particles, including meteoritic material [Cziczko *et al.*, 2001]. The main trace metal constituents found in meteoritic particles are Fe, Mg, Al, Ca, Na, Ni, Mn, and K. These trace species may influence important properties of the sulfate aerosol. For instance, if these trace substances are present as solids, they may serve as heterogeneous nuclei for cloud formation. If present in dissolved form, metal ions may catalyze liquid-phase reactions in the sulfate particles. The exact physical form (solid or aqueous) of the metals in the sulfate particles is not currently known.

[4] The question of metal solubility is complex, depending on equilibrium thermodynamics, dissolution rates, and chemical form. For instance, Fe²⁺ salts such as FeSO₄ are highly soluble in water and in dilute sulfuric acid and rapidly achieve dissolution equilibrium. In contrast, the equilibrium solubility of Fe³⁺ such as Fe₂O₃ is orders of magnitude lower, dissolution kinetics is slow, and equilibration times are long [Stumm and Morgan, 1996]. Therefore a kinetic/mechanistic approach is necessary which initializes the system with the mass of each mineral present in an atmospheric particle at the temperature and composition of the surrounding aqueous sulfuric acid. Identified meteoritic materials including Ca²⁺, Mg²⁺, Na⁺, Ni²⁺, and K⁺ have a single common oxidation state. In contrast, Fe and Mn minerals can be found in much more soluble Fe²⁺ and Mn²⁺ states or much less soluble Fe³⁺ and Mn^{3+/4+} states [Cotton and Wilkinson, 1972]. Finally, meteoritic material may also contain any number of other minerals including insoluble oxides of silicon and aluminum. The current paper concentrates specifically on the subsystem Fe²⁺ and Mg²⁺. An important simplification found in the current work is that the Fe²⁺ and Fe³⁺ systems are decoupled (i.e., slow Fe²⁺ auto-oxidation kinetics), at least for the typical timescales and temperatures of atmospheric sulfate particles.

[5] We have determined the solubility of the parent metals of MgSO₄, FeSO₄, and a mixture of metal sulfates representative of meteorite samples in sulfuric acid solutions from 20–90 wt % over the temperature range 200–300 K. We have also investigated the kinetics of Fe²⁺ oxidation by O₂ under these conditions. Finally, we have performed bulk freezing experiments to determine the influence of soluble metal ions on the freezing temperatures of sulfuric acid solutions.

2. Experiments

2.1. Solubility Experiments

[6] In all experiments, reagent grade 96.4 wt % H₂SO₄ was diluted to 20–90 wt % using distilled water. Analysis of the distilled water using an ARL-3410+ inductively coupled atomic emission spectrometer (ICP/AES) showed negligible amounts of dissolved metals. Therefore no further purification process was employed. The H₂SO₄ concentration was determined prior to each experiment by titration with a standardized NaOH solution. Each standardization and titration was performed multiple times, and the standard deviation of these trials was used to produce H₂SO₄ concentration error bars in each experiment. In all experiments the H₂SO₄ weight percent concentrations are calculated taking into

account only H₂SO₄ and H₂O present in the system, with no corrections due to metal sulfate dissolved. The waters of hydration present in the FeSO₄•7H₂O were included in the determination of the H₂SO₄ concentration. Temperature was measured using a Type T copper/constantan thermocouple. The uncertainty in the temperature measurement was always <1°C (specified by Omega Engineering, Inc.). This uncertainty was used to produce temperature error bars in the solubility experiments.

[7] The maximum solubility of Fe²⁺ and Mg²⁺ in 20–90 wt % H₂SO₄ was first determined at room temperature by separately mixing FeSO₄•7H₂O and MgSO₄ into the H₂SO₄ until solid dissolution ceased. The solutions were mixed for ~72 hours to ensure that the metals in solution were in equilibrium with the undissolved solid. After mixing, the solutions were centrifuged for 20 min at 4000 rpm to remove all solids from the saturated solutions. The supernatant was then analyzed for Fe and Mg content using ICP/AES. Total iron analyzed here ([Fe]_T) is the sum of Fe²⁺(aq), Fe³⁺(aq), and any aqueous complexes (e.g., sulfates) of each. The same holds for [Mg]_T. As discussed further below, we measure negligible amounts of Fe³⁺ in our systems. Thus we abbreviate hereafter [Fe²⁺] for [Fe]_T and similarly for [Mg²⁺].

[8] To ensure that the 3 day period was adequate to obtain solubility equilibrium, H₂SO₄ solutions were left to mix with an abundance of FeSO₄ and MgSO₄ for a period of 28 days. Each week a sample of each solution was analyzed for metal content. Because the metal content was the same within error in the solutions mixed for 3 days and over the period of a month, we concluded that the 3 day mixing period was adequate for the determination of equilibrium solubility.

[9] The setup used in our low-temperature solubility experiments was an insulated methanol bath that was chilled using a recirculating flow of methanol from a Neslab refrigerator through a copper coil. Using this method, the methanol bath in the cooler was chilled from 0°C to -70°C and solubility experiments were carried out at a desired temperature in this range. To determine Fe²⁺ and Mg²⁺ solubility in 20–50 wt % H₂SO₄ at low temperatures, a metal sulfate saturated H₂SO₄ solution at room temperature was placed in a test tube in the cold bath. Because the solution was supersaturated with respect to the metal sulfate at colder temperatures, solid metal sulfate precipitated out of solution to reach equilibrium. After precipitation, the supernatant was sampled and analyzed for metal content using ICP/AES. If the metal sulfate solution froze, a lower metal sulfate concentration was used that did not freeze but still resulted in solid precipitation upon cooling.

[10] Because no solid precipitated in 60–70 wt % H₂SO₄ at low temperatures, a different method was employed to determine Fe²⁺ and Mg²⁺ solubility. Initially, H₂SO₄ with no metal in it was placed in the bath at the desired temperature. Once the H₂SO₄ reached the bath temperature, crystalline metal sulfate was added stepwise into the H₂SO₄ until solid dissolution ceased. This solid was removed by passing the solution through 0.1 μm syringe filter that was chilled to the bath temperature. The filtrate was analyzed for metal content using ICP/AES.

[11] To measure how the metal ion solubility was affected by other metal ions, we also measured mixed metal sulfates

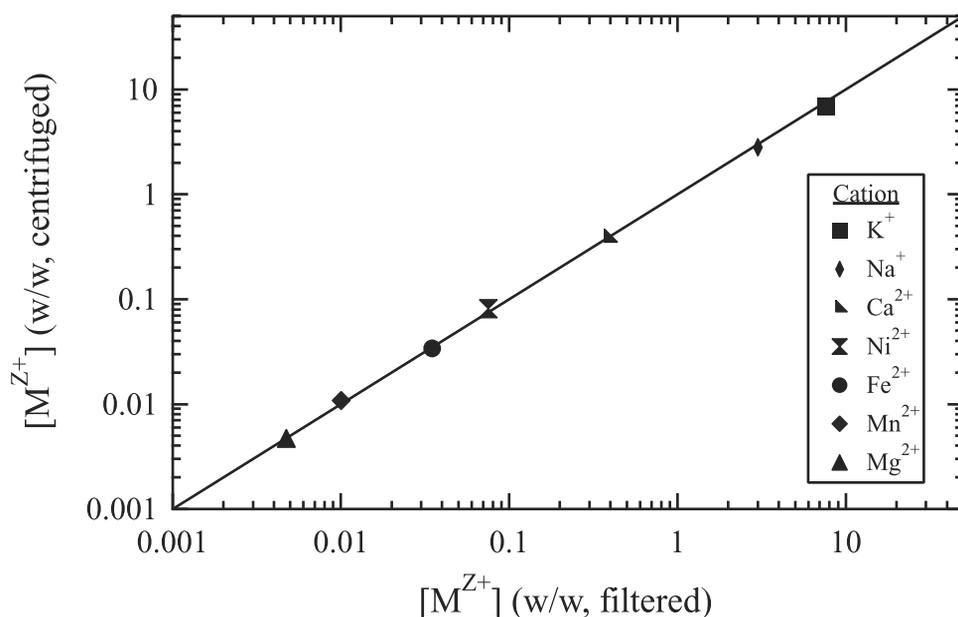


Figure 1. Weight percent soluble metal, $[M^{Z+}]$ (where M is metal studied and z is 1 or 2), using the “centrifuge method” versus using the “filter method” of removing solid particles from solution. Each symbol represents a different metal studied in 89.1 wt % H_2SO_4 at 22.9°C.

of composition dictated by that likely found in meteoritic samples. Previous work has shown that stratospheric particles contain ~0.75 wt % extraterrestrial Fe [Cziczo *et al.*, 2001]. Using this percentage, the weight percent of other major meteoritic constituents such as Ca, K, Mn, Na, Ni, and Mg were estimated by Cziczo *et al.* [2001]. These metals in ratios consistent with actual stratospheric particles were simultaneously added as sulfate salts to 40–70 wt % H_2SO_4 that was previously cooled to a specific temperature in the cold bath. These solutions were mixed and then forced through a 0.1 μm syringe filter chilled to the bath temperature. The filtered solution was then analyzed for metal content using ICP/AES.

[12] To determine if the syringe filter affected metal solubility, 89.1 wt % H_2SO_4 was mixed separately with each metal sulfate tested as described in the room temperature solubility experimental section. Half of each solution was centrifuged to remove solid particles and the supernatant analyzed for metal content. The other half was filtered to remove solid particles with the 0.1 μm syringe filter. Parent metal solubility using the “centrifuge” preparation method is plotted versus parent metal solubility using the “filter” preparation method in Figure 1. Each metal exhibits different solubility in 89.1 wt % H_2SO_4 with K^+ exhibiting the greatest solubility at ~10 wt % and Mg^{2+} exhibiting the lowest solubility at less than 0.01 wt %. There is good agreement with the two preparation methods. It is thus unlikely that any undissolved metal sulfate is contributing to our solubility values.

[13] To determine the oxidation state of soluble Fe in our experiments, we sampled Fe saturated H_2SO_4 solutions once a week for a period of 28 days. One sample from each H_2SO_4 concentration was analyzed for total Fe content using ICP/AES. A second sample was analyzed for ferrous ion content using a Hach[®] DR/2000 direct reading spectrophotometer. Specifically, each solution was reacted with

1,10-phenanthroline and sodium bicarbonate in a Hach[®] AccuVac Ampul. After a three-minute reaction period, the solution was placed in the spectrophotometer and analyzed for ferrous ion content using 510 nm light. Because this method requires ferrous iron concentrations to be between 0.02 and 3 mg/L and pH values to be between 3 and 9, each solution was diluted by a factor of 1000 to 50,000 with distilled water. It was determined that once diluted, the experimental limits of this method were not violated. To investigate the kinetics of Fe^{2+} auto-oxidation, compressed air was bubbled through only the 20 and 70 wt % H_2SO_4 samples. Ferrous ion content was determined each week for a period of 28 days using the method outlined above.

2.2. Freezing Experiments

[14] To probe the influence of metal ions on the sulfuric acid freezing temperature, ~10 mL of 20–70 wt % H_2SO_4 was mixed with a small amount of solid $FeSO_4$, $MgSO_4$, or meteoritic components present as sulfate salts. The amount of metal sulfate added to the H_2SO_4 corresponded to the least amount of metal soluble determined by the low-temperature solubility experiments. This precluded solid precipitation during the experiment. The sample was contained in a plastic tube and was sealed with a screw cap. The screw cap had a thermistor mounted in it so that when the cap was screwed tight, the thermistor was submerged in the sample. The thermistor head was covered with plastic insulation and the headspace of the tube was capped with nitrogen to minimize any heterogeneous nucleation that the thermistor or tube might facilitate.

[15] Two types of freezing experiments were performed. In the first, the plastic tubes were submerged in a liquid methanol bath that was cooled from 273 to 183 K at a rate of ~0.5 K/min. Freezing was indicated by a rise in temperature, which was caused by the heat of fusion and was sensed by the submerged thermistors. Because the

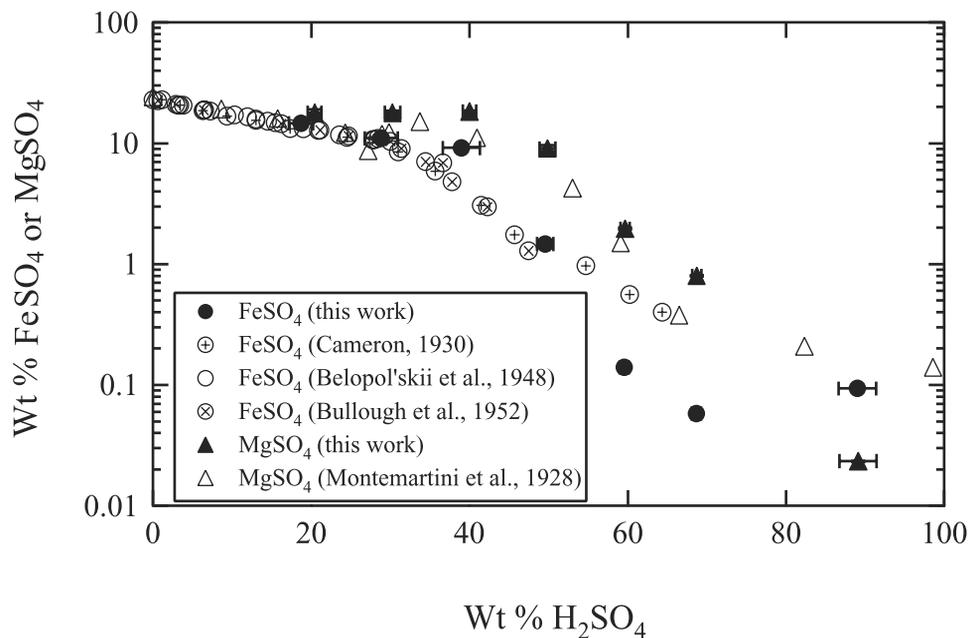


Figure 2. FeSO_4 and MgSO_4 solubility as a function of wt % H_2SO_4 at 22.9°C (solid symbols) compared to previous studies at 25°C for FeSO_4 and 12.6°C for MgSO_4 (open symbols). Conversion is as follows: wt % H_2SO_4 is $m_{\text{H}_2\text{SO}_4}/(m_{\text{H}_2\text{SO}_4} + m_{\text{H}_2\text{O}})$ and wt % FeSO_4 is $m_{\text{FeSO}_4}/(m_{\text{FeSO}_4} + m_{\text{H}_2\text{SO}_4} + m_{\text{H}_2\text{O}})$. At “18.7 wt % H_2SO_4 ” and “14.6 wt % FeSO_4 ” actual solution composition by mass (in g) is then {17.2, 18.7, and 81.3} for { FeSO_4 , H_2SO_4 , and H_2O }.

thermistors were not accurate at low temperatures, a thermometer submerged in the methanol bath (calibrated to ± 0.2 K) was used to determine the actual temperature of the samples at the time of freezing. For samples with the same wt % H_2SO_4 and metal content, three to six freezing experiments were performed.

[16] In the second type of freezing experiment, the samples were cooled from 273 K down to 227 K at a rate of ~ 0.5 K/min. Once the sample temperature reached 227 K, the temperature was held constant for 30 min. After this time period, the temperature was reduced by ~ 4 K and held for another 30 min. This stepwise decrease of the sample temperature by 4 K every 30 min was performed until all of the samples froze or the temperature reached 190 K.

3. Results and Discussion

3.1. Solubility Experiments

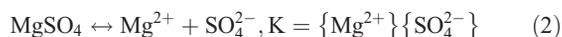
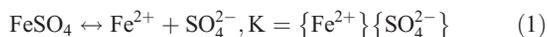
[17] Fe^{2+} and Mg^{2+} solubility measurements were carried out in 20–90 wt % H_2SO_4 at $22.9 \pm 1.0^\circ\text{C}$. From the mass of soluble metal, we calculated the mass of soluble metal sulfate by assuming a 2+ oxidation state for each metal and adding the corresponding mass of sulfate. These results are summarized in Figure 2 along with previous results for these systems at near room temperature [Belopol'skii et al., 1948; Bullough et al., 1952; Cameron, 1930; Montemartini and Losana, 1929]. The room temperature results show FeSO_4 solubility of greater than 14 wt % in 18.7 wt % H_2SO_4 (e.g., 17.2 g FeSO_4 , 81.3 g H_2O , and 18.7 g H_2SO_4). However, as the H_2SO_4 concentration increases, we find that the amount of soluble FeSO_4 decreases to a value of less than 0.10 wt %. Solubility of FeSO_4 in 20–50 wt % H_2SO_4 is in good agreement with the previous solubility

studies while solubility in more concentrated H_2SO_4 differ slightly. Cameron [1930] found that $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (present as deep green monoclinic crystals) is the stable solid phase in contact with solutions of up to 45.6 wt % H_2SO_4 at room temperature. At H_2SO_4 concentrations greater than 45.6 wt % H_2SO_4 , the stable solid phase in contact with the solution is $\text{FeSO}_4 \cdot \text{H}_2\text{O}$, which is present as a white, crystalline fine powder. We are in qualitative agreement with this study: we observed a change in color from green to white of any solids in H_2SO_4 solutions of 50 wt % and above. While the phases are known at room temperature [Cameron, 1930], the phase diagram has not been determined at low temperature where the region of stability may shift.

[18] MgSO_4 shows the same solubility trends as FeSO_4 , though more soluble than FeSO_4 , over the acid concentrations studied. MgSO_4 solubility is slightly higher in our measurements than in the previous solubility studies, but our measurements were obtained at 22.9°C , whereas the literature values were determined at $\sim 12.6^\circ\text{C}$. Because the solubility of MgSO_4 in H_2SO_4 is higher at warmer temperatures, our solubility values at 22.9°C are in good agreement with the literature values at 12.6°C . As with the FeSO_4 solubility study, MgSO_4 solubility differs slightly from the literature values at the highest H_2SO_4 concentration. Montemartini and Losana [1929] report several stable solid phases of MgSO_4 in contact with the solutions depending on acid content. Below 28 wt % H_2SO_4 , the predominant stable solid phases are $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. Between 28 and 60 wt % H_2SO_4 , the predominant solid phases are $\text{MgSO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 3\text{H}_2\text{SO}_4$. Above 60 wt % H_2SO_4 , the predominant solid phase is $\text{MgSO}_4 \cdot 3\text{H}_2\text{SO}_4$. Because all of these phases appear as white solids, it could not be determined if we were in

agreement with the previous study. Again the phases have only been studied at room temperature.

[19] The temperature dependence of the Fe^{2+} and Mg^{2+} solubilities in H_2SO_4 was also examined. General equilibrium reactions for the metal sulfates in solution are formally written in equations (1) and (2) [Krauskopf and Bird, 1995]:



where K is the solubility equilibrium constant and $\{M^{Z+}\}$ is the chemical activity of species M^{Z+} . The thermodynamic formulation of the temperature dependence of mineral solubility is given by equation (3) [Krauskopf and Bird, 1995].

$$\log K_T = - [(\Delta H^\circ/2.303R)(1/T)] + [-\log K_{T_{\text{ref}}} + (\Delta H^\circ/2.303R)(1/T_{\text{ref}})] \quad (3)$$

where ΔH° is the enthalpy change under standard state conditions, R is the universal gas law constant, and $K_{T_{\text{ref}}}$ is a known solubility equilibrium constant at some T_{ref} (usually 25°C). Equation (3) assumes that the standard enthalpy change is invariant with temperature and that the difference between standard entropy change at the reference temperature and the standard entropy change at the temperature of interest can be neglected.

[20] Total metal solubility in concentrated H_2SO_4 is complicated by the presence of aqueous HSO_4^- , SO_4^{2-} , and aqueous metal complexes in solution. At equilibrium the solubility and speciation equations must all be simultaneously satisfied. A complete description of temperature dependence of solubility must quantify the temperature dependence of all equilibrium constants, including not only the solubility product but also the speciation constants. The constants are also strictly for ion activities, rather than concentrations, and the activity coefficients and their temperature dependencies are unknown in the concentrated acids we are studying. In short, a complete detailed analysis requires more information than available. An alternative in these cases is the use of a conditional equilibrium constant, $K^{\text{cond } MZ^+}$ [Stumm and Morgan, 1996], which we calculate using equation (4):

$$K^{\text{cond } MZ^+} = [M^{Z+}]_T [\text{SO}_4^{2-}]_T \quad (4)$$

where $[M^{Z+}]_T$ denotes the molarity of metal in solution and $[\text{SO}_4^{2-}]_T$ denotes the molarity of sulfate in solution due to mineral dissolution. The conditional equilibrium constant holds only for a specific and defined range of chemical and physical conditions, which are limited to a single sulfuric acid composition in the current study.

[21] As an empirical approximation, we write an analogue to equation (3):

$$\log K^{\text{cond } MZ^+} = -a(1/T) + b \quad (5)$$

with the thermodynamic values replaced as empirical fitting parameters "a" and "b." This empirical equation satisfactorily fits all of the collected data. Further, we use it in section 3.2 to extrapolate the amount of soluble metal to

temperatures representative of the atmosphere. Because our solubility data are extrapolated to at most 30 K colder than our experimental temperatures, we feel that the equation (5) will give a reasonable approximation of metal solubility at actual atmospheric temperatures.

[22] The temperature dependence of Fe solubility in sulfuric acid is shown in Figure 3. Figure 3a shows the Fe^{2+} conditional equilibrium constant as a function of inverse temperature in 20–50 wt % H_2SO_4 , and Figure 3b shows data for 60–70 wt % H_2SO_4 . A straight line fit can be placed through the 20–40 wt % Fe solubility points; however, at lower temperatures the 50 wt % points deviate slightly from a straight line. For H_2SO_4 concentrations between 60 and 70 wt %, as temperature decreases the mole fraction of soluble Fe remains the same within error for both concentrations of acid. A completely different behavior of metal solubility in high acid concentrations is not surprising because as the concentration of H_2SO_4 increases, the amount of water in solution decreases. Thus the solution ceases to behave like an aqueous H_2SO_4 solution with an abundance of free water participating in the equilibrium. Also note that $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ becomes the stable solid at room temperature at the highest H_2SO_4 concentrations and that this may be the cause of the different behavior. Table 1 shows the calculated constants based on straight line fits to equation (5) when FeSO_4 is dissolved in 20–70 wt % H_2SO_4 .

[23] The temperature dependence of the Mg solubility in H_2SO_4 is shown in Figure 4. Figure 4a shows the data for 20–50 wt % H_2SO_4 and Figure 4b shows data for 60–70 wt % H_2SO_4 . As was the case for Fe, the Mg solubility decreases as temperature decreases for 20–50 wt % H_2SO_4 . For the Mg data, a straight line fit can be placed through the entire 20–50 wt % data set, and only at the lowest temperatures do the points deviate slightly from a straight line. For H_2SO_4 concentrations between 60 and 70 wt % the solubility was temperature independent. Again, this may be due to a limited amount of water and a change in the stable solid. Table 1 shows the calculated constants based on straight line fits to equation (5) when MgSO_4 is dissolved in 20–70 wt % H_2SO_4 .

[24] In addition to the solubility studies of FeSO_4 and MgSO_4 separately in H_2SO_4 , we also probed the solubilities of combinations of these and other metals, as occurs for meteoritic material. To test how the presence of the other meteoritic metals influences Fe and Mg solubility, mixtures of various metal sulfates in various concentrations of H_2SO_4 with mass loadings representative of actual meteoritic material were made [Cziczo *et al.*, 2001]. Some of the metals dissolved substantially while others slightly dissolved. The solubility results for these "artificial" meteoritic mixtures and extrapolated Fe and Mg solubility values from the binary metal sulfate/ H_2SO_4 study (at the meteoritic experimental conditions) are shown in Table 2. While the results show quite complex behavior, the overall solubility of Fe and Mg is roughly comparable (within a factor of 2) to the solubility when the metals were added separately.

3.2. Ionic State and Phase of Fe and Mg in Atmospheric Particles Based on Solubility Study

[25] It could be possible that $\text{Fe}^{2+}_{(\text{aq})}$ (ferrous iron) in the presence of atmospheric O_2 oxidizes to $\text{Fe}^{3+}_{(\text{aq})}$ during the

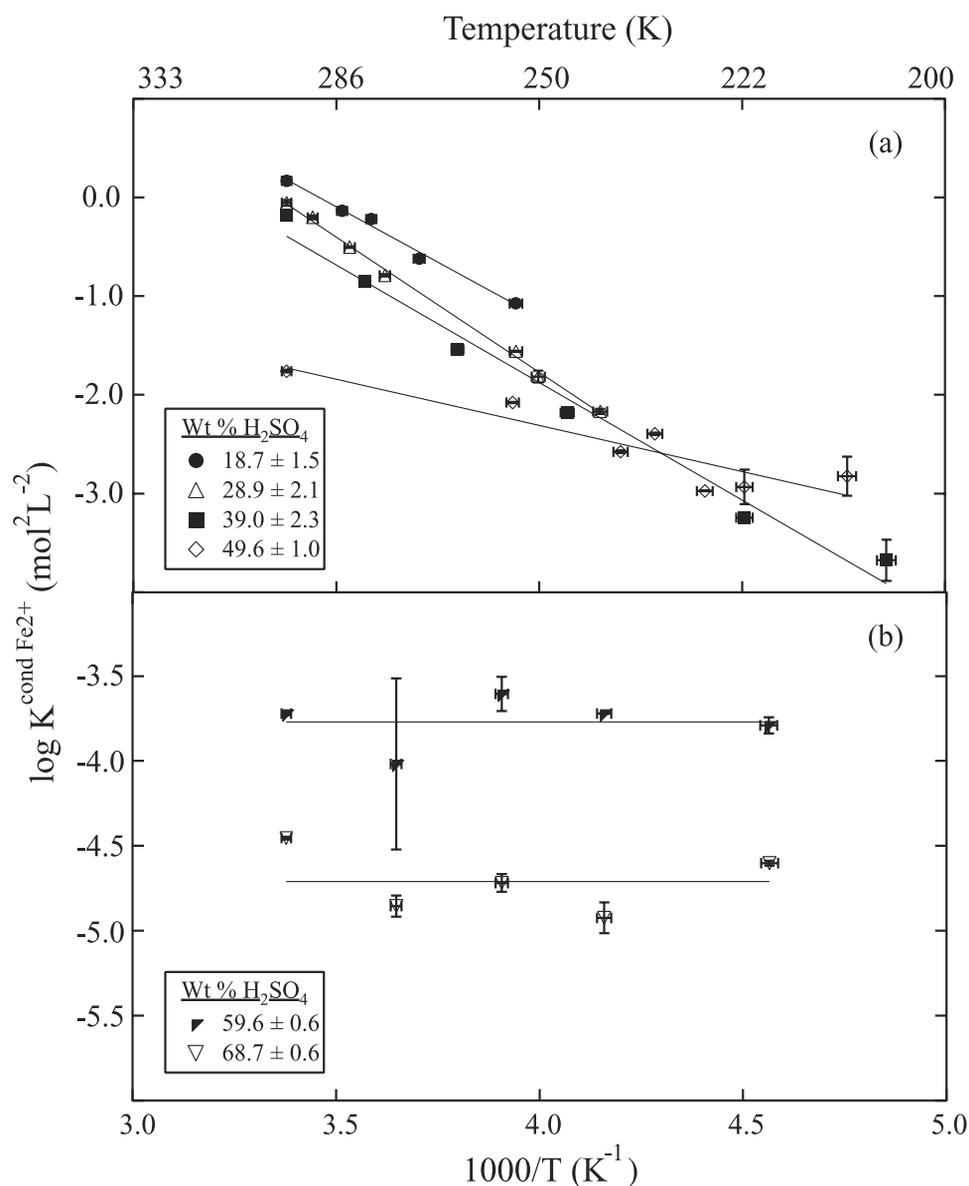


Figure 3. Fe²⁺ conditional equilibrium constant as a function of inverse temperature in (a) 20–50 wt % H₂SO₄ and (b) 60–70 wt % H₂SO₄. Each symbol represents a different wt % H₂SO₄ studied, and the lines represent a linear fit through each data set.

residence time of atmospheric aerosol. In our experiments, there is insufficient O₂ in the sealed tubes to significantly perturb the Fe²⁺: Fe³⁺ ratio. To test this we measured the ferrous and total Fe content in each of our 20–70 wt % H₂SO₄ solutions (contained in sealed tubes) each week for a period of 28 days. We found that over this time period the amount of ferrous iron in all solutions was the same (within error) as the total iron content. To overcome this experimental limitation, which would not be encountered by atmospheric particles (i.e., open systems), we bubbled air through one 20 wt % and one 70 wt % H₂SO₄ solution at room temperature and sampled them once a week for a period of 28 days. In the 20 wt % H₂SO₄ solution, the ferrous iron content was reduced to ~70% [Fe]_T over the duration of the experiment. We verified that the majority of the iron remained in the ferrous form, at least for <70 wt %. In the 70 wt % H₂SO₄ solution, it cannot be exactly

determined to what extent the iron remained in the ferrous form because, in some cases, the amount of ferrous iron in solution determined by the Hach[®] method slightly exceeded that of total iron determined by ICP/AES.

Table 1. Calculated Constants Based on Straight Line Fits to Equation (5)^a

wt % H ₂ SO ₄ ^b	a (Fe)	b (Fe)	a (Mg)	b (Mg)
~20	2.24	7.75	2.79	10.11
~30	2.74	9.21	2.79	10.11
~40	2.38	7.65	2.79	10.11
~50	0.94	1.42	2.79	10.11
~60	0	-3.77	0	-1.55
~70	0	-4.71	0	-1.89

^aLog K^{cond}_{MZ⁺} = -a(1/T) + b.

^bActual percentages are 18.7, 28.9, 39.0, 49.6, 59.6, and 68.7 for Fe and 20.4, 30.3, 40.0, 49.9, 59.6, and 68.7 for Mg.

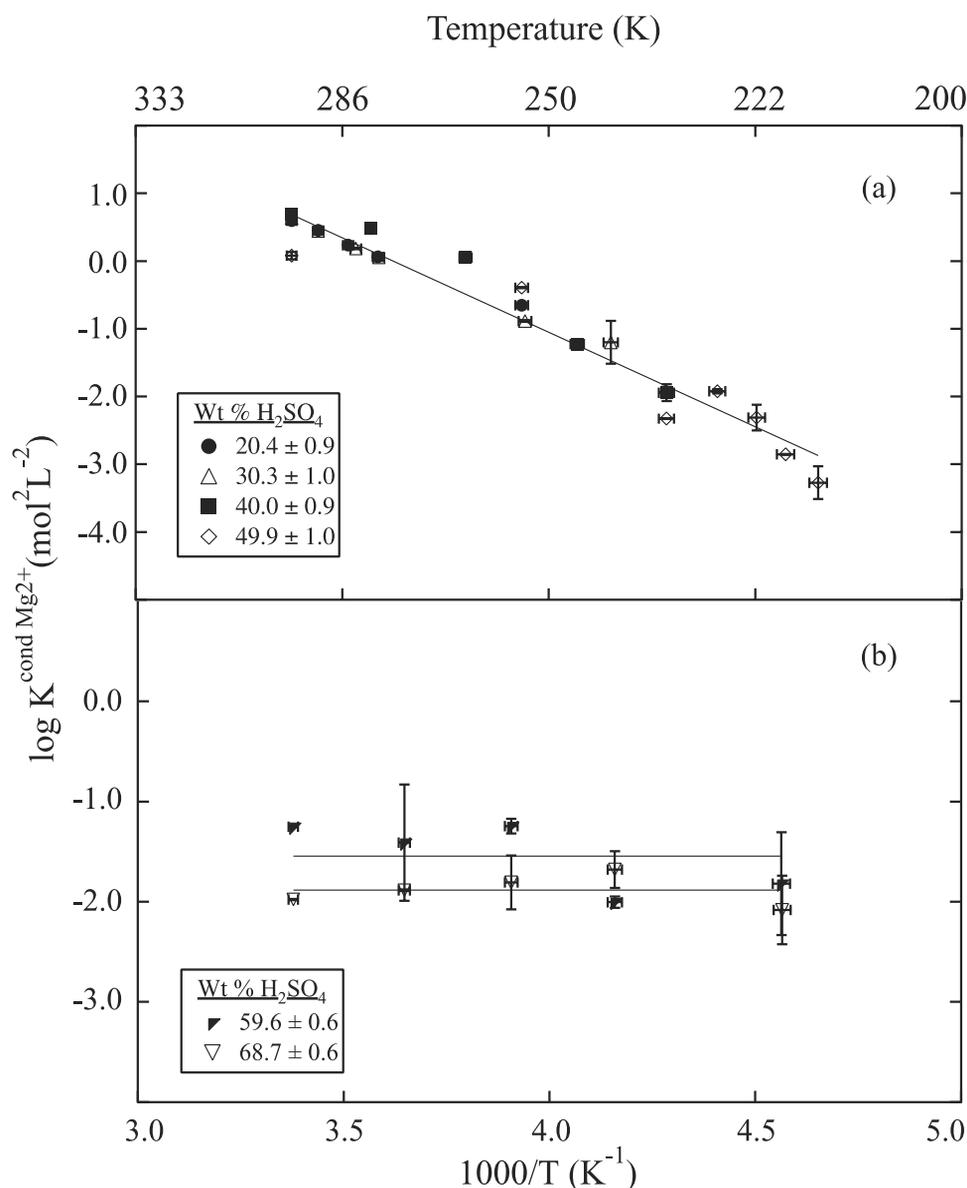


Figure 4. Mg²⁺ conditional equilibrium constant as a function of inverse temperature in (a) 20–50 wt % H₂SO₄ and (b) 60–70 wt % H₂SO₄. Each symbol represents a different wt % H₂SO₄ studied, and the lines represent a linear fit through each data set.

Because there is so little iron in the 70 wt % solutions, small experimental errors most likely account for this discrepancy. Assuming a typical stratospheric climatology of 210–225 K and 40–70 wt % H₂SO₄, we infer that most of the iron initially present as ferrous ion inside atmospheric H₂SO₄ droplets will remain in the ferrous form, rather than oxidize, in the presence of oxygen. Other

atmospheric oxidants such as O₃ were not included in these studies.

[26] Extrapolations of the linear fits in Figures 3a and 3b and 4a and 4b can be made to estimate the amount of soluble Fe and Mg in solution for H₂SO₄ particles under upper tropospheric and lower stratospheric conditions. The estimation of Fe and Mg solubility under these conditions is

Table 2. Solubility of Artificial Meteorite Metal in Sulfuric Acid Solutions

H ₂ SO ₄ , wt %	T (K)	Component Soluble, wt %						
		Ca	K	Mn	Na	Ni	Fe ^a	Mg ^a
40.5	215.4	0.0030	0.0027	0.0017	0.0284	0.0169	0.0517 (0.0853)	0.0470 (0.0709)
49.0	223.8	0.0005	0.0017	0.0011	0.0194	0.0081	0.1289 (0.1700)	0.0684 (0.1161)
60.0	219.1	0.0006	0.0045	0.0001	0.0425	0.0253	0.0643 (0.0488)	0.1227 (0.2752)
69.1	219.1	0.0004	0.0016	0.0001	0.0046	0.0410	0.0193 (0.0155)	0.0923 (0.1744)

^aParentheses indicate metal solubility extrapolated from binary solubility experiments.

Table 3. Estimated Amount of Soluble Fe^{2+} and Mg^{2+} in Atmospheric Sulfuric Acid Particles

Atmospheric Region	H_2SO_4 , ^a wt %	Fe^{2+}			Mg^{2+}	
		T , ^b K	$K^{\text{cond}} \text{Fe}^{2+}$, $\text{mol}^2 \text{L}^{-2}$	Soluble, ^c wt %	$K^{\text{cond}} \text{Mg}^{2+}$, $\text{mol}^2 \text{L}^{-2}$	Soluble, ^d wt %
UT	~20	219	3.16×10^{-3}	0.278	2.38×10^{-3}	0.104
UT	~30	222	6.88×10^{-4}	0.121	3.72×10^{-3}	0.122
LS	~40	193	2.00×10^{-5}	0.019	4.37×10^{-5}	0.012
LS	~50	197	4.84×10^{-4}	0.088	8.88×10^{-5}	0.017
LS	~60	204	1.70×10^{-4}	0.049	2.84×10^{-2}	0.275
LS	~70	214	1.95×10^{-5}	0.015	1.30×10^{-2}	0.174

^aActual percentages are 18.7, 28.9, 39.0, 49.6, 59.6, and 68.7 for Fe and 20.4, 30.3, 40.0, 49.9, 59.6, and 68.7 for Mg.

^bCalculated assuming UT water of 3×10^{-2} mbar and LS water of 4×10^{-4} mbar.

^cCalculation: wt % soluble $\text{Fe}^{2+} = [(K^{\text{cond}} \text{Fe}^{2+})^{1/2}(55.85)]/[(10)(\rho\text{H}_2\text{SO}_4)]$.

^dCalculation: wt % soluble $\text{Mg}^{2+} = [(K^{\text{cond}} \text{Mg}^{2+})^{1/2}(24.31)]/[(10)(\rho\text{H}_2\text{SO}_4)]$.

shown in Table 3. To determine extrapolated temperatures, it was assumed that the 20–30 wt % H_2SO_4 solutions were in equilibrium with a relevant upper tropospheric water partial pressure of 3.0×10^{-2} mbar. Likewise, it was assumed that the 40–70 wt % H_2SO_4 solutions were in equilibrium with a relevant lower stratospheric water partial pressure of 4×10^{-4} mbar. As seen in Table 3, we estimate that Fe and Mg have solubilities of ~0.01–0.28 wt % of the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions at temperatures and acid compositions representative of the atmosphere. Compared to composition measurements done by mass spectrometry of atmospheric particles showing ~0.75 wt % Fe and 0.20 wt % Mg, we conclude it is plausible that solid Fe^{2+} and Mg^{2+} minerals often occur inside atmospheric sulfuric acid particles.

3.3. Freezing Experiments

[27] Bulk freezing experiments were performed to determine if the dissolved metal ions could impact the freezing of sulfuric acid solutions. Each solution contained Fe^{2+} ,

Mg^{2+} , or a mixture of meteoritic metals in concentrations below those determined from the low-temperature solubility experiments. With this approach, solid inclusions, which could lead to heterogeneous nucleation, are absent. An example of the temperature change produced in a 60 wt % “fast freezing” experiment is shown in Figure 5. Temperature is plotted as a function of time with the bath temperature shown as a thick solid line and sample temperatures (measured using thermistors mounted in the samples) as thin solid lines. Each experiment was performed multiple times on an identical sample and is labeled according to metal content and sample number in Figure 5 (i.e., Fe 2 is sample number 2 containing iron). In 60 wt % H_2SO_4 , a solid nucleated from one of the samples containing iron at ~217.9 K causing a steep rise in temperature due to the release of the latent heat of fusion. Each of the other samples containing iron subsequently froze, until the last sample froze at ~211.1 K. In contrast, no nucleation occurred for samples containing magnesium until ~196.6 K where one sample froze, while the remaining samples froze by 193.4 K.

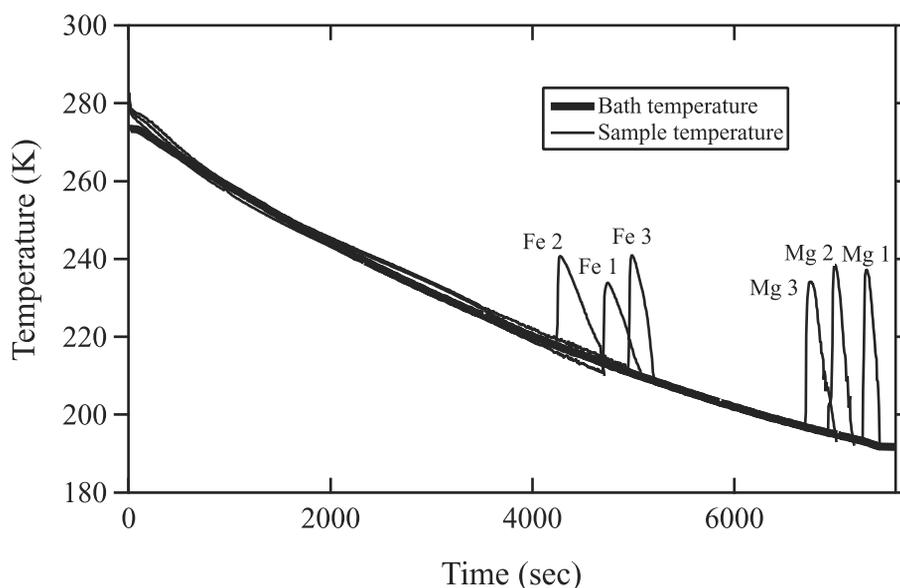


Figure 5. Temperature as a function of time in a 60 wt % H_2SO_4 “fast freezing” experiment with the cooling bath temperature designated as a thick line and solution temperatures designated as a thin lines. The temperature spikes denoted as “Fe” were the point at which the bulk solutions containing soluble Fe froze, and the temperature spikes denoted as “Mg” were the points at which the solutions containing soluble Mg froze.

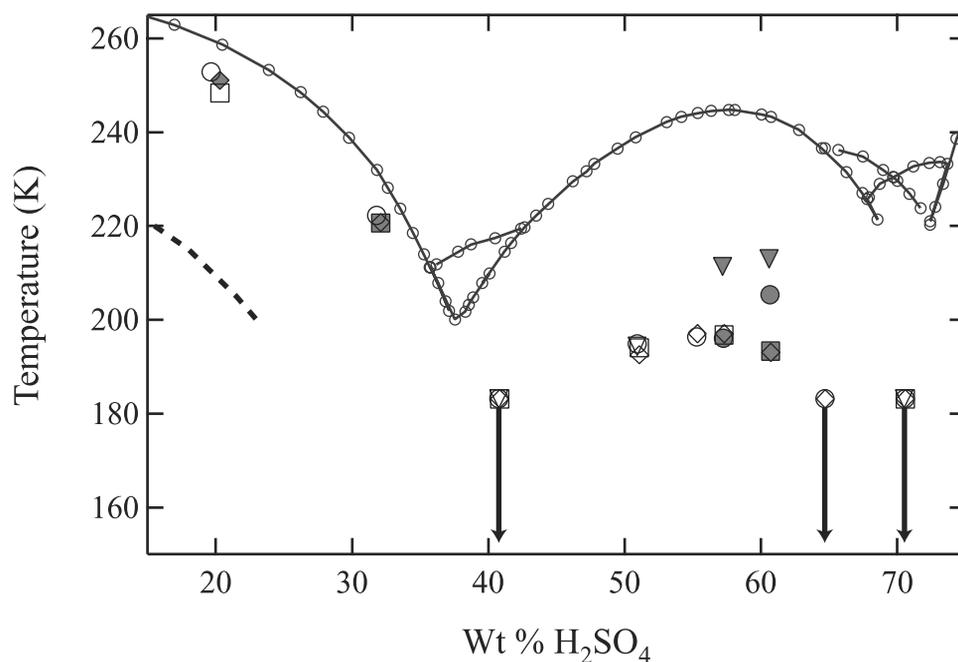


Figure 6. Lowest freezing temperatures of various solutions as a function of wt % H_2SO_4 . The line with circles designates the equilibrium $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ phase diagram from *Gable et al.* [1950]; the dashed line designates temperatures of ice nucleation from sulfuric acid/water aerosols from *Prenni et al.* [2001]; the triangles, circles, and squares represent the lowest temperature at which a 10 mL H_2SO_4 solution containing “artificial meteorite”, Fe^{2+} , and Mg^{2+} , respectively, froze. The diamonds represent the lowest temperature at which “blank” 10 mL H_2SO_4 solutions froze. Each freezing experiment was performed at least 3 times on the same solution. Some freezing experiments were performed 6 times and are noted by shaded symbols in Figure 6. All of the samples froze by the indicated temperatures, or none of the samples froze (as indicated by a downward arrow).

The spread of freezing points in solutions containing the same amount of mineral appears somewhat scattered. This is not surprising because of the stochastic nature of freezing; however, it appears that the presence of iron in 60 wt % H_2SO_4 increases the freezing point of the solution substantially.

[28] The lowest observed freezing temperatures for 10 mL samples of binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions and for $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions containing metals is plotted as function of wt % H_2SO_4 in Figure 6. Also shown in Figure 6 is the equilibrium binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ phase diagram [*Gable et al.*, 1950] and parameterized ice nucleation data [*Prenni et al.*, 2001]. Each solution containing different metal sulfates are plotted as a different symbol on the graph along with “blank” H_2SO_4 solutions that contain no metal sulfates. Each freezing experiment was performed at least 3 times on the same solution and in every case, all of the samples froze by the noted temperatures or none of the samples froze (as indicated by a downward arrow). If there was a solution that was of particular interest to us, we performed three additional freezing experiments on a separate solution that contained approximately the same amount of metal. The solutions on which we performed additional freezing experiments are indicated by shaded symbols in Figure 6. In every case, these solutions froze at approximately the same temperature as the first solution we tested. We also performed “slow freezing” experiments with certain solutions to determine if the speed at which we lowered the

solution temperature affected the freezing point. In every case, the “slow freezing” experiments yielded approximately the same freezing temperature as the “fast freezing” experiments.

[29] The only solutions that exhibit an increase in freezing temperature over the “blank” solutions are the 57.6 wt % (SAT composition) solution containing meteoritic metal and the 60 wt % solutions containing meteoritic metal and Fe separately. These solutions froze $\sim 12\text{--}20$ K higher than solutions containing no soluble metal. The remaining solutions containing metal sulfates froze at the same temperature as the “blank” solution.

[30] Bulk freezing experiments have several limitations that are not present in aerosol freezing experiments. For example, particles present in the sample or imperfections in the tube walls can trigger the heterogeneous nucleation of SAT, which may explain the deviation in our ice freezing points from *Prenni et al.* [2001]. Quantitative results may not be attainable in these bulk experiments but the qualitative results are intriguing. *Luo et al.* [1994] used theoretical calculations to report a maximum SAT homogeneous nucleation rate of $\sim 5 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1}$ between 50 and 60 wt % H_2SO_4 at about 205 K. *Koop et al.* [1997] refined these calculations by introducing updated values of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ parameters such as diffusion activation energies and solid/liquid interface energy. They calculated a maximum SAT homogeneous nucleation rate of $\sim 1 \times 10^{-3} \text{ cm}^{-3} \text{ s}^{-1}$ at about 52 wt % H_2SO_4 and 187 K. It is consistent with

these theoretical studies that our bulk solutions exhibited an increase in freezing temperature in the same H₂SO₄ concentration range. Therefore it is not surprising that solutions in the SAT equilibrium regime did not freeze unless the H₂SO₄ concentration was between 50–60 wt %.

[31] The most interesting results are the solutions that exhibited an increase in freezing temperatures in the presence of dissolved metal ions. Even if heterogeneous effects, such as adsorption of metals on inner walls and alterations of heterogeneous nucleation efficiency, play a role in the freezing of these solutions, they still freeze ~12–20 K higher than solutions containing no metals or solutions containing solely Mg. We hypothesize that soluble Fe played a role in the increased freezing temperature for these solutions. However, the 57.6 wt % solution showed an increase in freezing temperature with the meteoritic metal solution and not with the solution containing only Fe. This result was surprising because both solutions contained approximately the same amount of Fe. We then performed freezing experiments on 57.6 wt % solutions containing each meteoritic metal separately and all of them froze at the same temperature as the “blank” solution within error. Therefore a combination of soluble metals increases the freezing temperature of the 57.6 wt % solution.

[32] Using the formalism of *Koop et al.* [1995], the upper bound of the freezing rate ω (s⁻¹) can be calculated from a single freezing experiment with $\omega = \tau^{-1} \ln [1/(1 - x)]$, where τ is the freezing time period and x is the confidence level. Using a typical freezing period of 100 s and a confidence level of 99 %, we can calculate the upper bound of the freezing rate to be $\omega \approx 0.046$ s⁻¹. Using this freezing rate we can also calculate an upper bound for the homogeneous nucleation rate coefficient, J_{hom} , using the relation $J_{\text{hom}} = \omega/V$, where V is the volume of the solution (10 mL). For our bulk freezing experiments, $J_{\text{hom}} \leq 0.0046$ cm⁻³ s⁻¹ and 220 K. Obviously, a stratospheric aerosol droplet with a very small volume would not freeze homogeneously under these circumstances. However, the homogeneous nucleation rate varies dramatically with temperature and supersaturations. Therefore small aerosol droplets might still freeze at temperatures less than 220 K but greater than 195 K, thus providing a mechanism for PSC formation in the stratosphere.

4. Conclusions and Atmospheric Implications

[33] The solubility of sulfates of Fe²⁺, Mg²⁺, and meteoritic metals has been determined in 20–70 wt % H₂SO₄/H₂O solutions at low temperatures and in 20–90 wt % H₂SO₄/H₂O solutions at room temperature. The solubilities of FeSO₄ and MgSO₄ in various H₂SO₄ solutions at room temperature agree well with previous solubility measurements. On the basis of the solubilities measured, soluble Fe and Mg could comprise ~0.01–0.28 wt % of atmospheric H₂SO₄ particles at temperatures and acid compositions representative of the atmosphere. It was also determined that the majority of Fe dissolved in H₂SO₄ remained in the ferrous form even when we intentionally tried to oxidize it with air for a period of a month. The amount of Fe²⁺ and Mg²⁺ soluble in meteoritic mixtures at low temperatures are roughly comparable to the amount separately soluble.

[34] *Cziczo et al.* [2001] determined that stratospheric sulfate particles contain ~0.75 wt % Fe and 0.20 wt % Mg by mass, respectively. Because the analytical technique employed by *Cziczo et al.* [2001] destroys the aerosol sampled, it is not directly known whether the aerosol contains any solid metal. Our solubility data suggest that the majority of solid, if introduced as the sulfate salt, will remain in the solid form in the atmosphere. However, a small percentage of the solid would dissolve in solution. Therefore heterogeneous nucleation of a solid (e.g., SAT) inside a particle containing metal sulfates is possible. Mineral inclusions have previously been shown to increase the ease of the crystallization of ammonium sulfate and nitrate from solutions at room temperature [*Han and Martin*, 1999; *Han et al.*, 2002; *Martin et al.*, 2001].

[35] To determine if soluble metal in solution had an effect on solid formation from H₂SO₄ solutions, we performed bulk freezing experiments on solutions that contained soluble metals. For the majority of acid concentrations and metal sulfates studied, there was no effect on the freezing temperatures of the solutions. However, for 57.6 wt % H₂SO₄ containing dissolved “artificial” meteorites and 60 wt % H₂SO₄ containing dissolved Fe or dissolved “artificial” meteorites, there was an increase in freezing temperature of ~12–20 K. From the bulk experiments we estimate an upper limit to homogeneous nucleation of $J_{\text{hom}} < 0.0046$ cm⁻³ s⁻¹ at 220 K. While this nucleation rate is too slow to suggest minerals cause SAT formation at 220 K, they may induce SAT formation at lower atmospheric temperatures.

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References

- Belopol'skii, A. P., V. N. Kolycheva, and S. Y. Shpunt, System ferrous sulfate-sulfuric acid-water. III. The solubility of ferrous sulfate heptahydrate in aqueous solutions of sulfuric acid at temperatures from 10° to 50°, *Zh. Prikl. Khim.*, 21, 794–801, 1948.
- Bullough, W., T. A. Canning, and M. Strawbridge, The solubility of ferrous sulfate in aqueous solutions of sulfuric acid, *J. Appl. Chem.*, 2, 703–707, 1952.
- Cameron, F. K., The solubility of ferrous sulphate, *J. Phys. Chem.*, 34, 692–710, 1930.
- Cotton, F. A., and G. Wilkinson, *Advanced Inorganic Chemistry: A Comprehensive Text*, 1145 pp., John Wiley, Hoboken, N. J., 1972.
- Cziczo, D. J., D. S. Thomson, and D. M. Murphy, Ablation, flux, and atmospheric implications of meteors inferred from stratospheric aerosol, *Science*, 291, 1772–1775, 2001.
- DeMott, P. J., and D. C. Rogers, Freezing nucleation rates of dilute solution droplets measured between –30°C and –40°C in laboratory simulations of natural clouds, *J. Atmos. Sci.*, 47, 1056–1064, 1990.
- Gable, C. M., H. F. Betz, and S. H. Maron, Phase equilibria of the system sulfur trioxide-water, *J. Am. Chem. Soc.*, 72, 1445–1448, 1950.
- Han, J., and S. T. Martin, Heterogeneous nucleation and the efflorescence of (NH₄)₂SO₄ particles internally mixed with Al₂O₃, TiO₂, and ZrO₂, *J. Geophys. Res.*, 104(D3), 3543–3553, 1999.
- Han, J. H., H. M. Hung, and S. T. Martin, Size effect of hematite and corundum inclusions on the efflorescence relative humidities of aqueous ammonium nitrate particles, *J. Geophys. Res.*, 107(D10), 4086, doi:10.1029/2001JD001054, 2002.
- Koop, T., U. M. Biermann, W. Raber, B. P. Luo, P. J. Crutzen, and T. Peter, Do stratospheric aerosol droplets freeze above the ice frost point?, *Geophys. Res. Lett.*, 22(8), 917–920, 1995.
- Koop, T., B. Luo, U. M. Biermann, P. J. Crutzen, and T. Peter, Freezing of HNO₃/H₂SO₄/H₂O solutions at stratospheric temperatures: Nuclea-

- tion statistics and experiments, *J. Phys. Chem. A*, 101(6), 1117–1133, 1997.
- Krauskopf, K. B., and D. K. Bird, *Introduction to Geochemistry*, 647 pp., McGraw-Hill, New York, 1995.
- Luo, B., T. Peter, and P. Crutzen, Freezing of stratospheric aerosol droplets, *Geophys. Res. Lett.*, 21(13), 1447–1450, 1994.
- Martin, S. T., J.-H. Han, and H.-M. Hung, The size effect of hematite and corundum inclusions on the efflorescence relative humidities of aqueous ammonium sulfate particles, *Geophys. Res. Lett.*, 28(13), 2601–2604, 2001.
- Montemartini, C., and L. Losana, Equilibrium between double sulfates and aqueous solutions of sulfuric acid at various concentrations. III, *Ind. Chim.*, 4, 199–205, 1929.
- Prenni, A. J., M. E. Wise, S. D. Brooks, and M. A. Tolbert, Ice nucleation in sulfuric acid and ammonium sulfate particles, *J. Geophys. Res.*, 106(D3), 3037–3044, 2001.
- Solomon, S., The mystery of the Antarctic ozone “hole,” *Rev. Geophys.*, 26, 131–148, 1988.
- Solomon, S., S. Borrmann, R. R. Garcia, R. Portmann, L. Thomason, L. R. Poole, D. Winker, and M. P. McCormick, Heterogeneous chlorine chemistry in the tropopause region, *J. Geophys. Res.*, 102(D17), 21,411–21,429, 1997.
- Stumm, W., and J. J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 1022 pp., John Wiley, Hoboken, N. J., 1996.
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