HETEROGENEOUS REACTIONS WITH NaCl IN THE EL CHICHON VOLCANIC AEROSOLS

Diane V. Michelangeli
Space Science Division, NASA Ames Research Center

Mark Allen
Earth and Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology

Yuk. L. Yung
Division of Geological and Planetary Sciences, California Institute of Technology

Previous investigations of the effects of the 1982 eruption of the El Chichon volcano could not explain all the observations of changes in O3, HCl, NO and NO2 simultaneously without proposing unproven chemical reactions. Since reactions between solid NaCl and gaseous CINO3 and N2O5 rapidly produce photochemically active chlorine species and solid NaN O3 in laboratory experiments, we suggest that these reactions could have occurred with the NaCl observed to be present in the El Chichon sulfuric acid aerosols. As a consequence, we predict that HCl should increase substantially, while NO should decrease, in agreement with the measurements after the eruption. Ozone should only be slightly affected by these reactions. Reactions between solid NaCl and the acids H2SO4 and HNO might prove to be important, but we lack sufficient evidence regarding their efficiency and the presence of HNO3 in the aerosols to be more conclusive.

Introduction

The eruption of the El Chichon volcano in Mexico in March–April 1982 [see for example Pollack et al., 1983] provided stratospheric chemists with an excellent opportunity to test their models by trying to simulate the effects of this known perturbation to the atmosphere. SO2 was directly injected into the stratosphere [Krueger, 1983] and rapidly converted to sulfuric acid aerosols [Hoffmann and Rosen, 1984]. The aerosol cloud, located between 16 and 30 km [DeLuisi et al., 1983] was still observable one year after the eruption [Hoffmann and Rosen, 1983; Thomas et al., 1983; Adriani et al., 1983; Spinhirne and King, 1985; Jäger and Carnuth, 1987].

Michelangeli et al. [1989] investigated the chemical changes in the stratosphere during the first three months after the formation of the aerosol cloud. They used a one dimensional radiative transfer multiple scattering code [Michelangeli et al., 1990] to evaluate the changes in the total actinic flux after the eruption. The particles were efficient forward scatterers which lead to a total radiation increase of up to 8% between 3000 and 8000 Å in the aerosol layer (for more details see Michelangeli et al. [1989] and Michelangeli et al. [1990]). Michelangeli et al. [1989] included both this radiation change and 3°C temperature changes (observed by Labitzke et al. [1983] and modelled by Pollack and Ackerman [1983]) in a one dimensional chemical kinetics model of the stratosphere. While they obtained a decrease in ozone which agreed with the observations of Heath and Schlesinger [1984] and Chandra [1987], they could not explain the measured 40% increase in HCl [Mankin and Coffey, 1984; B. W. Gandrud and A. L. Lazrus, private communication, 1983], as well as the large NO and NO2 decreases [McFarland et al., 1986; Roscoe et al., 1986], even after including direct injections of HCl, Cl2 and H2O from the volcano into the stratosphere.

Therefore, Michelangeli et al. [1989] explored the role of heterogeneous reactions on sulfuric acid aerosols in reproducing the available measurements. This was suggested by the importance of reactions between the ice particles of the polar stratospheric clouds and gas phase molecules (N2O5, CINO3, HCl, H2O) for explaining the Antarctic ozone hole [Solomon et al., 1986; McElroy, 1986; Molina et al., 1987; Tolbert et al., 1988]. Using the laboratory results of Rossi et al. [1987], Tolbert et al. [1988] and Worsnop et al. [1988] for the efficiency (or sticking coefficient, γ) of reactions on HSO4/H2O drops, Michelangeli et al. [1989] simulated the effects of various heterogeneous reactions involving ClO and NO species in their model. They concluded that the speculative heterogeneous reaction CINO3 + HCl (with product NO retained in the aerosol) was the most effective process. Other reactions considered led to changes in the opposite sense to what was observed and/or in the correct sense, but too small in magnitude. Unfortunately, there are currently no laboratory results proving the direct heterogeneous conversion of CINO3 to HCl. Hoffmann and Solomon [1989] did a similar study of heterogeneous reactions with a two-dimensional model, but they did not include simultaneously the radiation and temperature changes.

Finlayson-Pitts [1983] and Finlayson-Pitts et al. [1989] presented results that indicated that gaseous (g) NO2, N2O5 and CINO3 react with solid (s) NaCl in the following manner:

\[ 2\text{NO}_2(g) + \text{NaCl}(s) \rightarrow \text{NOCl}(g) + \text{NaN}_2\text{O}_5(s) \] (1)

\[ \text{CINO}_3(g) + \text{NaCl}(s) \rightarrow \text{Cl}_2(g) + \text{NaN}_2\text{O}_3(s) \] (2)

\[ \text{N}_2\text{O}_5(g) + \text{NaCl}(s) \rightarrow \text{CINO}_2(g) + \text{NaN}_2\text{O}_3(s) \] (3)

An early measurement (as quoted in Finlayson-Pitts, 1983) indicated that \( \gamma \approx 10^{-6} - 10^{-7} \) for reaction (1). Re-
cent experiments [F.E. Livingston and B. Finlayson-Pitts, 1991] suggested that $\gamma$ for reaction (1) is smaller ($10^{-6}$) and that $\gamma > 5 \times 10^{-3}$ for reaction (3). No sticking coefficient information is available for reaction (2).

The reactions proceed at 298 K, but no data are available at the colder stratospheric temperatures (~225 K at 28 km, the peak of the aerosol layer). Finlayson-Pitts et al. [1989], on the basis of Molina et al. [1987], suggest that the reactions might be more efficient at low temperatures because of the increased residence time of the species on the particles. The reactions on the surface are ionic in nature and should not have an activation barrier. The lack of quantitative experimental information at low temperatures inhibits detailed numerical simulations of the effects of reactions (1)–(3), but a qualitative assessment of their possible impact is feasible.

Results and Discussion

The first question we need to address is whether or not NaCl is present in volcanic aerosols. The only direct evidence for the presence of halite in the El Chichon aerosol cloud is from the in situ measurements of Woods et al. [1985] using a quartz crystal microbalance cascade impactor on a U–2 aircraft between 18 and 21 km. On May 5th, 1982, they estimated that 7% of the total aerosol mass (or 0.5 $\mu$g m$^{-3}$) was NaCl. No halite was measurable during flights in July, November and December. Woods et al. [1985] claim that the detection of halite and its apparent disappearance by July could explain the large depolarization ratios measured in early May 1982 by Hayashida et al. [1984] and a return to normal values in late May.

Woods et al. [1985] explain the disappearance of NaCl by invoking the reaction $\text{H}_2\text{SO}_4 + 2\text{NaCl (s)} \rightarrow \text{Na}_2\text{SO}_4 (s) + 2\text{HCl}$. To validate their theory they searched for $\text{Na}_2\text{SO}_4 (s)$ in their samples, and only found it present in the May 5th sample when it was reexamined in November. This suggests that the reaction occurred within the sample after it was collected, but does not prove that it was important in the atmosphere. Woods et al. [1985] state that the NaCl started to convert to $\text{Na}_2\text{SO}_4$ only after one month. Pinto et al. [1989] argue that this reaction might be limited by the sedimentation of NaCl within a month, and the lack of sufficient regeneration of $\text{H}_2\text{SO}_4$ from $\text{SO}_2$.

While there is uncertainty regarding the presence of $\text{Na}_2\text{SO}_4 (s)$, as well as the lifetime of NaCl (s), it seems clear that halite was still present at significantly high concentrations one month after the eruption. Since $\text{H}_2\text{SO}_4$ is not thought to react during that time according to Woods et al. [1985], it leaves time for reactions (1)–(3) to occur, and then helps explain the disappearance of halite by July. From the Woods et al. [1985] measurements we deduce that the concentration of [NaCl] = 5.15 x 10$^9$ cm$^{-3}$ near 20 km. To obtain the concentration at 28 km (peak of aerosol cloud) we use the lidar measurements of DeLuisi et al. [1983] for the aerosol scattering: 40% of the aerosols were located at 28 km, while 7% were present at 20 km. A simple scaling leads to an NaCl amount at 28 km of 2.94 x 10$^{10}$ cm$^{-3}$. While this figure is probably a large overestimate, it gives the order of magnitude we are considering. We can then compare this to the standard gas abundances in the non-perturbed photochemical model: $[\text{NO}_2] = 2.6 \times 10^6$ cm$^{-3}$, $[\text{CINO}_2] = 4.4 \times 10^6$ cm$^{-3}$, and $[\text{N}_2\text{O}_5] = 5.7 \times 10^8$ cm$^{-3}$ at 28 km. From these numbers it is clear that the amount of NaCl will not be the limiting factor in the rates of reactions (1)–(3).

Livingston and Finlayson–Pitts (1991), while studying reaction (3) concluded that HNO$_3$ (g) + NaCl (s) → HCl (g) + NaNO$_3$ (s) might also be occurring in their system. However, no quantitative kinetic rates were reported. Conceivably this could also take place in the stratosphere with very high efficiency. While this reaction could be very effective at reducing NO$_x$ and increasing HCl, it requires that HNO$_3$ be in, or in contact with, the aerosols, which are already very acidic, consisting roughly of 75% H$_2$SO$_4$. This might prove to be the main limitation to the efficiency of this reaction. So far there is no evidence suggesting the presence of HNO$_3$ in volcanic aerosols. The reaction would also lead to a significant reduction in HNO$_3$ which was not observed after the eruption [Mankin and Coffey, 1986; Arnold et al., 1990].

All three proposed reactions ((1)–(3)) take newly injected Cl from NaCl and convert it to photolytically unstable chlorine-containing compounds (Cl$_2$, NOCl, CINO$_2$). The Cl produced is active and can possibly lead to an increase in HCl, the most stable chlorine-containing species. Furthermore, reaction (2) has the added advantage of taking Cl from the more inert CINO$_3$ and converting it to reactive Cl$_2$. Therefore, for every NaCl that reacts with CINO$_2$, we produce 2 Cl atoms. This would lead to a very large source of extra chlorine, and therefore could lead to an HCl increase.

As far as increasing HCl is concerned, there are two differences with the cases presented by Michelangeli et al. [1989]. First, reaction (2) differs from the reaction between CINO$_2$ and HCl by not destroying HCl directly, and by introducing an extra Cl source to the stratosphere. Second, in the previous work, the simulations of a direct Cl$_2$ or HCl injection into the stratosphere failed to produce an overall HCl increase after three months, because the chemistry was perturbed in a single pulse, and then left to relax back to the steady state. The large gradient in HCl was quickly smoothed out by diffusion. Pinto et al. [1989] also suggest that HCl should be washed out rapidly. In the case we propose now, the heterogeneous reactions would progress at a slower rate, releasing Cl gradually to the stratosphere. It would then be possible for a new state to be reached after three months. Even though NaCl was injected in a pulse, observations discussed earlier suggest it was present in the aerosol for at least one month. Contrary to this, both of the reactions between NaCl and acid ($\text{H}_2\text{SO}_4$ or HNO$_3$), if they occur, produce HCl directly, and probably very rapidly. This would then result in a situation very similar to that of the direct HCl injection, and therefore would not be effective at increasing HCl three months after the eruption.

Reactions (1)–(3) have the added advantage of having an impact on NO$_x$ chemistry as well. All three reactions convert active NO$_x$ species ($\text{NO}_2$, CINO$_2$, N$_2$O$_5$) to NaNO$_3$(s) in the aerosols which can fall out of the atmosphere. NaNO$_3$ will not return NO$_x$ to the stratosphere, such as would the NOCl(g) and CINO$_2$(g) produced in (1) and (3). Even in these two reactions NaNO$_3$(s) is
produced and, therefore, they might be effective in at least reducing NO\textsubscript{x}. In addition, NO\textsubscript{2} is now directly involved in heterogeneous reactions. In this case, a reaction between NaCl and HNO\textsubscript{3} would be very effective at reducing NO\textsubscript{x}. Unfortunately, this cannot be quantified for lack of data on the reaction.

These results are extremely uncertain owing to the unknown heterogeneous reaction efficiencies at low temperatures. However, we can see whether these processes ((1)–(3)) have the potential of being important. They will be in competition with reactions such as

\[
\begin{align*}
N_2O_3 + h\nu &\rightarrow NO_2 + NO_3 \\
OH + NO_2 + M &\rightarrow HNO_3 + M \\
CINO_3 + h\nu &\rightarrow Cl + NO_3 
\end{align*}
\]  

Some simple calculations show the relative importance of these reactions. First, we assume that when a gas molecule (NO\textsubscript{2}, CINO\textsubscript{3} or N\textsubscript{2}O\textsubscript{3}) sticks to a particle, it is in contact with NaCl and can react. We therefore can calculate the loss frequency due to collisions with NaCl(s) by

\[
\nu_{\text{NaCl}} = \frac{1}{4\gamma v AN_0}
\]

where \(v\) is the mean speed of the impacting molecule, \(v = \sqrt{8kT/\pi m}\), \(A\) is the mean surface area (\(6.4 \times 10^{-8}\) cm\(^2\), assuming that the geometrical and optical cross sections are the same), and \(N_0\) is the number density of the aerosols (\(26\) cm\(^{-3}\) at \(28\) km). Assuming sticking coefficients for NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{3} are \(\gamma = 10^{-8}\) and \(5 \times 10^{-9}\), respectively, we obtain the corresponding loss frequencies for heterogeneous reaction with NaCl, \(J_{\text{NaCl}} = 1.4 \times 10^{-10}\) and \(4.5 \times 10^{-9}\) s\(^{-1}\), respectively. The loss frequency due to CINO\textsubscript{3} is not known, but is probably close to that for N\textsubscript{2}O\textsubscript{3}. We compare these with the loss frequencies for reactions (4)–(6), which are

\[
\begin{align*}
J_4 &= 3.82 \times 10^{-5} \text{ s}^{-1} \\
J_5 &= 1.32 \times 10^{-5} \text{ s}^{-1} \\
J_6 &= 1.08 \times 10^{-4} \text{ s}^{-1}
\end{align*}
\]

The loss frequencies of reactions (4)–(6) are higher than for the reactions between NO\textsubscript{2} and NaCl, but are not so different for N\textsubscript{2}O\textsubscript{3} and possibly CINO\textsubscript{3}. The heterogeneous reactions represent a permanent sink for NO\textsubscript{x} and can produce a Cl increase, followed by an HCl increase.

If we assume that one NO\textsubscript{2}(g) is lost for each NaNO\textsubscript{3}(s) formed, the NO\textsubscript{2} concentration at 28 km will decrease by 50% (\(1.3 \times 10^6\) molecules cm\(^{-3}\); McFarland et al., 1986; Roscoe et al., 1986) after 14 hours by reaction (3). At the same altitude, reaction (2) could lead to a 40% increase in HCl (\(1.72 \times 10^6\) molecules cm\(^{-3}\); B. W. Gandrud and A. L. Lazarus, private communication, 1983) in 3.4 days. If the loss timescale for HCl due to vertical transport is ~1 month, the elevated HCl abundance can be sustained with \(\gamma\) for (2) as small as \(10^{-5}\). Therefore, the proposed heterogeneous chemistry can be relatively inefficient and still reproduce observations. Reaction (1) is, however, too slow to have any impact. Since these reactions occur rapidly, there should be no problem caused by NaCl sedimentation, since we know halite is present for a month.

An important uncertainty is the location of the reaction. Once the surface layer of NaCl has been oxidized to NaNO\textsubscript{3}, it is not clear whether or not the reaction will continue in the interior and release HCl(g). Livingston and Finlayson-Pitts (1991) suggest that reaction (3) occurs on the surface of the halite crystals in their experimental system. Further laboratory investigations are required to understand and quantify this process more precisely. Also, the presence of NaCl in volcanic aerosols has not been extensively reported in the literature, and therefore remains an uncertainty. It is crucial that, in the event of another volcanic eruption more in situ aerosol measurements be taken, and that the abundance of NaCl be definitively established. In addition, it would be important to look for NaNO\textsubscript{3} and Na\textsubscript{2}SO\textsubscript{4} in the aerosols.

Since the ultimate fate of the NaNO\textsubscript{3} is to fall out of the stratosphere, a close examination of the Greenland and Antarctic ice cores would be worthwhile. The acidic layer corresponding to El Chichon has been detected in Greenland ice cores. It would be interesting to look for the presence of NaNO\textsubscript{3} or Na\textsubscript{2}SO\textsubscript{4} after the eruption. Unfortunately, due to the rapid fall times limiting the amount of NaNO\textsubscript{3} (s) and Na\textsubscript{2}SO\textsubscript{4} (s) that can reach the polar regions, and the large tropospheric contribution of Na\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{-}, and SO\textsubscript{4}\textsuperscript{2-}, this will probably be very difficult, if not impossible.

If the impact of reactions (1)–(3) is similar to that of the speculative chemistry proposed in Michelangeli et al. (1989) which reproduces the HCl and NO\textsubscript{x} measurements, an ozone decrease of a few percent can be expected. This is not considered a disagreement with the observations since there is easily a few percent uncertainty in all the assumed parameters for the model calculation. However, because of the complex nature of the various interactions between the NO\textsubscript{x} and CINO\textsubscript{3} species and O\textsubscript{3} in the stratosphere, the ultimate fate of O\textsubscript{3} can only be determined by detailed photochemical modeling.

Heterogeneous reactions with NaCl seem to have the potential of having a major impact on stratospheric chemistry after the eruption of El Chichon. A detailed numerical study awaits further laboratory results. The ultimate question is whether or not this mechanism might have been even more significant during earlier larger volcanic eruptions.

Acknowledgements. We thank M.-T. Leu for valuable discussions and B. Finlayson-Pitts for communication of laboratory results prior to publication. We also are grateful to the anonymous reviewers for pointing out the deficiencies of our initial presentation. This work was supported by NAGW-413 to California Institute of Technology. One of us (DVM) acknowledges support of a NASA NRC Fellowship. Contribution number 4898 from the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

References


DeLuise, J. J., E. G. Dutton, K. L. Coulson, T. E. DeForest, and B. G. Mendonca, On some radiative features of


Hayashida, S., et al., Water Research Institute, Middle Atmospheric Program, note 3, 1984.


Diane V. Michelangeli, Space Science Division, NASA Ames Research Center, Moffett Field, California 94035

Yuk L. Yung, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

Mark Allen, Earth and Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109

(Received: August 24, 1990; revised: November 28, 1990; accepted: February 12, 1991.)