

HETEROGENEOUS REACTIONS WITH NaCl IN THE EL CHICHON VOLCANIC AEROSOLS

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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 ClNO₃ and N₂O₅ rapidly produce photochemically active chlorine species and solid NaNO₃ 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_x 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 HNO₃ 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

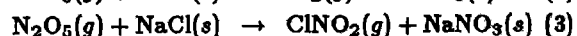
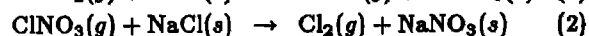
The eruption of the El Chichon volcano in Mexico in March-April 1982 [see for example Pollack *et al.*, 1983] provided stratospheric chemists with an excellent opportunity to test their models by trying to simulate the effects of this known perturbation to the atmosphere. SO₂ was directly injected into 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, ClNO₃, 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 H₂SO₄/H₂O drops, Michelangeli *et al.* [1989] simulated the effects of various heterogeneous reactions involving ClO_x and NO_x species in their model. They concluded that the speculative heterogeneous reaction ClNO₃ → HCl (with product NO_x 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 ClNO₃ 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 ClNO₃ react with solid (s) NaCl in the following manner:



An early measurement (as quoted in Finlayson-Pitts, 1983) indicated that γ ≈ 10⁻⁶-10⁻⁷ for reaction (1). Re-

cent experiments [F.E. Livingston and B. Finlayson-Pitts, 1991] suggested that γ for reaction (1) is smaller (10^{-8}) 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 $0.5 \mu\text{g m}^{-3}$) 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 $\text{H}_2\text{SO}_4 + 2\text{NaCl (s)} \rightarrow \text{Na}_2\text{SO}_4 \text{ (s)} + 2\text{HCl}$. To validate their theory they searched for $\text{Na}_2\text{SO}_4 \text{ (s)}$ 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 Na_2SO_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 H_2SO_4 from SO_2 .

While there is uncertainty regarding the presence of $\text{Na}_2\text{SO}_4 \text{ (s)}$, 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 H_2SO_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 $[\text{NaCl}] = 5.15 \times 10^9 \text{ cm}^{-3}$ near 20 km. To obtain the concentration at 28 km (peak of aerosol cloud) we use the lidar measurements of DeLuizi *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 $2.94 \times 10^{10} \text{ cm}^{-3}$. 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: $[\text{NO}_2] = 2.6 \times 10^9 \text{ cm}^{-3}$, $[\text{ClNO}_3] = 4.4 \times 10^8 \text{ cm}^{-3}$, and $[\text{N}_2\text{O}_5] = 5.7 \times 10^8 \text{ cm}^{-3}$ 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 $\text{HNO}_3 \text{ (g)} + \text{NaCl (s)} \rightarrow \text{HCl (g)} + \text{NaNO}_3 \text{ (s)}$ 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_2SO_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].

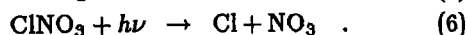
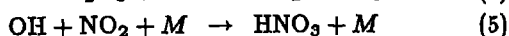
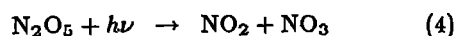
All three proposed reactions ((1)–(3)) take newly injected Cl from NaCl and convert it to photolytically unstable chlorine-containing compounds (Cl_2 , NOCl , ClNO_2). The Cl produced is active and can possibly lead to an increase in HCl, the most stable chlorine-containing species. Furthermore, reaction (2) has the added advantage of taking Cl from the more inert ClNO_3 and converting it to reactive Cl_2 . Therefore, for every NaCl that reacts with ClNO_3 , 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 ClNO_3 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 (H_2SO_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_y species (NO_2 , ClNO_3 , N_2O_5) to $\text{NaNO}_3 \text{ (s)}$ 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 $\text{ClNO}_2 \text{ (g)}$ produced in (1) and (3). Even in these two reactions $\text{NaNO}_3 \text{ (s)}$ is

produced and, therefore, they might be effective in at least reducing NO_x . In addition, NO_2 is now directly involved in heterogeneous reactions. In this case, a reaction between NaCl and HNO_3 would be very effective at reducing NO_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



Some simple calculations show the relative importance of these reactions. First, we assume that when a gas molecule (NO_2 , ClNO_3 or N_2O_5) 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 $J_{\text{NaCl}} = 1/4 \gamma v A N_a$ where v is the mean speed of the impacting molecule $v = \sqrt{8kT/\pi m}$, A is the mean surface area ($6.4 \times 10^{-8} \text{ cm}^2$, assuming that the geometrical and optical cross sections are the same), and N_a is the number density of the aerosols (26 cm^{-3} at 28 km). Assuming sticking coefficients for NO_2 and N_2O_5 are $\gamma = 10^{-8}$ and 5×10^{-3} , respectively, we obtain the corresponding loss frequencies for heterogeneous reaction with NaCl, $J_{\text{NaCl}} = 1.4 \times 10^{-10}$ and $4.5 \times 10^{-5} \text{ s}^{-1}$, respectively. The loss frequency due to ClNO_3 is not known, but is probably close to that for N_2O_5 . We compare these with the loss frequencies for reactions (4)–(6), which are $J_4 = 3.82 \times 10^{-5} \text{ s}^{-1}$, $J_5 = 1.32 \times 10^{-5} \text{ s}^{-1}$, and $J_6 = 1.08 \times 10^{-4} \text{ s}^{-1}$. The loss frequencies of reactions (4)–(6) are higher than for the reactions between NO_2 and NaCl, but are not so different for N_2O_5 and possibly ClNO_3 . The heterogeneous reactions represent a permanent sink for NO_x and can produce a Cl increase, followed by an HCl increase.

If we assume that one $\text{NO}_2(\text{g})$ is lost for each $\text{NaNO}_3(\text{s})$ formed, the NO_2 concentration at 28 km will decrease by 50% ($1.3 \times 10^9 \text{ molecules cm}^{-3}$; 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 ($1.72 \times 10^8 \text{ molecules cm}^{-3}$; B. W. Gandrud and A. L. Lazrus, 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 γ 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_3 , it is not clear whether or not the reaction will continue in the interior and release $\text{HCl}(\text{g})$. 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 pre-

cisely. 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_3 and Na_2SO_4 in the aerosols.

Since the ultimate fate of the NaNO_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_3 or Na_2SO_4 after the eruption. Unfortunately, due to the rapid fall times limiting the amount of $\text{NaNO}_3(\text{s})$ and $\text{Na}_2\text{SO}_4(\text{s})$ that can reach the polar regions, and the large tropospheric contribution of Na^+ , NO_3^- , and SO_4^{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_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_x and ClO_x species and O_3 in the stratosphere, the ultimate fate of O_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.

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