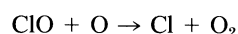
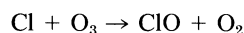


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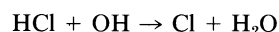
Volcanic Contribution of Chlorine to the Stratosphere: More Significant to Ozone Than Previously Estimated?

Abstract. *Earlier estimates of the chlorine emission from volcanoes, based upon evaluations of the preeruption magmatic chlorine content, are too low for some explosive volcanoes by a factor of 20 to 40 or more. Degassing of ash erupted during 1976 by Augustine Volcano in Alaska released 525×10^6 kilograms of chlorine (± 40 percent), of which 82×10^6 to 175×10^6 kilograms may have been ejected into the stratosphere as hydrogen chloride. This stratospheric contribution is equivalent to 17 to 36 percent of the 1975 world industrial production of chlorine in fluorocarbons.*

Fluorocarbons have been considered a threat to stratospheric ozone because they resist breakdown and rainout in the lower atmosphere and eventually rise into the stratosphere. In the stratosphere, ultraviolet radiation dissociates the common fluorocarbons (CFCl_3 and CF_2Cl_2), producing free chlorine atoms (1) that destroy ozone by the reaction chain (2)



Chlorine can also be released into the atmosphere from the HCl by the reaction (3)



Ordinarily, HCl does not pose a threat to stratospheric ozone because it is readily soluble in water and is rained out of the troposphere. Some large explosive volcanic eruptions, however, inject gas and ash directly into the stratosphere and thus bypass tropospheric processes that remove HCl. In this report, I present evidence that such eruptions may contribute much more HCl to the stratosphere than has previously been believed.

Eruptions that penetrate the stratosphere are much less common than those that do not, but in recent years such eruptions have occurred about once each year (4). In general, the most explosive eruptions occur at volcanoes characterized by (i) moderately to highly silicic magmas (andesite, dacite, and rhyolite); (ii) a relatively high preeruption content of volatile elements, especially water; and (iii) long repose periods (a decade or more). Although very explosive eruptions can occur in any volcanic region, they are most common at volcanoes along continental and island arcs, pri-

marily around the margins of the Pacific Ocean.

During an eruption, individual explosions are usually largest and eruption columns are highest during the initial and climactic phases, which generally last only a few hours or days. The waning phase, during which eruption columns rarely reach the stratosphere, may last months or years.

Eruption columns are formed when magma ascends to the surface and volatile elements, formerly kept in solution in the melt by high pressure, escape and expand as vapor. The gas thrust generated by this expansion carries the frothy, comminuted magma out of the vent at a rate of as much as 600 m/sec.

Gas may enter eruption columns by several processes, the most important and most tractable of which is probably

Table 1. Summary of measured preeruption chlorine contents of magmas from different magmatic provinces (20).

Geologic occurrence and magma type	Chlorine content (% by weight)
Ocean ridge tholeiitic basalt	?
Oceanic islands	
Tholeiitic basalt	0.01 to 0.04
Alkalic basalt	?
Silicic magmas	?
Continental arcs and island arcs	
Basalt	0.01 to 0.22
Andesite (21)	< 0.66
Rhyolite	?
Augustine Volcano (1976 eruption)	
Basalt	~ 0.25
Dacite	0.50 (± 0.1)
Intraplate regions	
Basic alkalic magmas (22)	> 0.17 to 0.48
Silicic alkalic magmas (22)	> 0.24 to 0.56

exsolution of the gas dissolved in the silicate melt. For H_2O and CO_2 , exsolution is extremely rapid and nearly complete; ash that falls from an eruption column generally contains only a small percentage of the preeruption content of these components. The release of sulfur, chlorine, and fluorine may be less complete, so that a significant percentage may remain in the quenched ash.

One can estimate the amount of any volatile element exsolved from the melt and released into the atmosphere during an eruption by comparing the preeruption concentration of the element in the silicate melt (generally not known) to that in the quenched ash. The chlorine output of erupting volcanoes has been estimated by assuming that magma contains 0.02 to 0.025 percent (by weight) of chlorine before erupting and releases all of it during an eruption (5). These values are based upon the composition of fumarolic emissions or the composition of gases released when already partially degassed volcanic rocks are melted, neither of which adequately reflects preeruption magmatic gas compositions.

Better estimates of preeruption chlorine contents of magmas have been obtained recently (i) by examining sea-floor basalt, which is not substantially degassed because of the pressure of superjacent water at the time of the eruption (6), and (ii) by analyzing, with the electron microprobe, inclusions of glass (formerly melt) trapped within crystals in volcanic rocks (7-9). Because they are encased in crystals, these inclusions do not lose their volatile elements as the magma ascends and erupts.

Thus far, few chlorine analyses have been obtained by either method. These analyses (Table 1) indicate that, in general, more chlorine is contained in silicic magmas, magmas of continental and island arcs (10), and alkalic magmas, particularly the silicic alkalic magmas that occur primarily in the interior of continents. The richest magmas may contain more than 0.5 to 1.0 percent chlorine, which exceeds by 20 to 40 times or more the earlier estimates upon which volcanic atmospheric impact has been estimated (5).

The moderately to highly silicic magmas of continental and island arcs, by virtue of their high chlorine content, extreme explosivity, and frequent eruptions are likely to have the greatest atmospheric impact. Silicic alkalic magmas are uncommon and thus of less importance.

I obtained the following data by examining ejecta of the explosive 1976 eruption of Augustine Volcano, Alaska, a

continental-arc volcano dominated by andesitic and dacitic magmas. The eruption occurred in three phases (8). The first, from 22 to 26 January, was the most violent; at least five major explosions generated eruption columns that rose to an altitude of 12 to 14 km and penetrated the tropopause at 9.8 km. These explosions produced ashfall throughout south-central Alaska and incandescent pumiceous ash flows that descended all flanks of the volcano. Fine ash injected into the stratosphere during an early explosion was detected by lidar 5 days later at an altitude of 14 km over the East Coast of the United States (11). After 10 days of quiescence, the second phase began on 6 February with an explosion that probably did not penetrate the tropopause but which produced minor regional ashfall. Explosions of gradually declining intensity continued for at least 2 weeks while a new lava dome emerged from the summit crater. Incandescent block-and-ash flows were emplaced on the north side of the cone, but no additional regional ashfall occurred. The last phase of the eruption, in mid-April, resembled the later part of the February phase and was associated with the final stage of growth of the new lava dome.

Glass inclusions in crystals in dacite ejecta contain 0.32 to 0.63 percent chlorine. The analyses loosely define a chemical differentiation trend that suggests that the dacite contained approximately 0.50 percent chlorine before eruption (8). Because of the complex preeruption history of the magmas, the uncertainty in this estimate is approximately ± 20 percent.

The glassy groundmass of degassed pumices and blocks contains 0.22 to 0.28 percent chlorine. Using an average post-eruption chlorine content of 0.25 percent, I calculate that the magma lost 0.25 percent chlorine (as HCl vapor) as it erupted.

Approximately 0.19 km^3 of new magma was erupted, corresponding to a mass of approximately $0.3 \times 10^{12} \text{ kg}$. This magma therefore emitted $525 \times 10^6 \text{ kg}$ of chlorine (± 40 percent) (12).

The amount of this HCl that reached the stratosphere is probably between that released by air-fall ash deposited by tropopause-penetrating eruption clouds, or $84 \times 10^6 \text{ kg}$ (± 40 percent), and that released from all deposits emplaced during the five explosions that reached the stratosphere in January, or $180 \times 10^6 \text{ kg}$ (± 40 percent). However, if the rate of degassing beneath the surface is rapid in comparison to the rates of magma ascent and eruption, then gas may have escaped in early explosions from magma that did

not erupt until later or perhaps did not erupt at all (13). In that case, the total atmospheric and stratospheric HCl injections may have been higher than these estimates. The amount of chlorine in the estimated total atmospheric and stratospheric injections corresponds to 107 and 17 to 36 percent, respectively, of the 1975 world production of chlorine in fluorocarbons (14).

Some HCl may have been released by other sources which cannot, at present, be reliably evaluated. One of these sources is free vapor, which may have accumulated in subsurface chambers during preeruption "boiling" of the magma. Although evidence suggests that the dacite was saturated with a chloride-rich aqueous vapor phase before eruption (8), the amount of such vapor present cannot be estimated without greater knowledge of the magma history, including magma volume. Petrologic studies may constrain the role played by this possibly major source of gas. Another possible source is groundwater, either marine or meteoric (15). It is unlikely that this source contributed more than a small fraction of the HCl released by magma degassing.

Although this discussion illustrates that potentially significant amounts of HCl can be injected into the stratosphere by explosive eruptions, the proportion of HCl that is ultimately converted to chlorine will depend upon the rate at which HCl is scavenged from the stratosphere by particles or aerosols (predominantly sulfuric acid). This depends in part upon the sulfur content of the magma, which is very low (100 to 400 parts per million) at Augustine Volcano (8). For the more sulfurous (1600 parts per million) magma erupted from Fuego Volcano, Guatemala, Rose (16) estimated that 17 percent of the chlorine injected into the atmosphere was removed by dissolution in aerosols subsequently scavenged by ash.

In tropospheric intraeruptive plumes emitted by Augustine Volcano during February 1976, ozone concentrations dropped from background values of 15 to 35 parts per billion to virtually zero (17). Stolarski and Butler (18) calculated that a stratospheric injection of $300 \times 10^6 \text{ kg}$ of ClX could reduce the ozone column by as much as 7.7 percent (if there was complete conversion to chlorine). Geologically major eruptions, such as caldera-forming eruptions that emit hundreds of cubic kilometers of magma, may have a long-term impact upon stratospheric ozone. For example, eruption of the Bishop Tuff from Long Valley Caldera, California, 700,000 years ago generated 100 km^3 of air-fall ash (19). If the magma

degassed 0.25 percent chlorine (equivalent to Augustine Volcano), this eruption may have injected $289 \times 10^9 \text{ kg}$ of HCl into the stratosphere, equivalent to about 570 times the 1975 world industrial production of chlorine in fluorocarbons.

Clearly, volcanic sources of stratospheric chlorine may be significant in comparison with anthropogenic sources. To assess human impact upon stratospheric chemistry, the nonuniform historic impact of volcanoes must first be assessed. Additional work will be required, in particular to determine (i) many more estimates of the preeruption and posteruption gas content of magmas; (ii) the mechanisms of concentration and release of gas in subsurface magma chambers, especially erupting chambers; (iii) the role of groundwater in volcanic eruption columns; (iv) the distribution of gas and particulates in tropospheric and stratospheric eruption columns, particularly those formed during climactic-phase eruptions; and (v) the efficiency of gas scavenging. Additional work is also needed to evaluate the volcanic contribution to the atmosphere of hydroxyl-, carbon-, nitrogen-, and sulfur-containing compounds, as well as trace hydrocarbons and fluorocarbons, and their combined effect upon ozone.

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9. With the electron probe, chlorine, sulfur, and fluorine can be measured to within ± 0.02 percent (by weight) absolute. Water can also be estimated if it is assumed to be the missing component in a major- and minor-element analysis that sums to less than 100 percent.
10. These magmas are part of what is known as the "calc-alkaline suite."
11. A. B. Meinel *et al.*, *Science* **193**, 420 (1976).
12. On the basis of 30 percent crystals and 70 percent melt in the magma. The corresponding mass of HCl is $540 \times 10^6 \text{ kg}$.
13. W. I. Rose, R. E. Stoiber, and L. L. Malinconico suggested that as much as four times the volume of erupted magma may have degassed below the surface during the 1974 activity of Fuego Volcano, Guatemala (talk presented at the 1979 annual meeting of the Pacific Northwest section of the American Geophysical Union, Bend, Oregon). Whether this could contribute to stratospheric plumes depends upon the actual rate of degassing, a function of the rate of magma ascent and cooling. This, at present, cannot be well constrained.
14. Estimated from information provided in F. S. Rowland and M. J. Molina, *J. Phys. Chem.* **80**, 2049 (1976).
15. The oxygen and hydrogen isotopic compositions of steam condensates [see Johnston (8); unpublished data] indicate that fumarolic emissions before, during, and after the 1976 eruption have

consisted predominantly of meteoric water with, at most, only minor amounts of marine water. It is possible, however, that a deeper stratum of groundwater, predominantly marine, is tapped during explosions.

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17. R. Rasmussen, R. Stordour, J. L. Moyers, J. G. Echardt, W. H. Zoller, talk presented at American Geophysical Union spring annual meeting, Washington, D.C., 1976. Plumes emitted by Augustine Volcano were directly sampled by aircraft during waning-phase eruptions in February [P. V. Hobbs, L. F. Radke, J. L. Stith, *Science* 195, 871 (1977)] and during intraeruptive periods in early and late February 1976 [E. A. Lepel, K. M. Stefansson, W. H. Zoller, *J. Geophys. Res.* 83, 6212 (1978)]. Waning-phase eruptions are not associated with large eruption plumes, do not generate regional ashfall, and create coarser, less vesicular ejecta than climactic-phase eruptions.

Hence, comparison of the sampled plumes to those of the earlier, more explosive activity in January is tenuous.

18. R. S. Stolarski and D. M. Butler, *Pure Appl. Geophys.* 117, 486 (1979).
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20. Data are from J. G. Moore and J. G. Schilling [*Contrib. Mineral. Petrol.* 41, 105 (1973)], Anderson (7), and Johnston (8)]. A question mark indicates that no values have been determined.
21. This value has been calculated (7). Few determinations are available, and higher chlorine concentrations may exist.
22. These concentrations were determined directly in extrusive rocks and are minimum values for the preeruption magmatic chlorine content [J. C. Stormer, Jr., and I. S. E. Carmichael, *Am. Mineral.* 56, 292 (1971)].

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N-Formylmethionyl Peptide Receptors on Equine Leukocytes Initiate Secretion but Not Chemotaxis

Abstract. *The chemotaxis of leukocytes appears to be initiated by the binding of chemotactic factors to the surface of these cells. N-Formylated peptides induce chemotaxis and lysosomal enzyme secretion of leukocytes; because these peptides are available in a purified radiolabeled form, they have been useful in the characterization of receptors for chemotactic factors. Equine polymorphonuclear leukocytes secrete lysosomal enzymes but do not exhibit chemotaxis in response to the N-formylated peptides, even though they have a high-affinity cell surface receptor for these agents. The specificity of the equine receptor resembles the specificity of the receptor on chemotactically responsive leukocytes from other species. Equine polymorphonuclear leukocytes may thus be an excellent model for the study of the events that lead to a biological response following receptor occupancy.*

Chemotaxis, the ability of certain cells to sense and migrate along chemical gradients, can be demonstrated in many organisms, including bacteria, protozoans, and slime molds, as well as in eukaryotic cells (1). In higher organisms, chemotaxis is particularly important for the normal functioning of the immune system because phagocytes such as polymorphonuclear leukocytes (PMN's) and macrophages appear to accumulate at inflammatory sites by responding to chemotactic signals produced there (2).

A major advance in the understanding of chemotaxis came about through the discovery that bacteria as well as PMN's and macrophages contain specific high-affinity surface receptors for chemotactic factors (3, 3a). In bacteria, the availability of chemotactically defective mutants has led to the definition of biochemical events that follow the coupling of chemotactic factors to their receptors and result in a unidirectional migratory response (4). The availability of a reliable source of eukaryotic cells with specific defects of chemotactic responses may have similar significance for the eventual understanding of chemotaxis in higher life forms. To this end, we surveyed the chemotactic response in vitro of PMN's from several mammalian species. We found that equine PMN's, while able to respond chemotactically to the 5a com-

ponent of complement (C5a) and zymosan-activated horse plasma (5), did not respond to the N-formylated chemotactic peptides (6), even though there are high-affinity receptors for these peptides on their surface. Since the equine PMN's did secrete lysosomal enzymes in response to the N-formylated peptides, leukocytes from this species appear to lack the mechanisms that specifically produce a chemotactic response upon

occupancy of the N-formylated peptide receptor.

Blood containing 10 units of heparin per milliliter was obtained from healthy horses maintained at the Duke University Medical Center farm. The PMN's were isolated by sedimentation of the blood in dextran T-500 (Pharmacia) followed by Ficoll-Hypaque density centrifugation (7). The resultant cells routinely contain > 95 percent PMN's. Chemotaxis was quantified in modified Boyden chambers with 5- μ m nitrocellulose filters (8), was scored by determining the average number of PMN's that migrated through the filter, and is expressed as the percentage of the maximal response (8). Partially purified horse C5a was isolated from zymosan-activated horse plasma by methods used for the isolation of human C5a (5, 9). N-Formylated methionyl peptides used were: N-formylmethionylleucylphenylalanine (fMet-Leu-Phe), fMet-Met-Met-Met, fNle-Leu-Phe (Nle, norleucine) (Peninsula Laboratories, Palo Alto, California), and fMet-Leu (Andrulis Research Corp., Bethesda, Maryland). Receptor binding studies were performed with fMet-Leu-[³H]Phe (specific activity, 56.9 Ci/mole; New England Nuclear). A glass fiber vacuum filtration method was used with PMN's at a concentration of 5×10^7 per milliliter of phosphate-buffered saline (PBS) (3a, 10).

To test whether equine PMN's contained specific receptors for fMet-Leu-Phe, we incubated isolated PMN's with 1 to 6 nM fMet-Leu-[³H]Phe in the presence or absence of 10 μ M unlabeled fMet-Leu-Phe. The reaction mixtures were rapidly vacuum filtered onto glass fiber disks and washed, and specific

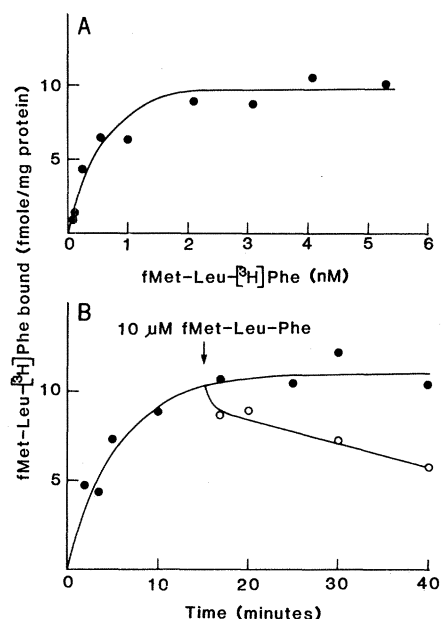


Fig. 1. (A) Binding of fMet-Leu-[³H]Phe to equine PMN's as a function of fMet-Leu-[³H]Phe concentration. Five million equine PMN's were incubated with the indicated concentration of fMet-Leu-[³H]Phe in the presence and absence of 10 μ M unlabeled fMet-Leu-Phe for 25 minutes at 25°C. Reactions were terminated by dilution with ice-cold incubation buffer followed by immediate filtration onto glass fiber disks. Specific binding (11) was calculated after quantification of radioactivity by liquid scintillation counting. Each value represents the mean of duplicate determinations. (B) Time course of fMet-Leu-[³H]Phe binding to PMN. The fMet-Leu-[³H]Phe (5 nM) was incubated with equine PMN's for the indicated time intervals at 25°C, and specific binding (11) was assayed (●). To some incubation mixtures (○) a large excess of unlabeled fMet-Leu-Phe (10 μ M) was added after 15 minutes of incubation, and fMet-Leu-[³H]Phe binding was assayed at subsequent time intervals as indicated. Each value represents the mean of determinations from two separate incubation mixtures.