from the relation $^{146}Sm/^{147}Sm \simeq \lambda_{147}t\,(^{142}Nd/^{143}Nd)_{ch}(^{142}\delta/^{143}\delta)/1.11$, where t is the age of Allende CD (assumed 4.56×10^9 years), λ is the decay constant of ^{147}Sm, δ is defined in Table 2, ch is chondritic, and 1.11 is the ratio of the recoil ranges of ^{142}Nd and ^{143}Nd.
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El Chichón: Composition of Plume Gases and Particles

Abstract. *Aircraft measurements were made of trace gases, atmospheric particles, and condensed acid volatiles in the plume of El Chichón volcano, Chiapas, Mexico, in November 1982. Hydrogen sulfide was the primary gaseous sulfur species in the plume at the time of collection. Concentrations of 28 elements were determined by neutron activation analysis of particulate material from the plume. Rates of trace element emission to the atmosphere for each species were estimated by normalization to the simultaneously determined total sulfur emission rate. The volatile elements sulfur, chlorine, arsenic, selenium, bromine, antimony, iodine, tungsten, and mercury were enriched relative to bulk pyroclastic material by factors of 60 to 20,000. Arsenic, antimony, and selenium were associated predominantly with small ($\leq$ 3 micrometer) particles. Calcium and sodium were present almost exclusively on larger particles and aluminum and manganese were bimodally distributed. Ash-laden particulate material injected into the stratosphere during the early violent eruptions was enriched by factors of 10 to 30 relative to ash in some of the same elements observed in the quiescent plume.*

Gases and particulate material emitted to the atmosphere by volcanic activity have been suggested as a major source of anomalously enriched elements in remote background aerosols (*1*). Aircraft studies (*2–4*) have confirmed ground studies (*5, 6*) showing that noneruptive volcanic outgassing produces aerosols highly enriched in volatile and chalcophilic elements.

The Mexican volcano El Chichón underwent violent eruption in late March and early April 1982, injecting large quantities of gas and ash above the tropopause, producing the largest stratospheric cloud of volcanic origin observed this century. Atmospheric turbidity and temperature anomalies have been reported (*7, 8*) and are still being monitored. We investigated the chemical nature of the material emitted that is most likely to exert long-range effects on the global background aerosol. This study of the emissions from El Chichón was pursued as a part of the Research on Atmospheric Volcanic Emissions (RAVE) project, a joint effort by the National Aeronautics and Space Administration in cooperation with five universities.

All samples collected by us were obtained with NASA aircraft 429, a Lockheed Electra turboprop modified for tropospheric gas and particle collection (*9*). Continuous total gaseous sulfur measurement was provided by an onboard Meloy flame photometric detector (FPD) interfaced to a chromatographic system for the in-plume determination of H_2S and SO_2.

Samples were collected on 3 November 1982, at which time El Chichón was emitting a visible plume to an altitude of 0.7 km. The plume had a width of 3 km approximately 1 km downwind from the crater rim. Two sets of filter samples and one cascade impactor sample were collected while the plane flew coaxially in the plume. Teflon filters were selected for their high flow rate and low blank characteristics. Two types of multiple filter stacks were employed. One type contained a single Teflon filter followed by four cellulose filters that had been treated with 1*M* ^7LiOH in 30 percent glycerol to trap acid volatiles (such as SO_2, HF, HCl, and HBr). The second consisted of a quartz fiber filter followed in sequence by two nylon filters and two cellulose filters that had been treated with 1*M* $NaHSO_4$ in 10 percent glycerol for the collection of acidic gases (HCl and HNO_3) and ammonia, respectively. The cascade impactor collected size-segregated particles on polycarbonate films on seven stages followed by a polycarbonate backup filter. Blanks were collected for all filter and film types by exposing them for 30 seconds. Background air filter samples were collected while the plane flew at an altitude of 3 km to and from the volcano.

In addition to our own samples, we analyzed a sample of ash injected above the tropopause by the March and April 1982 eruptions of El Chichón that was collected by the NASA-DOE (Department of Energy) WB57F aircraft. This sample was collected above 18 km in May 1982 over the continental United States.

All filters were preloaded in cassette holders, stored in cleaned polyethylene bags before sample collection, and returned to clean bags immediately thereafter. Teflon and ^7LiOH-glycerol–treated cellulose filters, returned to the University of Maryland, were prepared in a class 100 clean room and tested for 28

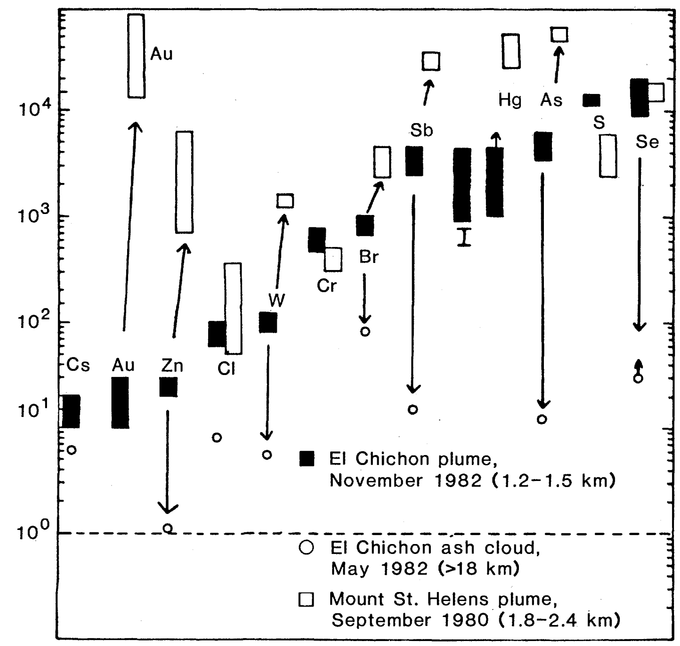

Fig. 1. Enrichment factors (relative to volcanic ash) for selected volatile elements on particles from the El Chichón plume.

elements by instrumental neutron activation analysis (INAA) (*10*). Particulate mercury values represent lower limits due to the possible loss of radioactive Hg° formed during the activation procedure (*11*). Soluble particulate SO_4^{2-} concentrations were determined by extraction of the quartz filters and ion chromatography at the University of Arizona.

The stratospheric sample of volcanic ash (300 ± 30 μg) was washed free of a silicone oil–coated collection flag with Freon-113 and suction-filtered through a polycarbonate filter (pore diameter, 0.1 μm), which was rinsed with hexane to ensure removal of the collection oil. Two blank filters were carried through an identical procedure, sealed, and shipped along with the sample to the University of Maryland for INAA.

The results presented in Table 1 represent the average blank-corrected concentrations of elements measured in background and plume particulate material. Also reported are the average total sulfur concentration measured by FPD simultaneously with the filter collection,

Table 1. Concentrations of elements in background and El Chichón plume particles, in the stratospheric ash sample, and in El Chichón crater pumice.

Element	Average regional background concentrations (ng/m^3), November 1982 ($N = 3$)	Average concentrations (ng/m^3) in plume, November 1982 ($N = 6$)	Composition of ash from stratosphere, May 1983 (ppm or %)	Composition of pumice from crater, January 1983 (ppm or %)
Sodium	35 ± 6	530 ± 200	6.8 ± 0.3 (%)	3.4 ± 0.6 (%)
Magnesium	< 70	460 ± 200	< 2 (%)	
Aluminum	47 ± 10	540 ± 200	14.6 ± 0.2 (%)	10.2 ± 0.2 (%)
Chlorine	22 ± 10	640 ± 300	6300 ± 900	1200 ± 100
Potassium	5 ± 2	260 ± 100	7.9 ± 0.3 (%)	2.2 ± 0.4 (%)
Calcium	60 ± 30	900 ± 400	5.4 ± 0.7 (%)	5.1 ± 0.4 (%)
Scandium	0.008 ± 0.006	0.039 ± 0.010	4.0 ± 0.2	6.9 ± 0.3
Titanium	≤ 20	≤ 50	1.0 ± 0.3 (%)	0.24 ± 0.04 (%)
Vanadium	0.12 ± 0.05	1.6 ± 0.3	110 ± 20	190 ± 40
Chromium	4.0 ± 0.7	24 ± 6	< 10	6 ± 2
Manganese	0.59 ± 0.04	40 ± 20	1800 ± 500	1300 ± 100
Iron	45 ± 10	200 ± 100	3.1 ± 0.2 (%)	4.7 ± 0.1 (%)
Cobalt	0.06 − 0.04	0.34 ± 0.30	6.3 ± 0.3	11 ± 1
Zinc	6 ± 2	13 ± 2	80 ± 10	120 ± 30
Arsenic	< 0.2	70 ± 40	19 ± 1	2.3 ± 0.3
Selenium	0.052 ± 0.003	1.3 ± 0.7	7 ± 2	< 0.4
Bromine	0.45 ± 0.19	11 ± 5	100 ± 50	2.2 ± 0.2
Rubidium	≤ 0.5	≤ 1	290 ± 10	87 ± 5
Strontium	≤ 0.2	≤ 0.2	1300 ± 100	1200 ± 200
Zirconium	≤ 0.001	≤ 0.001	260 ± 50	210 ± 60
Molybdenum	≤ 0.4	≤ 0.4	23 ± 7	3.7 ± 0.2
Antimony	0.040 ± 0.002	7 ± 3	3.4 ± 0.4	0.4 ± 0.1
Iodine	0.3 ± 0.2	1.8 ± 0.7	< 20	< 40
Cesium	0.010 ± 0.003	0.3 ± 0.1	13 ± 1	3.7 ± 0.2
Barium	≤ 0.8	≤ 0.8	1900 ± 100	820 ± 90
Lanthanum	0.005 ± 0.003	0.18 ± 0.08	85 ± 2	37 ± 3
Cerium	0.085 ± 0.040	0.32 ± 0.25	78 ± 4	57 ± 4
Samarium	0.0028 ± 0.0009	0.026 ± 0.009	8.7 ± 0.3	4.5 ± 0.3
Europium	0.0022 ± 0.0005	0.0074 ± 0.008	1.5 ± 0.1	1.4 ± 0.1
Ytterbium	≤ 3	≤ 3	3.0 ± 0.3	1.8 ± 0.2
Lutetium	≤ 200	≤ 700	0.5 ± 0.1	0.35 ± 0.02
Hafnium	0.006 ± 0.001	0.05 ± 0.03	7.3 ± 0.3	3.5 ± 0.3
Tantalum	≤ 0.1	≤ 0.1	1.5 ± 0.2	0.64 ± 0.03
Tungsten	0.15 ± 0.09	0.7 ± 0.5	2.5 ± 0.9	0.8 ± 0.4
Gold	0.008 ± 0.001	0.25 ± 0.09	≤ 0.05	0.0020 ± 0.0008
Mercury	≥ 0.035 ± 0.010	≥ 0.3 ± 0.1	≤ 5	≤ 5
Thorium	0.006 ± 0.002	0.029 ± 0.007	26 ± 1	9.3 ± 0.3
Particulate sulfur	900 ± 200	5,600 ± 2,000		
Total sulfur	< 7,000	140,000 ± 15,000		
Particulate fraction (%)	≥ 11	4.0 ± 0.6		
Particulate chlorine	< 50	620 ± 300		
Total chlorine	420 ± 50	16,000 ± 8,000		
Particulate fraction (%)	< 11	3.9 ± 0.6		
Particulate bromine	0.66 ± 0.09	12 ± 3		
Total bromine	4.7 ± 0.5	40 ± 15		
Particulate fraction (%)	12 ± 2	30 ± 5		

the elemental composition of the stratospheric ash sample, and the composition of El Chichón pyroclastic material. The expressed standard deviations are those arising from analytical error only. Organic-soluble fractions of the elements associated with the ash particles were probably lost in the rinses before analysis.

It is of interest to identify those elements associated with plume aerosols that are enriched relative to bulk pyroclastic material erupted from the same volcano. To this end we calculated the ash enrichment factor (EF_{ash}), as given by

$$EF_{\mathrm{ash}} = \frac{(X/\mathrm{Sc})_{\mathrm{plume}}}{(X/\mathrm{Sc})_{\mathrm{ash}}}$$

where $(X/\mathrm{Sc})_{\mathrm{plume}}$ is the ratio of the concentration of an element to that of scandium measured in the plume aerosol and $(X/\mathrm{Sc})_{\mathrm{ash}}$ is that ratio determined for representative ash material. Scandium was selected because it is accurately determined by INAA and, unlike aluminum, does not form volatile halides that could be enriched by high-temperature volcanic activity (*12*). Hoffer *et al.* (*13*) reported that the early eruptions in March and April produced light gray pumice and ash, andesitic in composition and largely juvenile in origin. An interior sample of fresh, primarily juvenile pyroclastic material, retrieved from the crater of El Chichón in January 1983, was pulverized and analyzed in triplicate by INAA.

Table 2. Estimated flux of selected volatile elements (thousands of kilograms per day).

Element	El Chichón, November 1982	Mount St. Helens, September 1980 (*4*)
Sulfur (total)*	400	450
SO_4 (particulate)	16	24
Ash	15	60
Chlorine (total)*	53	
Chlorine (particulate)	2	3
Arsenic (particulate)	0.2	0.8
Selenium (particulate)	0.004	0.1
Bromine (total)*	0.1	
Bromine (particulate)	0.03	0.02
Antimony (particulate)	0.02	0.03
Mercury (particulate)	≥ 0.0009	≥ 0.003
Gold (particulate)	0.0007	0.003

*Total acidic gaseous species.

The ranges of calculated EF_{ash} values for volatile elements found to be enriched in the plume aerosols are plotted in Fig. 1. Included for comparison are the individual EF_{ash} values of the stratospheric ash sample as well as the ranges of EF_{ash} values for the elements measured in the Mount St. Helens plume aerosol (*4*). In Fig. 2 the observed concentrations of seven elements are plotted as a function of particle diameter. More than 70 percent of the mass of the enriched volatile elements arsenic, antimony, and selenium is associated with particles ≤ 3 μm in diameter. Aluminum and manganese have a bimodal distribution, with peaks at ~ 0.4 μm and 3 to 6 μm, whereas sodium and calcium are associated almost exclusively (> 80 percent) with particles > 3 μm. The results again point to the possible volatilization of aluminum and manganese as halide compounds that subsequently condense on the surface of particles, yielding a bimodal size distribution.

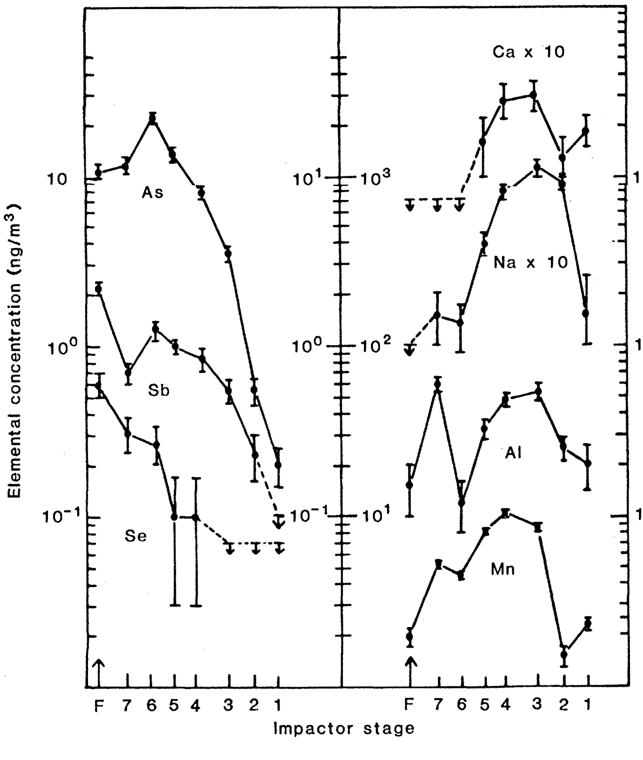

Fig. 2. Concentrations of elements in the El Chichón plume aerosol, plotted as a function of particle size. Impactor stage numbers correspond to effective cutoff diameters: *1*, 30 μm; *2*, 15 μm; *3*, 7.0 μm; *4*, 2.6 μm; *5*, 1.4 μm; *6*, 0.7 μm; and *7*, 0.35 μm. *F* indicates backup filter.

Chromatography and treated filters were used in the analysis of the gas-phase sulfur species (SO_2 and H_2S) and the acid-base species of sulfur, chlorine, bromine, and nitrogen (HNO_3 and NH_3). These experiments demonstrated that the primary gaseous sulfur species emitted at the time of sampling was H_2S. Chromatographic analysis showed H_2S concentrations as high as 400 parts per billion by volume (ppbv) and SO_2 concentrations less than 100 ppbv. It was not possible, with the chromatographic system used, to estimate the concentrations of other sulfur-containing gases, such as CS_2 and COS. Previous studies (*14*–16), however, demonstrated that SO_2 and H_2S are the predominant sulfur species present in volcanic emanations. Thus it is reasonable to suggest that sulfur from El Chichón was emitted predominantly as H_2S, either directly or as a consequence of the interaction of lake and ground water. The apparent highly reducing nature of these emissions at this stage of the venting process is very unusual, and the volcanologic implications are unknown (*17*). If the observed concentrations of sulfur in the plume are representative of those at the time of the initial large eruptive event in April 1982, then the potential impact on stratospheric chemistry may need to be evaluated.

Inorganic gaseous chlorine and bromine concentrations were substantially larger than the aerosol concentrations of these elements. The aerosol fractions of total sulfur, chlorine, and bromine in the plume are included in Table 1. Less than 5 percent of the emitted sulfur and chlorine was present on particles in the plume at the distances where it was sampled, whereas almost one-third of the emitted bromine was associated with such particles. The concentrations of HNO_3 and NH_3 in the plume were equal to or less than the detection limits of 1 and 0.3 μg/m^3, respectively, suggesting that neither ammonia nor nitric acid is produced by this type of volcanic activity.

By normalizing the concentrations of enriched volatile elements to that of total sulfur, one can calculate their emission rates relative to that of H_2S. Enriched elements with emission rates on the order of 1 kg per day or greater are listed in Table 2 and compared to estimates of the emission rates made for the quiescent Mount St. Helens in September 1980 (*4*). Emission rates for most species appear to be comparable at the two volcanoes, with the exception of a significantly lower values for selenium from El Chichón.

In summary, during this investigation the sulfur emission from El Chichón, unlike that from other volcanoes at this stage, was primarily in the form of H_2S. Of the 29 elements measured in particulate material collected by aircraft from the plume of the volcano, sulfur, chlorine, arsenic, selenium, bromine, antimony, iodine, tungsten, and mercury were found to be enriched relative to bulk pyroclastic material by factors comparable to those determined at Mount St. Helens. Unlike the Mount St. Helens aerosols, however, these samples showed no significant enrichment in zinc or gold. Analysis of elemental composition as a function of particle size revealed that the enriched volatile elements were associated primarily with fine particles and can be expected to have long atmospheric residence times compared with the nonenriched, crustal elements found on larger, more rapidly settling particles. Fine ash injected into the stratosphere by the March eruption was also enriched in the volatile elements relative to ground ash, but these enrichments were significantly smaller than those measured in the quiescent plume samples. These findings support the occurrence of chemical fractionation during eruptions and posteruptive outgassing which is preserved as a signature that can be carried with small aerosols as they are transported over long distances.

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Ultraviolet Visual Pigment in a Vertebrate: A Tetrachromatic Cone System in the Dace

Abstract. *Microspectrophotometric measurements of optically isolated photoreceptors in the Japanese dace, a cyprinid fish, revealed four spectroscopically distinguishable cone pigments and one rod pigment. A visual pigment that absorbs in the near ultraviolet was found in small single cones.*

Sensitivity to ultraviolet (UV) light has been known to exist in ants for about a century and in bees for at least half that long (*1*). More recently, electrophysiological measurements have revealed flies, spiders, and other arthropods to be sensitive to UV light (*2*). A UV-absorbing visual pigment, a retinal-based chromoprotein, whose longest wavelength (alpha band) absorption peaks at about 350 nm, has been extracted from the neuropteran *Ascalaphus macaronius* (*3*). Pigeons (*4*) and hummingbirds (*5*) also respond to light in this spectral region. However, in these vertebrates neither the UV-sensitive receptor nor a UV-absorbing visual pigment has been identified. We now report finding short single cones in an aquatic vertebrate that could mediate UV responses.

Many species of bony fish have well-developed color vision. Among them, members of the cyprinid family (*6*), especially goldfish and carp, have been extensively investigated in vision research. Another cyprinid, the Japanese dace, *Tribolodon hakonensis* (Günther), with the common name "ugui," has been studied recently (*7*). A common fish in Japan, with a well-developed retina and receptors forming a highly regular cone mosaic, ugui has also been studied by electrophysiology, anatomy, and microspectrophotometry (*8*). The horizontal

Table 1. Numerical distribution of ugui photoreceptors as a function of peak absorptions of their visual pigments.

λ_{max} (nm)	Cones						Rods	To-tal
	Double		Single					
	Long	Short	Long	Me-dium	Short 1	Short 2		
600 to 620	7		32	1				40
570 to 590	16		17	2				35
520 to 535		17	2	25	1		28	73
500 to 515		11	3	46	1		12	73
405 to 415					13	1		14
350 to 370					1	14		15
Total	23	28	54	74	16	15	40	250

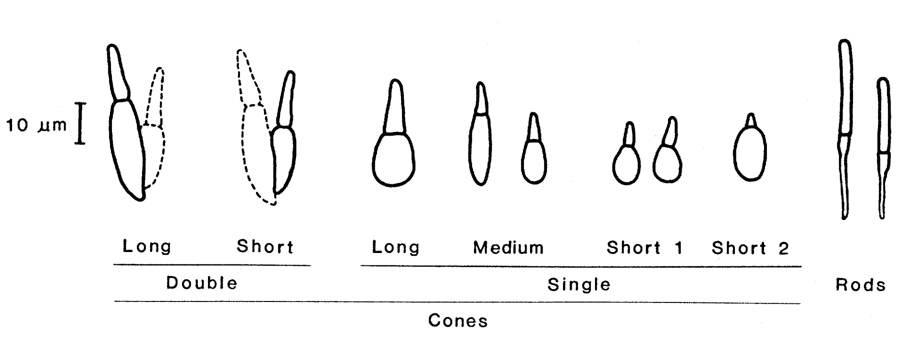

Fig. 1. Distal elements of ugui photoreceptors (devoid of myoid, nucleus, and synaptic processes). Morphology was determined at a magnification of ×1000; cell contours were traced from photomicrographs.