

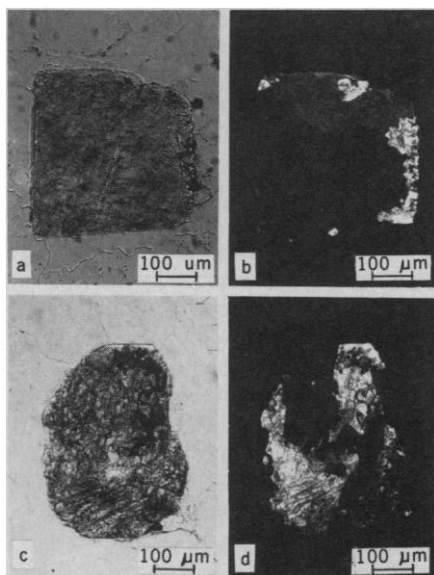


Fig. 2. Illustration of optical domains in post-shot anhydrite: (a) crystal in plane-polarized light; (b) crystal with crossed Nicols; (c) crystal in plane-polarized light; and (d) crystal with crossed Nicols. All depths, 2773 feet.

dergone a completely reversible phase transformation (3). Laboratory experiments on the preshot Tatum rock itself also showed evidence of the anhydrite phase change, but, because of dilution by the soft halite, the transformation was not evident below 24.5 kbar. This report describes the evidence for phase transformation as seen in postshot rock samples obtained from cores taken through the center, into the puddle of the cavity, and below the shot point.

The preshot anhydrite, enclosed in a matrix of halite, has a modal grain size of about 700 μm . The prismatic, euhedral grains are clear and free of gross imperfections (Fig. 1). Few twinned grains are observed. There is little evidence of strain; in all grains fractures are few, extinction is sharp and uniform, and undulose extinction is absent. The three pinacoidal cleavages are in evidence.

At depths from 2773 feet to approximately 2794 feet, the halite remains unfractured. However, the postshot anhydrite grains are at times partly cracked and contain distinctly different optical domains that may be seen quite easily under crossed Nicol prisms. Figures 2 and 3 illustrate this phenomenon in three different grains. A similar domain structure has been attributed to the high-temperature phase transformation of synthetic bromellite (4). At 2796 feet, strain induced by the shot is indicated by mechanical twins and slight undulose extinction; however, the optical domains are not distinct. X-ray analysis of the postshot anhydrite indicates the presence of only CaSO_4 .

Using Stephens' data as a guide, one can

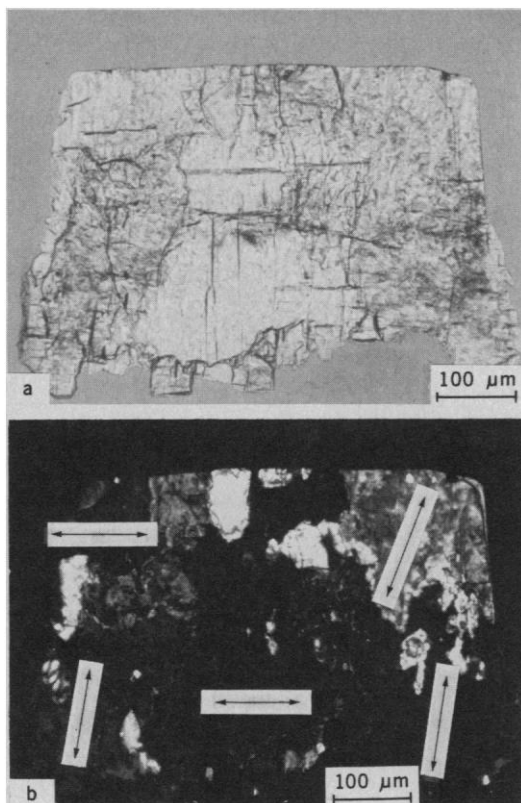


Fig. 3. Appearance of anhydrite grains in a postshot sample (depth, 2773 feet) of a Salmon core. (a) Plane-polarized light showing cleavage traces and cracks. Note cracks and cleavage traces within the cracked areas. (b) Same areas as (a) with crossed Nicols, showing optical domains. (c) Detail of crystallographic domains in anhydrite crystal, crossed Nicols. The relative misorientation due to the high-pressure transformation may be observed in the traces of the cleavages. Arrows indicate directions of the trace of the plane of the relatively faster vibration direction.

place a peak radial stress of approximately 25 kbar at 2796 feet or approximately 1.5 cavity radii. Rogers (2) estimates the peak radial pressure at 2796 feet to have been on the order of 30 kbar. Considering the difficulties associated with evaluating the activation energies for high-pressure reactions, the differences in the experimental environments, and the errors involved in estimating the pressures, one must conclude that the agreement between Rogers' calculations and field measurements and Stephens' experimental work is excellent. In addition, recently completed experimental laboratory work by Schock (5) for Borg and Smith (6) has confirmed the existence of a high-pressure polymorph of anhydrite. The monoclinic monazite structure ($P2_1/n$) is considered the most likely configura-

Because of the ease with which this pres-

sure change may be observed, it would appear that anhydrite may be an excellent pressure indicator in future high-pressure experiments.

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5 February 1975

Precipitation: Its Acidic Nature

Abstract. *A comparison of the free hydrogen ion concentration and the total hydrogen ion concentration of rain samples shows that rain is a weak acid. The weak acid nature of rain casts doubt on the concepts that the acidity of rain is increasing and that these increases are due to strong acids such as sulfuric acid.*

The term "acid rain" has come into widespread use to imply that precipitation may be influenced by anthropogenic activity in such a manner as to cause a decrease in the pH. Likens and Bormann (1) discuss

the most commonly held opinions on "acid rain." They report that precipitation in the northeastern United States is acidic and is presumably due to air pollution. The relationship to air pollution is based upon two

assumptions: (i) that the *pH* of precipitation without anthropogenic activity would be 5.7 (this is the *pH* of a solution of CO₂ in water in equilibrium with the partial pressure of CO₂ in the atmosphere); (ii) that precipitation with a *pH* less than 5.7 must contain a strong acid of anthropogenic origin; the strong acid usually suggested is H₂SO₄ generated by the oxidation of SO₂.

The assumption that the H⁺ found in rainfall at the present time is due to the presence of strong mineral acids such as H₂SO₄ can be evaluated. Likens and Bormann (1) report that the sulfur content of rain has decreased in New York State but this decrease is not reflected in *pH* measurements. They attribute this finding to the neutralization of H₂SO₄ by particulate matter. Granat (2) was not able to correlate the sulfate concentrations to the *pH* of precipitation in a large number of samples collected in Europe.

We undertook a study of the nature of the acidity of precipitation to determine if precipitation is a dilute solution of a strong acid such as H₂SO₄ or a solution of a weak acid. The precipitation-collecting station was located in Allegheny County, Pennsylvania, 11.2 km due north of the confluence of the Monongahela, Allegheny, and Ohio rivers, at an elevation of 400 m above sea level. The station was situated (in a residential area) so as to be unaffected by local sources.

Each sample was collected in a polyethylene bottle fitted with a polyethylene funnel 15.2 cm in diameter; the bottle was secured on a wooden platform 1.5 m above the ground. The precipitation collectors were cleaned in the laboratory with triple distilled water, air dried, assembled, and covered with plastic film to prevent dust from settling on the funnel and bottle. The collectors were placed out shortly before the onset of precipitation and were recovered either at the end of the precipitation event or when the collecting bottle was almost full, whichever occurred first. The collected samples were then capped and stored in a freezer.

The *pH* measurements were carried out on a *pH* meter (Corning model 12) equipped with a combination glass electrode (Fisher catalog number 13-639-90). The *pH* meter has an expanded scale which permits an accuracy of ± 0.005 *pH* unit in the buffer range and ± 0.01 *pH* unit outside the buffer range. An error of 1.00 *pH* unit corresponds to a potential difference of 59 mv. A 1-mv error in measurement will give a 3 percent error in the hydrogen ion concentration, [H⁺] (3). There is an additional error caused by the difference in ionic strength of the standardizing buffer and the precipitation sample. These

Table 1. Dilute H₂SO₄ titration.

Initial <i>pH</i>	4.01
<i>V</i> _s (ml)	51.73
Final <i>pH</i>	8.95
<i>V</i> _T (ml)	1.702
<i>M</i> NaOH	0.003049
OH ⁻ _T (mmole)	5.19×10^{-3}
OH ⁻ _{xs} (mmole)	4.76×10^{-4}
HA _T (mmole)	4.71×10^{-3}
<i>M</i> HA _T	9.10×10^{-5}
<i>M</i> free H ⁺	9.77×10^{-5}

sources of error in the *pH* measurements limit the accuracy of the procedure.

We carried out acid-base titrations by using a constant drive syringe pump to deliver the titrant. We followed the course of the titration by means of a strip chart recorder (Hewlett-Packard) attached to the *pH* meter.

Carbonate-free NaOH was prepared by dissolving 5 g of electrolytic NaOH pellets in 10 ml of distilled water. The insoluble Na₂CO₃ was filtered, and the filtrate was diluted to 1 liter with freshly boiled distilled water. The working solution (approximately 10⁻³ *M*) was prepared by diluting 10 ml of the 0.1 *M* NaOH to 1 liter with freshly boiled distilled water.

The working solution of NaOH was standardized against potassium acid phthalate immediately prior to the analysis of precipitation samples and after every four samples during a series of titrations.

Table 2. Comparison of the free acid to the total acid in precipitation.

Date of event	<i>pH</i>	Free [H ⁺] ($\times 10^5$)	[HA] _T (mmole/ml) ($\times 10^5$)
20 Dec. 1973	4.57	2.69	10.6
25-26 Dec. 1973	5.62	0.24	7.27
30 Dec. 1973-			
1 Jan. 1974	4.12	7.59	19.0
9 Jan. 1974	5.29	0.51	10.4
18-19 Jan. 1974	4.64	2.29	9.44
21 Jan. 1974	4.31	4.89	12.8
26-27 Jan. 1974	4.30	5.01	11.8
28 Jan. 1974	4.39	4.07	7.66
6-7 Feb. 1974	4.45	3.55	10.7
9-11 Feb. 1974	5.67	0.21	8.21
16-17 Feb. 1974	4.39	4.07	10.7
23-24 Feb. 1974	4.52	3.02	12.4
24-25 Feb. 1974	4.26	5.50	19.3
28 Feb. 1974-			
1 Mar. 1974	4.26	5.50	12.1
8 Mar. 1974	4.40	3.98	13.8
9 Mar. 1974	5.78	0.17	9.54
15-16 Mar. 1974	4.73	1.86	15.4
21 Mar. 1974	4.56	2.75	8.69
29-31 Mar. 1974	5.08	0.83	13.3
3-4 Apr. 1974	4.41	3.89	12.5
7-9 Apr. 1974	4.12	7.58	15.5
14 Apr. 1974	5.51	0.31	36.9
25-26 Apr. 1974	4.82	1.51	44.0
11-12 May 1974	4.63	2.34	25.6
17 May 1974	4.29	5.13	28.8
23 May 1974	4.60	2.51	43.3

The *pH* meter was calibrated with buffer solutions (Fisher Certified) at *pH* values of 4, 6, and 8.

The frozen precipitation samples were thawed in a water bath at 40°C for 30 minutes and then allowed to cool to room temperature for 60 minutes. A magnetic stirrer was used. The starting *pH* was measured on the expanded scale of the *pH* meter. The titrant was then added by the constant drive pump at a rate of 1.15 ml/minute. The course of the titration was followed on the normal scale of the *pH* meter, and the pump was stopped when the *pH* of the sample was near a value of 9. The final *pH* was measured on the expanded scale of the meter.

The acid present can be considered to be a monobasic acid (HA) such that:



with an equilibrium constant

$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (1)$$

For a strong monobasic acid

$$[\text{HA}]_T = [\text{A}^-] = [\text{H}^+] \quad (2)$$

but for a weak acid

$$[\text{HA}]_T = [\text{HA}] + [\text{A}^-] \quad (3)$$

where [HA]_T is the total acid present in the solution, and

$$[\text{H}^+] = [\text{A}^-] \neq [\text{HA}]_T \quad (4)$$

The [H⁺] is determined by measurement with a *pH* electrode. The [HA]_T is determined by titration with standard NaOH. Because the concentrations are quite low, the following indirect procedure for determining the total acid present was used.

An excess of standard base was added to a precipitation sample, and the quantity of HA_T present was determined from

$$\text{mmole HA}_T = \text{mmole OH}^-_T - \text{mmole OH}^-_{xs} \quad (5)$$

where OH⁻_T is the total base and OH⁻_{xs} is the excess base.

The [OH⁻]_{xs} was determined by measuring the *pH* of the solution at the end of the titration

$$[\text{OH}^-]_{xs} = \frac{10^{-14}}{[\text{H}^+]} \quad (6)$$

$$\text{mmole OH}^-_{xs} = [\text{OH}^-]_{xs} \times (V_s + V_T) \quad (7)$$

where *V*_s is the volume of sample titrated and *V*_T is the volume of titrant (in milliliters). The total base added is simply

$$\text{OH}^-_T = (\text{concentration of base}) \times V_T \quad (8)$$

For comparison purposes, dilute H₂SO₄ solutions were titrated by the above procedure: to 50 ml of distilled water 10⁻² *M* H₂SO₄ was added until the *pH* of the solu-

tion was approximately 4, and the titration procedure was carried out. The results of the titration are shown in Table 1. The $[HA]_T$ as determined by the titration procedure agrees with the $[H^+]$ as determined by the pH measurement. The 7 percent error is what one would expect from a procedure which requires two pH measurements.

Samples of rain or snow were collected from 38 precipitation events from December 1973 to June 1974. Of the 38 events sampled, sufficient sample was collected from 26 events for acidity measurements. The results are shown in Table 2. The pH of the precipitation ranges from a low of 4.12 to a high of 5.78. The average pH is 4.68. The range and average found in this study agree with those from a 1971–1972 study by Jones (4), who found an average pH of 4.5 in precipitation samples collected in the area around the Tennessee Valley Authority Cumberland Steam Plant. The results also agree with data published by Likens *et al.* on annual weighted pH for precipitation in New York State for the years 1966–1967, 1967–1968, and 1968–1969 (5).

The presence of weak acids in these precipitation samples (Table 2) is shown by

the titrations with standard base. All precipitation samples contain bound H^+ in amounts ranging from 2 to 100 times the free $[H^+]$. The precipitation is best characterized as a weak acid rather than a strong acid such as H_2SO_4 . These results also show that pH measurements alone cannot describe the acidic nature of precipitation.

The presence of weak acid species in precipitation casts additional doubt on the idea that the pH of rainfall was ever controlled by the solubility of CO_2 in the precipitation and discredits the assumption that strong acids account for the presently observed pH value.

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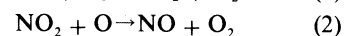
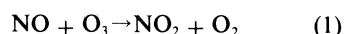
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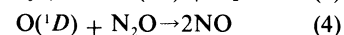
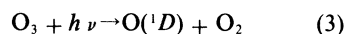
Solar Proton Events: Stratospheric Sources of Nitric Oxide

Abstract. *The production of nitric oxide (NO) in the stratosphere during each of the solar proton events of November 1960, September 1966, and August 1972 is calculated to have been comparable to or larger than the total average annual production of NO by the action of galactic cosmic rays. It is therefore very important to consider the effect of solar proton events on the temporal and spatial distribution of ozone in the stratosphere. A study of ozone distribution after such events may be particularly important for validating photochemical-diffusion models.*

It is now generally recognized that NO and NO_2 molecules are very important in limiting the natural content of ozone in the earth's atmosphere below 45 km due to the pair of catalytic reactions (1)



According to present knowledge the most important natural source for NO (and NO_2) is the reaction of nitrous oxide (N_2O) with excited oxygen $O(^1D)$ atoms, which are produced from ozone photolysis at wavelengths shorter than about 310 nm (2)

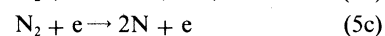
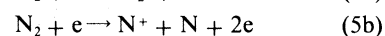
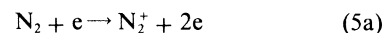


Estimates of the average global rate of production of stratospheric NO from this pair of reactions vary between 2.5×10^7 and 25×10^7 molecules $cm^{-2} sec^{-1}$ (2). An additional source of NO in the strato-

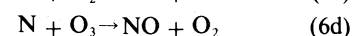
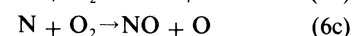
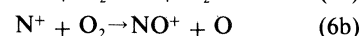
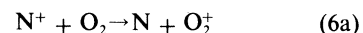
sphere is provided by the ionizing and dissociative action of fast secondary electrons, which are produced by galactic cosmic rays (GCR's) and in solar proton events. The GCR source of NO has been considered by a number of authors (3, 4) and its variable effect on total ozone during the solar cycle has played a significant role in the discussions about the possible environmental effects to be expected from future supersonic aviation in the stratosphere (4). The aim of the present report is to show that solar proton events, leading to so-called polar cap absorption (PCA), should also be considered as sources of NO in the stratosphere with potentially important consequences for the ozone layer. Both of these sources of NO operate mainly at high geomagnetic latitudes ($\geq 60^\circ$).

The primary particles in both galactic and solar cosmic radiation are energetic protons, with smaller fluxes of alpha-parti-

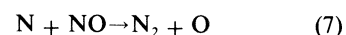
cles and heavier nuclei. The primary particles themselves are too energetic to be efficient in dissociating nitrogen, but they produce substantial fluxes of secondary electrons with energies in the range of tens to hundreds of electron volts. The following reactions lead to ionization and dissociation of nitrogen by energetic electrons



Nitric oxide is then formed via the reactions



A fraction of the N atoms will, however, react with NO



leading to a net loss of NO. Reaction 6c is slow and highly temperature dependent (5) for ground state $N(^4S)$ atoms, but not for electronically excited $N(^2D$ or $^2P)$ atoms. It is therefore important to know the electronic states of the N atoms formed in reactions 5b and 5c. Since such knowledge is not available from laboratory experiments, calculations of NO production rates in this paper were done with the two extreme assumptions of either complete or no production of N atoms in the excited states.

The calculation of ion-pair production rates utilizes the flux and spectrum of solar protons as measured by satellite-borne particle detectors and the standard range-energy relation for protons in air. Calculations of this kind have been carried out previously (6) and the details will not be described here. Certain assumptions, however, deserve mention. First, we have assumed that the proton fluxes are isotropic over the upward-looking hemisphere at the top of the atmosphere; this is almost invariably a good assumption, except for short periods during an event when substantial anisotropies may exist. Second, we have assumed that the fluxes observed by the satellites are the same as those entering the atmosphere; again, many past observations have shown that this is normally valid, even when the satellites are beyond the earth's magnetosphere. Third, we have neglected the effects of the alpha-particles and heavier nuclei that generally accompany the solar protons, and we have also neglected the effects of primary solar electrons; the latter make negligible contribution in the stratosphere, and the alpha-particles might add 10 percent or so to the ionization and NO production rates. For the purpose of making rough estimates of