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 *p*H measurement. The 7 percent error is what one would expect from a procedure which requires two *p*H 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 *p*H of the precipitation ranges from a low of 4.12 to a high of 5.78. The average *p*H 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 *p*H 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 *p*H 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 *p*H 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 *p*H 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 *p*H value.

JOHN O. FROHLIGER
ROBERT KANE
Department of Occupational Health,
Graduate School of Public Health,
University of Pittsburgh,
Pittsburgh, Pennsylvania 15261

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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*)

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1}$$

$$NO_2 + O \rightarrow NO + O_2 \tag{2}$$

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*)

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{3}$$

$$O(^1D) + N_2O \rightarrow 2NO \tag{4}$$

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 stratosphere 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 ($\geq 60°$).

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

$$N_2 + e \rightarrow N_2^+ + 2e \tag{5a}$$

$$N_2 + e \rightarrow N^+ + N + 2e \tag{5b}$$

$$N_2 + e \rightarrow 2N + e \tag{5c}$$

Nitric oxide is then formed via the reactions

$$N^+ + O_2 \rightarrow N + O_2^+ \tag{6a}$$

$$N^+ + O_2 \rightarrow NO^+ + O \tag{6b}$$

$$N + O_2 \rightarrow NO + O \tag{6c}$$

$$N + O_3 \rightarrow NO + O_2 \tag{6d}$$

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

$$N + NO \rightarrow N_2 + O \tag{7}$$

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 the magnitude of the effect, however, their neglect is justifiable.

The three events examined in this study took place during 12 to 16 November 1960, 2 to 5 September 1966, and 2 to 10 August 1972. In the case of the 1966 event, the proton data used were obtained from satellite 1963-38C (*7*), and the 1972 data were obtained from Explorer 43 (*8*). The proton data adopted for the November 1960 event are well documented in an article by Freier and Webber (*9*). The highest energy thresholds at which the fluxes were measured directly for the 1966 and 1972 events were respectively 25 and 60 Mev. In dealing with stratospheric ionization, we are mainly concerned with energies above about 10 Mev (reaching an altitude of 60 km at vertical incidence), which lies within the detector range. At an altitude of 30 km, however, the corresponding proton energy is about 100 Mev, which lies outside the directly observed range for two of the events, so that extrapolation of the observed fluxes is needed. The extrapolation was carried out by assuming an exponential-rigidity spectrum (*9*) defined by the observed fluxes, which probably gives accurate results in the upper stratosphere, but which is subject to some uncertainty below about 30 km. However, most of the production of NO which we have calculated took place above 30 km. The ionization rates during these events were very large, particularly in the case of the 1972 event. At the peak of this event ionization rates were as high as 6×10^4 cm^{-3} sec^{-1} at 60 km and 3×10^4 cm^{-3} sec^{-1} at 40 km and at 30 km.

With knowledge of the ionization rates and the electron impact cross sections of N_2 (*10*), it is possible to calculate the total amount of NO produced in the high latitude stratosphere during the PCA events, including local destruction of NO by reaction 7. As these events lasted for only a few days it is reasonable to neglect the effect of winds. The results of the calculations together with estimates of the total maximum and minimum annual production of NO by the action of GCR are presented in Fig. 1. The assumed background concentrations of NO_x ($NO + NO_2$) are compatible with calculations in which oxidation of N_2O by reaction 4 is the main source of NO in the stratosphere (*2*).

For the three PCA events the following yields of NO below 60 km at geomagnetic latitudes higher than 60°, expressed as molecules per square centimeter, were calculated: 2×10^{15}, November 1960; $6 \times$ $\times 10^{14}$, September 1966; 6×10^{15}, August 1972. The total annual production from GCR varies between 1.2×10^{15} and 1.8×10^{15} molecules cm^{-2} at similar latitudes (*3, 4*). Our calculations therefore indicate that the amount of NO formed in the stratosphere during these three PCA events was comparable to or larger than the total annual production of NO from the action of GCR and its variations over the solar cycle. As an additional comparison, the annual production of NO from the oxidation of N_2O mainly at latitudes lower than 60° is estimated to be between 7.5×10^{14} and 7.5×10^{15} molecules cm^{-2} (*2*). This indicates that, even compared to this source of NO, the PCA event in August 1972 was important.

Past ozone records have revealed interesting variations in total ozone (*11, 12*) which were explained by natural variations in NO production (*4*) and by the effects of additional NO deposited in the stratosphere due to nuclear bomb explosions, especially during 1961 and 1962 (*12*). Johnston *et al.* (*12*) estimated the yield of NO molecules from nuclear bombs to be between 0.17×10^{32} and 1×10^{32} per megaton TNT. Considering that during solar proton events NO is produced over one-sixth of the earth's surface, the input of NO from the August 1972 solar proton event was roughly equal to the stratospheric deposition of NO from a 50 to 300 megaton nuclear explosion. We propose, therefore, that for the explanation of ozone records, it is also important to consider the effects of solar proton events. Studies of ozone distributions in the stratosphere at high latitudes in periods following certain solar proton events may be very important in validating photochemical models of the stratosphere.

PAUL J. CRUTZEN
Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado 80302 and *National Center for Atmospheric Research, Upper Atmosphere Project, Boulder 80303*

IVAR S. A. ISAKSEN, GEORGE C. REID
Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder 80302

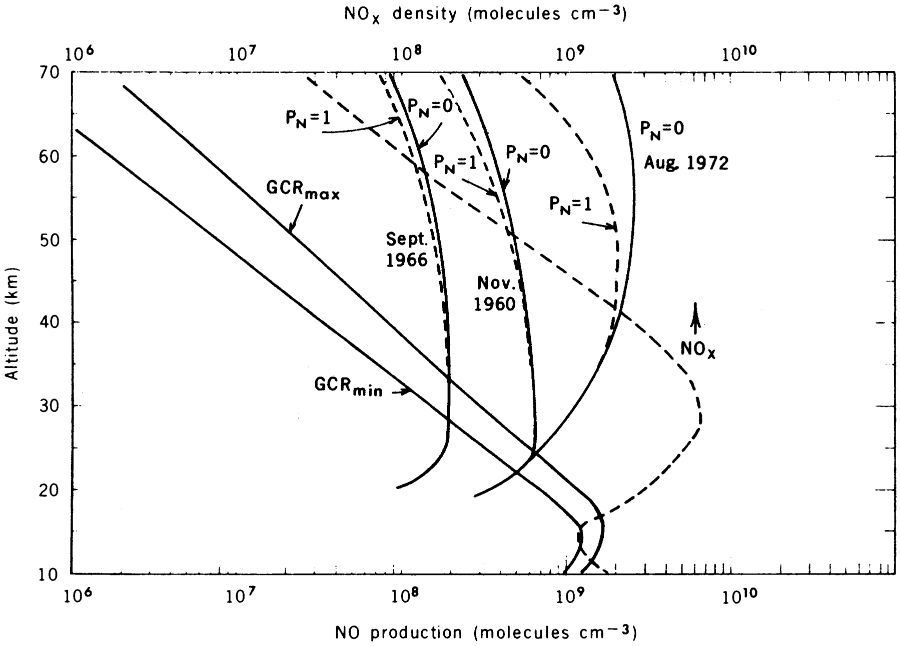

Fig. 1. Total production of NO during the solar proton events of November 1960, September 1966, and August 1972 (lower scale) is given for heights between 70 and 20 km. The curves labelled P_N = 0 and P_N = 1 give the production obtained by assuming that all nitrogen atoms are in excited (^2P,^2D) states and in the ground (^4S) state, respectively. The total maximum (GCR_{max}) and minimum (GCR_{min}) annual production of NO from galactic cosmic rays are included. The adopted background distribution of NO_x ($NO + NO_2$) is also given (upper scale).

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Turquoise Mine and Artifact Correlation for Snaketown Site, Arizona

Abstract. *Trace element analyses on turquoise from 24 mines in the southwestern United States indicate that the turquoise artifacts from Snaketown site in south-central Arizona came from the Himalaya mine near Halloron Springs, California. The correlation of artifact and mine turquoise in the Southwest is a means of determining prehistoric exchange patterns.*

Turquoise artifacts are found in archeological sites throughout the southwestern United States. The geographic distribution of the mineral, however, is limited to the margins of the Colorado Plateau in Arizona, New Mexico, and Colorado, and to a group of mines trending northeast in Nevada. Trace element analyses of turquoise (*1*) have demonstrated significant differences between individual localities (*2*). By means of trace element techniques, it is thus possible to identify the source of the mineral by comparing the trace element content of the artifact with that of turquoise from established geologic sources. The identification of source areas for archeological sites will provide needed information on the nature of prehistoric procurement systems and aid in defining exchange routes.

Thirteen turquoise beads from Snaketown site and multiple samples from each of 24 turquoise mines (Fig. 1) in the Southwest were analyzed by instrumental neutron activation analysis (INAA) in order to determine the source of the Snaketown turquoise. Trace element patterns for each of the beads were compared and found to be similar, suggesting a single source area for all of the beads. The trace element patterns for the beads correlated with that of turquoise from the Himalaya group of mines near Halloron Springs, California, but not with data from the other mines analyzed. This correlation was unexpected since there are several turquoise mines with prehistoric workings geographically closer to Snaketown (*3*).

Snaketown site is a 121-hectare village of single-unit dwellings occupied by the pre-Columbian Hohokam culture group from the beginning of the Christian Era until A.D. 1200. The village is situated on the Gila River Indian Reservation 20.9 km southwest of Chandler, Arizona. Excavations in 1936 and 1964 to 1965 revealed numerous house floors, wells, cremations, and platform mounds along with an abundance of ceramic and artifact material (*4*). The earliest turquoise artifacts known for the Southwest were found at Snaketown. The disk-shaped beads analyzed by INAA were found in the fill of house 8, which was occupied during the Gila Butte Phase (A.D. 500 to 700) of the site.

The Himalaya group of mines, 8 km northeast of Halloron Springs, California, have evidence of extensive prehistoric activity. The prehistoric workings consist of saucer-shaped pits up to 10 m across and 2 m deep. Stone tools were common in the pits, and nearby caves had fire-blackened ceilings, tools, and pottery fragments with incised designs. Rock carvings have been noted on basalt cliffs and boulders in the vicinity (*5*).

Trace element analysis of geologic materials by the INAA method has been described (*6*). Prior to analysis, geologic samples were coarsely crushed, and fragments of turquoise were hand-picked from matrix material under a petrographic microscope. Artifacts were thoroughly washed in an ultrasonic cleaner before irradiation to eliminate surface contaminations. The 13 beads varied in color from light blue to dark blue-green, and weighed between 100 and 300 mg.

The samples were subjected to a series of 1-minute and 6-hour irradiations in the University of Arizona TRIGA reactor in a neutron flux of 10^{12} neutrons cm^{-2} sec^{-1}. The resultant activity was counted on a 55-cm^3 (9.6 percent efficiency) Ge(Li) semiconductor detector connected to a 4096-channel analyzer after the appropriate periods of decay. The turquoise samples were analyzed by comparison with specific activities produced in synthetic turquoise standards activated at the same time. U.S. Geological Survey standard rock GSP-1 was used to check the analytical procedure (*7*).

INAA proved to be a valuable technique for detecting significant differences in trace element concentrations of turquoise from different geographic localities. Co, Cr, Eu, Sb, Sc, and Ta were most useful in this correlation despite the fact that 30 elements were investigated for each sample. Values for Au, Ba, La, Lu, and Fe were not particularly diagnostic since they varied as much within mines as between them. The concentrations of most trace elements in the Himalaya and Snaketown samples were low, relative to concentrations in samples from other areas. Specifically, the values for both Co and Cr clustered between 1 and 2 ppm for the Himalaya-Snaketown samples, while the range in the 23 other mines was 8 to 1000 ppm for Co and 18 to 260 ppm for Cr. Concentrations of Mn, V, Ag, Rb, Sn, Nd, Tb, Yb, Zr, Ta, Hf, and W were below the analytical detection

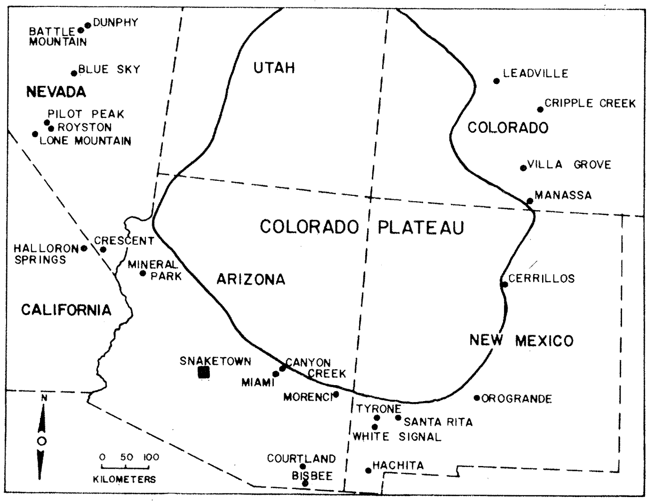

Figure 1. Location of turquoise mines and Snaketown site.