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CHEMICAL COMPOSITION OF A HIGH ALTITUDE FRESH SNOWFALL IN THE LADAKH HIMALAYAS

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Introduction

Studies of the chemical constituents in Antarctic and Greenland snow and ice cores have proven to be extremely useful for determining the composition of the atmosphere during past climatic events (Boutron and Delmas, 1980; Herron, 1982) and hence provide data concerning climatic change. Despite the potential for the collection of similar types of information from high altitude temperate glacier snow and ice cores, their study has been limited. In addition, unlike polar ice sheets, high altitude temperate glaciers are not only close to populated areas, but have higher accumulation rates. Owing to the latter, preservation of detailed records on sub-annual and sub-seasonal scales can be extracted from high altitude temperate glacier cores.

As part of the 1980 University of New Hampshire Nun Kun coring program a suite of surface snow samples were collected from the one snowfall event that occurred during the field season. Determinations of deuterium, reactive phosphate, reactive silicate, reactive iron, chloride, nitrate plus nitrite, pH, and ammonium measured on the eight samples collected from this snowfall are presented in this paper. Although limited in number these samples are unique and as such their interpretative use has been extended to define source(s) for the chemical species found within the snow samples and effects created on the distribution of these species by the mountainous terrain of Nun Kun. Results from these samples will be useful in the interpretation of the time-series record currently being analyzed from this area and in helping to improve our knowledge of the ice and snow chemistry of high altitude temperate glaciers.

Sampling Area

Nun Kun (75°51' - 76°08' E. long., 34°57' - 35°02' N. lat.) is a roughly rectangular massif (fig. 1) situated at the northwestern end of the Zanskar Range in Ladakh, India. The massif has at its center a snow and ice-covered plateau from which radiate several alpine glaciers. Except in the east where the plateau is joined to the main portion of the Zanskar Range by a pass the walls of the plateau rise steeply from river bed level at 3200 m to over 4140 m over distances of only 3-5 km. The surface of the plateau is crossed by several high ridges which act as containers for snowfields. These 4500-5000 m high ridges are punctuated by several peaks higher than 6000 m.

Although Ladakh is a relatively arid portion of the Himalayas the northern border of Nun Kun, Suru Valley, receives as much as 0.9 $m \cdot yr^1 H_2O$ equivalent (Qazi, 1973). Most of this precipitation enters the region during the summer monsoon period, July to August (Boucher, 1975). At this time surface air flow into the region is from the southwest off the Arabian Sea. At the 500 mb level air flow is eastward along northern portions of the range and westward along southern portions of the range (Boucher, 1975).

The surface samples used in this study were collected along a roughly south to north line (fig. 1) running from one of the southernmost peaks on the plateau (5512 m) to part way down (5125 m) one of the northward flowing glaciers exiting the plateau. The samples discussed were deposited in an approximately 5 cm thick layer on 22 July 1980 and were collected within less than 1 day of this snowfall event.

Sampling and Analytical Procedures

Each sample immediately upon sectioning from the core was collected and placed in precleaned plastic bags. Precleaning of the plastic bags involved a soap and water wash with rinsing several times in distilled-deionized water. Once melted in the plastic bags each sample was transferred to two 30 ml and one 125 ml LPE containers, precleaned in the same way as the bags, and one 125 ml (LPE) container that was precleaned by acid-washing in concentrated hydrochloric acid followed by rinsing several times in distilled-deionized water.

The portion of the sample in the soap and water cleaned 125 ml container was used for analysis of chloride, (Zall *et al*., 1956) and of reactive phosphate, ammonium and nitrite plus nitrate employing autoanalyzer techniques (Glibert and Loder, 1977). The portion of each sample in the acid-cleaned 125 ml container was used for analysis of reactive silicate and reactive iron by autoanalyzer using the techniques of Glibert and Loder (1977) and Stookey (1970), respectively. All of the aforementioned were analyzed at the University of New Hampshire.

The two 30 ml LPE containers were used for collecting portions of the melted samples that were analyzed for deuterium and pH. These containers were sealed with wax to prevent diffusion. Deuterium analyses were made in the CNRS Laboratoire de Glaciologie in Grenoble, France. pH was analyzed in the field within 36 hours of acquisition using an Orion Ionanalyzer T.M. model 399 A portable pH meter with an Orion 91-06 combination pH electrode after standardization using NBS buffers of pH=4.01 and pH=7.00.

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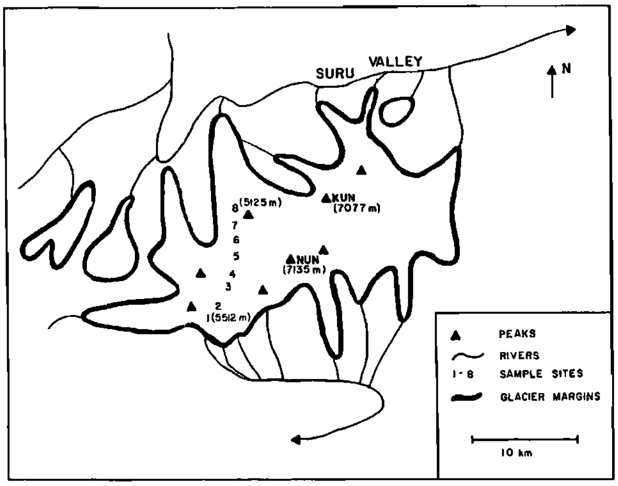

Fig. 1. Sketch map of the Nun Kun glaciers and the surrounding stream pattern.

pH analysis were made without stirring the sample.

Duplicate analyses of standards were used to determine the precision of analyses for chloride, reactive iron, reactive silicate, ammonium, reactive phosphate and nitrite plus nitrate. Analytical precision of replicate analyses of standards was ±1%, ±1%, ±1%, ±7%, ±4% and ±1% respectively.

Results and Discussion

Implications derived from the analyses of the 22 July 1980 snowfall samples are based on the assumption that the chemistry of the surface snow is representative of the air chemistry at the time of deposition. The validity of this assumption is currently being tested and the answer may alter some of the interpretations presented in this paper. To date the question of air/snow fractionation is divided between studies conducted in the Antarctic by Boutron and Lorius (1979) and in the Arctic by Rahn and McCaffrey (1979). The former found little difference between the chemical composition of air and related surface snow while the latter found a relatively large difference. The uniqueness of the samples in this study, however, requires that they be as fully interpreted as possible despite this controversy.

Elevational distribution of deuterium, reactive phosphate, reactive silicate, reactive iron, chloride, nitrate plus nitrite, pH and ammonium are plotted in figure 2. The implications of these relationships with particular reference to the change in distribution, notable from figure 2 in the elevation range 5200 to 5350 m, are discussed below.

Deuterium concentrations range from relatively light, -137.8 to -151.6°/oo, above 5250 to 5300 m, to relatively heavy, -68.1 to -82.2°/oo, below this level. These values averaged over the total 387 m elevation range sampled in this study, yield a per 100 m change of -14.4 to -21.5°/oo which is close to the -14.8 to -18.0°/oo per 100 m, computed from oxygen isotope gradients converted to deuterium concentrations, using data and relations from Niewodniczanski *et al.* (1981). Their work is based on a summary of data from several mountainous areas including sites in the Himalayas. Interestingly enough the closest sample site to Nun Kun used by Niewodniczanski *et al.* (1981), the Garwhal Himalayas, displayed no appreciable change in oxygen isotopic composition with elevation for the range 4400 to 6050 m. Using an average deuterium value of -98°/oo for the Garwhals, converted from the oxygen isotope values of Niewodniczanski *et al.* (1981), the Nun Kun deuterium values that are most similar are found below the elevation range 5250 to 5300 m, average -76.3°/oo. Examination of fig. 2 reveals that most of the total difference in deuterium, for our study, is accounted for over the elevation range 5250 to 5300 m. We suggest that the isotopically heavier deuterium samples, lower elevation sample group, were precipitated from a relatively warm air mass while the isotopically lighter deuterium samples, higher elevation sample group, were precipitated from a relatively colder air mass.

Analytically reactive forms of phosphate, silicate and iron all display similar patterns in concentration as a function of elevation with high values (average 0.7, 33.3 and 11.1 µM, respectively) below 5350 m dropping to very low or close to zero above 5300 m. Phosphate has as its possible sources anthropogenic and biogenic activity (Lyons and Mayewski, in press). Anthropogenically produced aerosols from fuel burning from Himalayan villages have been shown to influence the chemical composition of freshly fallen snow (Davidson *et al.*, 1981). This effect should be more pronounced in the winter months. Localization of phosphate concentrations to lower elevations does suggests a source from Suru Valley or from fertile areas, such as the Indo-Gangetic Plain to the south. The similarity of the reactive phosphate distribution to those of reactive iron and reactive silicate suggests that the phosphate measured by us is associated with soil particles possibly adsorbed into iron oxide coatings. Therefore, the localized phosphate concentration is probably of biogenic origin or anthropogenically introduced by the use of fertilizers.

Silicate and iron are derived primarily from crustal weathering (Rahn, 1976; Lyons and Mayewski, in press). Ratios of silicate/iron for the surface samples below 5300 m are 3/1 which is suggestive of continental aerosols with an anthropogenic admixture (Rahn, 1976). The ratios may, however, not be entirely comparable since the values presented in this study for silicate and iron represent only concentrations leached during the analytical technique and are not, therefore, total values. The abrupt decline of silicate and iron above 5300 m suggests either a local origin and/or transport of these species into the study area via lower elevation air masses.

Chloride displays a peak in concentration below 5350 m, 2.9 to 4.9 µM, and a range of values of 0.4 to 4.9 µM over the full elevation spectrum sampled. As summarized by Delmas *et al.* (1982) from their study of snow at the South Pole the primary source of chloride is due to the formation of gaseous hydrochloric acid

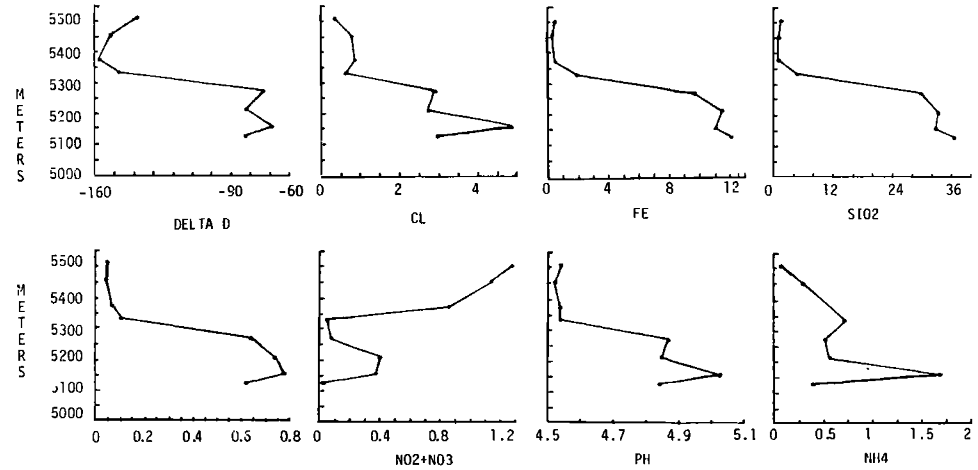

Fig. 2. Elevation (in meters) versus deuterium (DELTA D in °/₀₀), reactive phosphate (PO4 in μM), reactive silicate (SIO2 in μM), reactive iron (FE in μM), chloride (CL in μM), nitrate plus nitrate (NO2 + NO3 in μM), pH (in pH units) and ammonium (NH4 in μM).

promoted by sulfuric acid droplets in contact with sea salt particles (Yue et al., 1976). Samples of fresh snow collected in June-September from Gulmarg, approximately 75 km west of Nun Kun, by Sequeira and Keilkar (1978) have an average chloride concentration of 8.7 μM and are believed by them to be marine-transported. Considering the additional transport distance and elevation needed to get chloride to Nun Kun as opposed to Gulmarg, the lower elevation sample group from Nun Kun appears to have concentrations in the correct range for a marine source that has travelled past the region of Gulmarg. The sample group with low chloride concentrations, higher elevation, is so sharply juxtaposed against the high concentration group that it is most likely representative of an air mass that has been out of contact with an oceanic source longer than the lower elevation air mass and is therefore longer travelled.

Nitrite plus nitrate peak in concentration above and below 5300 m and range in concentration from close to zero to 1.3 μM. Sources for nitrite plus nitrate include biogenic and/or anthropogenic activity, lightning and volcanism (Lyons and Mayewski, in press). The lower peak is suggestive of a biogenic and/or an anthropogenic source produced by the use of fertilizers. The nitrate plus nitrate peak at the higher elevations is thought to reflect the chemistry of the pristine air aloft. Huebert and Lazrus (1980) have shown that in remote areas the concentration of nitric acid increases with elevation in the troposphere. Models of Logan et. al. (1981) suggest the same phenomenon.

pH values can be divided into two groups. Below 5300m they are relatively high, 4.87 to 5.03, and above 5300m they are relatively low, 4.52 to 4.54. If, as suggested by the deuterium results, two air masses came in contact during the 22 July storm event then the higher, isotopically lighter air mass as proposed, was colder and would have had based on CO_2 absorption, a relatively lower pH. The role of CO_2 in the measurement of pH in snow and ice samples of very low ionic strength is beyond the scope of this paper. Numerous recent works have discussed CO_2 as a "contaminant" in snow and ice (Koerner and Fisher, 1982; Oeschger et. al., 1982) and its contribution to the pH in our higher elevation samples can only be viewed as a possibility at this time. The pH decrease with elevation may also be due to increased sulfuric acid in these samples. As mentioned above nitrite plus nitrate does increase with elevation and the work of Ikegami et. al. (1978) have reported increased concentrations of sulfuric acid particles with elevation in Nepalese aerosols. Unfortunately we do not have sufficient sulfate data to investigate this matter. Based on the available information we propose as did Delmas et. al. (1982) for remote polar regions that the major source of aerosols to the high elevation pristine air above 5300 m are atmospheric trace gases SO_2 and NO_x plus possible additional of CO_2.

Ammonium concentrations decrease with elevation ranging from 0.1 to 1.75 μM. This distribution may be due to a local biogenic source similar to that of reactive phosphate. Disregarding a local source, however, this decrease with elevation of ammonium may reflect differences in chemistry of the regional aerosol. As an example, in Nepal the aerosol below 3000 m is dominated by particles of ammounium sulfate while that above 5600 m consists primarily of sulfuric acid particles (Ikegami et. al. (1978). In the latter case, the ammonium concentration of the snow may have been little affected by local anthropogenic or biogenic sources.

Summary

The distribution with elevation of the analytical results derived from samples of freshly fallen snow collected on the Nun Kun plateau appears to be best explained by invoking precipitation of the snow by two discrete air masses. One of these, the higher elevation air mass is characterized by relatively high concentrations of isotopically light deuterium and nitrate plus nitrate and relatively low pH. The other, lower elevation air mass contained relatively high concentrations of isotopically heavy deuterium, reactive phosphate, reactive silicate, reaction iron, chloride and ammonium and relatively high pH. The air mass configuration suggested by this study is similar to that described by Boucher (1975) in which northerly and southerly flowing air dominates at low levels and easterly and westerly flow dominates, at higher levels. The latter would contain the most long-travelled and, therefore, most pristine air.

Sources for the chemical species comprising the two air masses invoked include: biogenic activity (reactive phosphate, nitrite plus nitrate and ammonium), anthropogenic activity such as the use of fertilizers (reactive phosphate, nitrite plus nitrate), crustal weathering (reactive silicate and reactive iron) and marine (chloride).

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References

Boucher, K., Global Climate, Halstead Press, J. Wiley and Sons, New York, New York, 326 p. 1975.

Boutron, C. and C. Lorius, Trace metals in Antarctic snow since 1914, Nature, 277, 551-554, 1979.

Boutron, C. and R. Delmas, Assessing global atmospheric pollution through trace measurements in polar ice sheets, Ambio, 9(5), 210-215, 1980.

Davidson, C.I., T.C. Grimm and M.A. Nasta, Airborne lead and other elements derived from local fires in the Himalayas, Science, 214 (4527), 1344-1346, 1981.

Delmas, R., M. Briat and M. Legrand, Chemistry of South Polar snow, Jour. of Geophy. Res., 87 (C6), 4314-4318, 1982.

Glibert, P.M. and T.C. Loder, Automated Analysis of Nutrients in Sea Water: A Manual of Techniques, W.H.O.I., Tech Rept. 77-47, 46 p., 1977.

Herron, M., Impurity sources of F^-, Cl^-, NO_3^- and SO_4^{2-} in Greenland and Antarctic precipitation, Jour. of Geophys. Res., 87 (C4), 3052-3060, 1982.

Huebert, B.J. and A.L. Lazrus, Troposheric gas-phase and particulate nitrate measurements, Jour. of Geophys. Res., 85, (C-12), 7322-7328.

Ikegami, K., J. Inoue, K. Higuchi and A. Ono, Atmospheric aerosol particle observed in high altitude Himalayas, SEPPYO, 40, 86-89, 1978.

Koerner, R.M., and D. Fisher, Acid snow in the Canadian high Arctic, Nature, 295, 137-140, 1982.

Logan, J.A., M.J. Prather, S.C. Wofsy and M.B. McElroy, Troposheric chemistry: A global perspective, Jour. of Geophys. Res., 86 (C-8) 7210-7254, 1981.

Lyons, W.B. and P.A. Mayewski, Glaciochemical investigations as a tool in the historical delineation of the acid precipitation problem, EPA Critical Assessment Document, in press.

Lyons, W.B. and P.P. Mayewski and N. Ahmad, Acidity of recent Himalayan snow, 38th Eastern Snow Conf., in press.

Niewodiczanski, J., J. Grabczak, L. Baranski and J. Rzepka, The attitude effect on the isotopic composition of snow in high mountains, Jour. of Glaciology, 27 (95), 99-112, 1981.

Oeschger, H., B. Stauffer, A. Neftel, J. Schwander and R. Zumbrunn, CO_2 content in the past deduced from ice-core analyses, Ann. Glaciol. 3, 227-232, 1982.

Qazi, N.A., Water Resources Development in Suru Basin (Ladakh), Vacant Press, Srinagar, India, 51 p. 1973.

Rahn, K., The chemical composition of the atmospheric aerosol, Technical Report, Grad. School of Ocean., URI, 265 p., 1976.

Rahn, K.A. and R.J. McCaffrey, Compositional differences between Arctic aerosol and snow, Nature, 200, 479-480, 1979.

Sequeria, R. and D. Keilkar, Geochemical implications of summer monsoonal rainwater composition over India, Jour. of App. Metero., 17, 1390-1396, 1978.

Stookey, L.L., Ferrozine - A new spectrophotometric reactant from iron, Anal, Chem., 42, 779-881, 1970.

Yue, G.K., V.A. Mohnen and C.S. Kiang, A mechanism for hydrochloric acid production in clouds, Water Air Soil Pollut., 6, 277-294, 1976.

Zall, D.M., D. Fisher and M.D. Garner, Photometric determination of chloride in water, Anal. Chem., 28, 1665-1668, 1956.

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