

## ACIDITY OF RECENT HIMALAYAN SNOW

Wm. Berry Lyons  
Paul A. Mayewski

Department of Earth Sciences  
University of New Hampshire  
Durham, NH 03824 U.S.A.

and

Nasseruddin Ahmad

Geology Department  
Aligarh Muslim University  
Aligarh, India

### ABSTRACT

Surface snows collected at various elevations in the Indian Himalayas were analyzed in the field for pH as part of a broader study of the chemistry. The pH values are lower than the predicted =5.6 for unpolluted precipitation. Analysis of  $\text{NO}_3^- + \text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$  indicate that these low pH values are not completely due to the presence of strong mineral acids. The strong correlation of pH with elevation (i.e. temperature) suggests that the low pH values are due to the snow being supersaturated with  $\text{CO}_2$ .

### Introduction

Precipitation in the Northern Hemisphere has recently been recognized to have hydrogen ion concentrations 10 to 500 times higher than expected for precipitation assumed to be in equilibrium with atmospheric  $\text{CO}_2$  (i.e., pH=5.6) (Likens and Bormann, 1974; Cogbill and Likens, 1974; Lewis and Grant, 1980). However there has been some controversy regarding the nature of the acidity of the precipitation sampled and if, indeed, the pH of North American precipitation has increased over time (Frohlinger and Kane, 1975; Miller and Everett, 1979; Lerman, 1979; Stensland, 1980; Sequeria, 1981). pH records have been constructed rather imperfectly in most locations due to differences in sampling, handling and analytical procedures used (Galloway and Likens, 1976, 1978; Galloway et al., 1979). It is thought that the lower pH's measured in Northern Hemispheric precipitation are due to the input of sulfur and nitrogen oxides from fossil fuel-burning (Likens and Bormann, 1974). Yet little data are available on the pH of precipitation in areas of the Northern Hemisphere remote from North American and European sources of anthropogenic sulfur emissions. This paper reports the pH of snow samples from the Indian Himalayas. It is hoped that the data presented will add to the information required to define baseline values of global pH in snow and ice and eventually add to the body of knowledge needed to correctly evaluate the pH of worldwide precipitation.

### Methods

The snow samples come from within and adjacent to the Ladakh position of the Indian Himalayas (Fig. 1) and from an elevation range of 3400 to 5512 m. The samples are all surface snows (0-5 cm depth). Those from the Kangri and Sentik Glaciers were collected

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from a more arid environment than the others. A series of closely spaced samples were collected on the Kangri Glacier. These samples were precipitated from the same snow fall event within two days of collection. All other sites contained snow that could have been as old as one month.

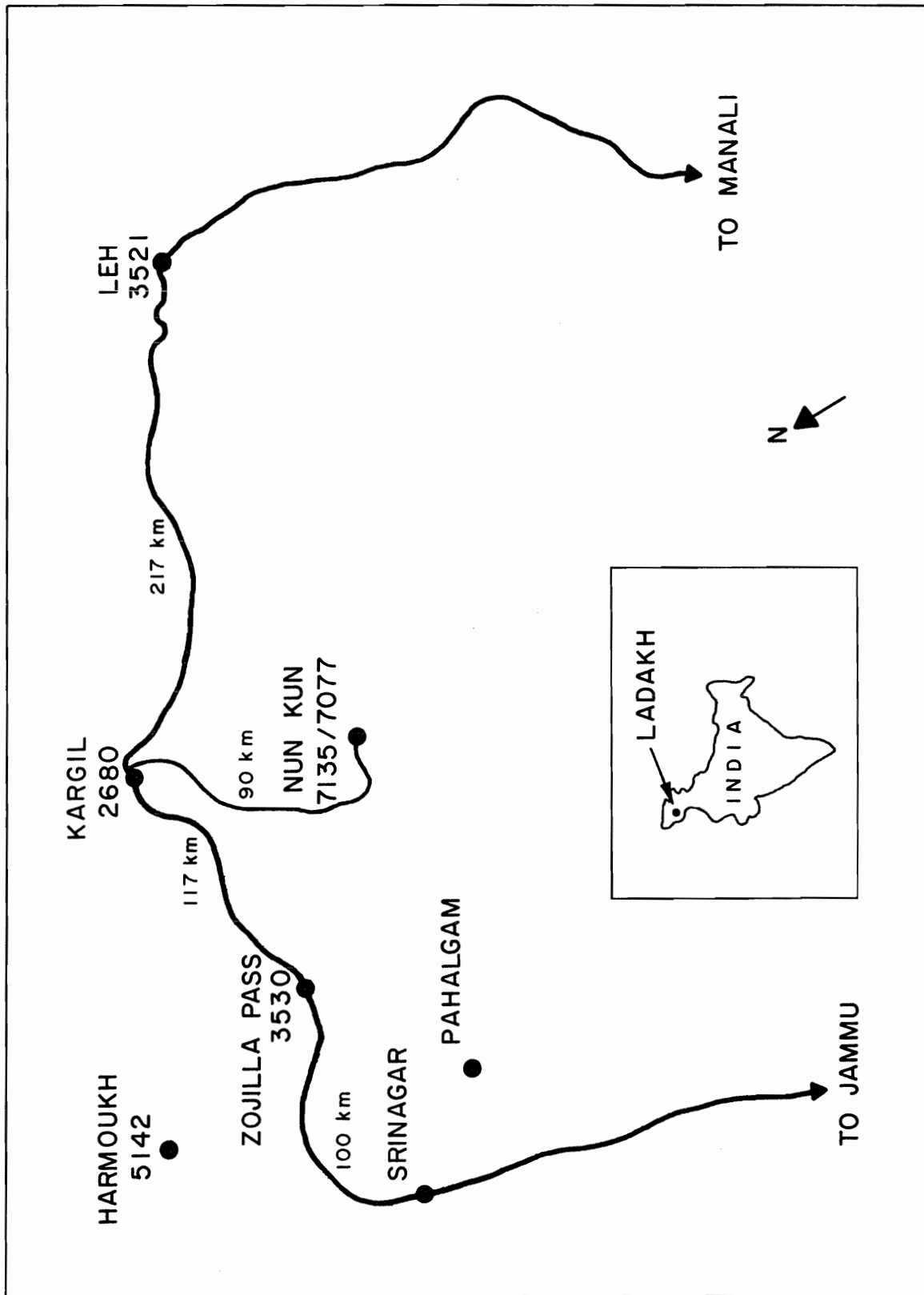


Figure 1. Sampling locations

A total of 23 samples were collected in 30 ml linear polyethylene (LPE) bottles and stored in these containers until analyzed. Thawed samples in their original sample bottles were analyzed for pH in the field within 36 hours of acquisition using an Orion Ionalyzer<sup>T.M.</sup> model 399A portable pH meter with an Orion 91-06 combination pH electrode after standardization using NBS buffers of pH = 4.01 and pH = 7.00. These samples were analyzed without stirring. The collection bottles were cleaned by washing in soap and water and then rinsed in tap water and finally rinsed at least 4-5 times in distilled-deionized water. The bottles were purchased for this use and were never exposed to acid solutions or acid vapors of any kind. Duplicate analyses were conducted on a number of snow and ice samples from this area while in the field, and the precision of the analysis reported as a coefficient of variation is  $\pm 0.05$  pH units.

In addition to the pH analysis, the eight closely spaced samples of recent snow on the Kangri Glacier were analysed colorimetrically for nitrate plus nitrite, reactive phosphate, ammonium, chloride, and sulfate. All analyses were performed utilizing a Technicon II - Auto Analyzer system and the methods of Gilbert and Loder (1977) for nitrate plus nitrite, ammonium and reactive phosphate, Zall et. al. (1956) for chloride and McSwain et. al. (1974) for sulfate. These data are shown in Table 1. The sub-samples analyzed for ammonium and reactive phosphate were acidified with ultrapure  $\text{HNO}_3$  to prevent loss of these constituents. Another subset was analyzed for chloride, sulfate and nitrate plus nitrite without the addition of a preservative. Galloway and Likens (1976) have shown that in precipitation samples chloride may be affected by long storage times without preservation but sulfate and nitrate are not.

Table 1: Chemistry of Kangri Glacier Snow samples.

Sample Elevation	$\text{Cl}^-$ $\mu\text{M}$	$\text{NO}_3^- + \text{NO}_2^-$ $\mu\text{M}$	$\text{NH}_4^+$ $\mu\text{M}$	$\text{SO}_4^{2-}$ $\mu\text{M}$	$\text{PO}_4^{3-}$ $\mu\text{M}$
5512	0.37	1.28	0.06	<4.5	0.05
5457	0.81	1.14	0.30	<4.5	0.05
5376	0.88	0.86	3.30	<4.5	0.07
5335	0.66	0.05	0.73	<4.5	0.10
5274	2.94	0.01	0.39	<4.5	0.56
5213	4.88	0.38	1.70	<4.5	0.53
5158	2.73	0.41	0.57	<4.5	0.79
5128	2.92	0.08	0.52	<4.5	0.52

### Results and Discussion

The pH values (Fig. 2) of all surface snows studied varied between 4.52 and 5.51. These pH values correspond to  $\text{H}^+$  concentrations that are higher than what is predicted for "unpolluted" precipitation. These data suggest that either the pH of pristine snow is lower than the quoted value of 5.6 for natural precipitation or even remote areas in the Northern Hemisphere away from anthropogenic atmospheric acid emissions have been affected by the global consumption of fossil fuel. Global budgetary considerations, however, indicate that a high percentage of anthropogenically introduced acid is removed within 1000 km of its source (Granat et al., 1976). Two rain samples from two different storm events 9 days apart at two different remote locations in Kashmir were collected in addition to the snow samples and analyzed utilizing the method previously discussed. The pH's of these samples were 5.34 and 5.78 supporting the notion that the precipitation in this area is not highly affected by man's activities.

Ionic budget considerations after Granat (1972) indicate that in the Kangri samples, strong mineral acids are not controlling the pH of the snow (Table 2). Recent work has suggested that there can be little relationship between pH and sulfate and nitrate in pre-

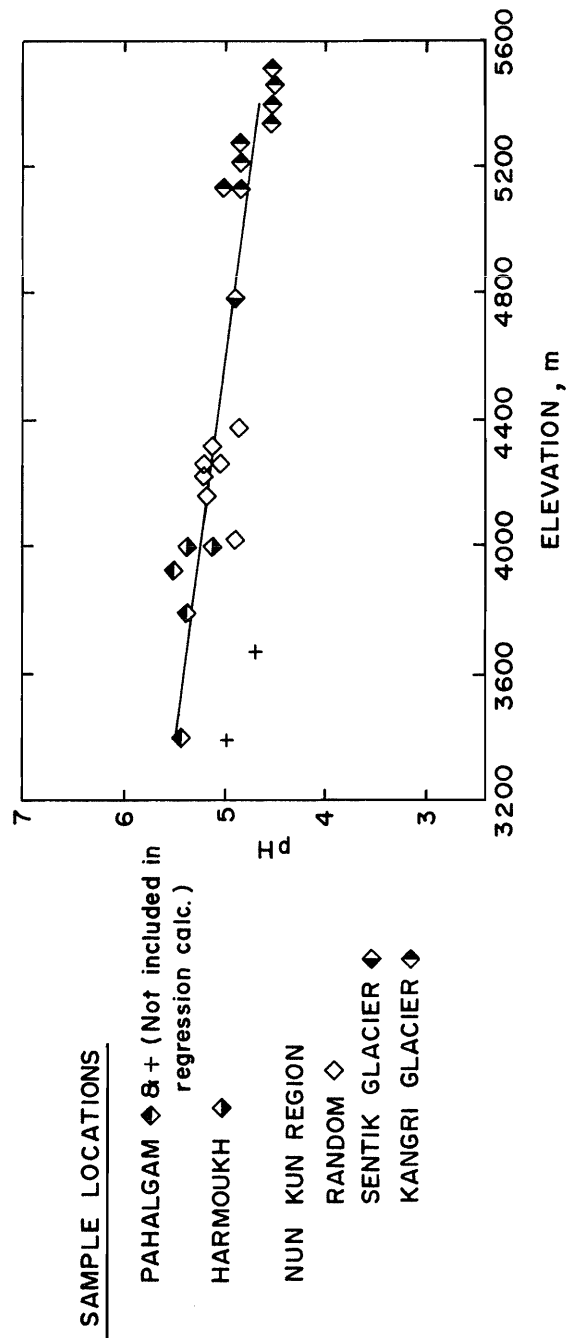


Figure 2. pH versus elevation

precipitation in various areas of the world (Stensland, 1980; Sequeria, 1981). This is due to the fact that all the nitrate and sulfate in the precipitation may not be present as acid but may be neutralized by other cations such as ammonium, calcium and magnesium. This may be particularly true for frozen precipitation (Bowersox and dePena, 1980), where weaker correlations between pH and strong mineral acids have been observed.

Table 2  $H^+$  values in microequivalents for the eight Kangri Glacier surface snow samples.

Elevation (m)	$\cdot H^+$	$*H^+$	$\Delta H^+$
5512	10	28	18
5457	11	29	18
5376	11	28	17
5335	9	28	19
5274	12	14	2
5213	11	15	4
5158	12	8	+4
5128	12	15	3

$\cdot H^+$  = calculated from ionic balance

$*H^+$  = from measured pH values

A number of workers (Scholander et. a., 1961; Berner et. al., 1978; Stauffer and Berner, 1978) have shown that polar ice and snow have higher concentrations of  $CO_2$  than that of the ambient atmosphere. Only recently have these higher than ambient  $CO_2$  values in ice been interpreted as trapped or absorbed  $CO_2$  in the ice lattice as opposed to equilibrium atmospheric gas values (Berner et. al., 1978; Delmas et al., 1980). Berner et al. (1978) have shown that most of the  $CO_2$  found in the polar ice was already present in freshly fallen snow.

It is possible that the pH's observed by us are due primarily to the dissolution of previously incorporated snow  $CO_2$  into the melted sample thus forming a solution supersaturated with respect to atmospheric  $CO_2$ . The combination pH electrode utilized by us fits snugly into the 30 ml collection bottle. This snug fit allows little to no contact with the ambient atmosphere so that the air space in the bottle over the sample is essentially in equilibrium with the water sample not the atmosphere. This is an extremely important fact for it allows us to measure as closely as possible the actual contribution of  $H_2CO_3$  to the pH of the snow under field conditions. Recently, Brosset (1980) has reported lake samples collected under ice cover that are supersaturated with respect to atmospheric  $CO_2$  even after bubbling with  $N_2$ . This coupled with the fact that the calculated ionic balances indicate excess  $H^+$  is not due to the strong mineral acids  $H_2SO_4$  and  $HNO_3$  supports the notion that volatile weak acids such as  $H_2CO_3$  are controlling the pH in these samples. For example, if the ionic balance,  $H^+ = Cl^- + 2 SO_4^{2-} + NO_3^- - NH_4^+$ , is considered in all samples, in all but one sample there is a strong acid hydrogen deficiency compared to the measured pH values in microequivalents (Table 2). These  $\Delta H^+$  values must be considered minimum values because: 1) undoubtedly a portion of the  $Cl^-$  is balanced by  $Na^+$  and 2) a value of  $4.5 \mu mol SO_4^{2-}$  was used in the calculations when all the  $SO_4^{2-}$  concentrations in these samples were below this value (our detection limits). Calculations indicate that the difference in  $H^+$  at the 5128 m to 5274 m can be explained by a less than ten fold increase in  $CO_2$  above ambient levels. These values are similar to those observed in polar ice (Berner et al, 1978; Delmas et al., 1980). The  $\Delta H^+$  above 5335m can be explained by a fifty-fold  $CO_2$  excess. The different pH values observed by us may then reflect as suggested by Berner et al. (1978) a difference in temperature at the time of formation of the snow crystal.

Little information is available concerning the pH of snow in remote alpine regions. Delmas and Aristarain (1979) have observed values ranging from 7.0 to less than 5.0 in a glacier ice core from the French Alps. The lowest pH's were observed in the snow which had accumulated in the past 6 years. These lower pH's were thought to be due to the addition of strong mineral acids from fossil-fuel burning from nearby industrial centers. However, actual pH measurements were not made and their strong acid titrations measurements may not have detected volatile weak acids such as  $H_2CO_3$  and hence may not be comparable to our data. Clement and Vaudour (1967) have reported pH values of snow from the southern French Alps in the range of 4.2 to 7.0 noting changes in pH with time, type of snow and elevation. These authors have suggested that, in general, low pH's correspond to winter snow accumulation, freshly fallen snows and higher elevations snows since all these conditions favor increased  $CO_2$  concentration. Miller (1979) has observed a similar relationship in Hawaiian rains with lower pH's observed at higher elevations. Although Miller suggested that this phenomenon was due to mid-troposphere transport of acid-forming pollutants, our anionic data indicate this is not the case in the Indian Himalayas.

In conclusion when pH is plotted versus elevation for the Himalayan surface snow sample in this study (Fig. 2), an association of low pH with high elevation (i.e., low temperature) becomes apparent.

The greatest departure from the observed trend comes for pH's at lower elevations where melting and refreezing of surface samples is most likely and pH overprinting is possible. Deleting two pH measurements in the low elevation range based on the likelihood that they may be overprinted yields a rather strong correlation ( $r = -0.88$ ). Clement and Vaudour (1967) found, over a smaller elevation range and utilizing fewer samples, a similar pH-elevation dependence. We suggest as did they, that the majority of the pH vs. elevation trend observed is a function of  $CO_2$  saturation and its dependence on temperature. If this is so, snow from high elevation, remote areas unaffected by man could be used as a paleotemperature indicator as well as a baseline for interpreting global pH values of snow and ice; if collected at sites in which no melting and overprinting has occurred.

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## References

- Berner, W., Stauffer, B. and Oeschger, H., 1978, Past atmospheric composition and climate, gas parameters measured on ice cores, *Nature*, 276: 53-55.
- Bowersox, V.C. and dePena, R.G., 1980, Analysis of precipitation chemistry at a central Pennsylvania site, *Jour. Geophys. Res.*, 85: 5614-5620.
- Brosset, C., 1980, A method for evaluating the acid-base balance in natural waters, *Water, Air and Soil Pollut.*, 14: 251-265.
- Clement, P. and Vaudour, J., 1967, Observations on the pH of melting snow in the southern French Alps, in: Arctic and Alpine Environments, ed. (Wright, H.E. and Osburn, W.H.) Indiana University Press, 205-213.
- Cogbill, C.V. and Likens, G.E., 1974, Precipitation in the northeastern United States, *Water Resour. Res.*, 10: 1133-1137.
- Delmas, R. and Aristarain, A., 1978, Recent evolution of strong acidity of snow at Mt. Blanc, in: Atmosphere Pollution, ed. (Benarie, M.M.) Elsevier Scientific, 233-237.
- Delmas, R.J., Ascencio, J.-M. and Legrand, M., 1980, Polar ice evidence that atmospheric CO<sub>2</sub> 20,000 yr BP was 50% of present, *Nature*, 284: 155-157.
- Frohlinger, J.O. and Kane, R., 1975, Precipitation: It's acidic nature, *Science*, 189: 455-457.
- Galloway, J.N. and Likens, G.E., 1976, Calibration of collection procedures for the determination of precipitation chemistry, *Water, Air and Soil Pollut.*, 6: 241-258.
- Galloway, J.N. and Likeus, G.E., 1978, The collection of precipitation for chemical analysis, *Tellus*, 30: 71-82.
- Galloway, J.N., Cosby, B.J. and Likeus, G.E., 1979, Acid precipitation: Measurement of pH and acidity, *Limnol. Oceanogr.*, 24: 1161-1165.
- Glibert, P.L. and Loder, T.C., 1977, Automated analysis of nutrients in seawater: A manual of techniques, W.H.O.I. Tech. Rpt. 77-47, 46 pp.
- Granat, L., 1972, On the relation between pH and the chemical composition in atmospheric precipitation, *Tellus*, 24: 550-560.
- Granat, L., Hallberg, R.O. and Rodhe, H., 1976, Nitrogen, Phosphorus and Sulfur - Global Cycles, SCOPE Rpt. 7, Ecol. Bull. #22, Stockholm, Sweden, 192 pp.
- Lerman, A., 1979, Geochemical Processes Water and Sediment Environment, John Wiley and Sons, New York, 481 pp.
- Lewis, Jr., W.M. and Grant, M.C., 1980, Acid precipitation in the western United States, *Science*, 207: 176-177.
- Likens, G.E. and Bormann, F.H., 1974, Acidrain: a series regional environmental problem, a serious regional environmental problem, *Science*, 184: 1176-1179.
- McSwain, M.R., Watrons, R.J. and Douglass, J.E., 1974, Improved methlthymol blue procedure for automated sulfate determinations, *Anal. Chem.*, 46: 1329-1331.
- Miller, J.M., 1979, The acidity of Hawaiian precipitation as evidence of long-range transport of pollutants, presented at the WMO Symposium on Long Range Transport of Pollutants, Sofia, Bulgaria.

- Miller, M.L. and Everett, G.E., 1979, A detailed analysis of the scientific evidence concerning acidic precipitation, Am. Chem. Soc. Meeting, Washington, D.C., 155-157.
- Scholander, P.F., Hemmingsen, E.A., Coachman, L.K. and Nutt, D.C., 1961, Composition of gas bubbles in Greenland icebergs, Jour. Glaciol. 3: 813-822.
- Sequeira, R., 1981, Acid rain: Some preliminary results from global data analysis, Geophys. Res. Lettrs., 8: 147-150.
- Stauffer, B. and Berner, W., 1978, CO<sub>2</sub> in natural ice, Jour. Glaciol., 21: 291-300.
- Stensland, G.J., 1980, Precipitation chemistry trends in the northeastern United States, in: Polluted Rain, ed. (Toribara, T.Y., Miller, M.W. and Morrow, P.E.), Plenum Press, New York, 87-108.
- Zall, D.M., Fisher, D. and Garner, M.D., 1956, Photometric determination of chloride in water, Anal. Chem., 28: 1665-1668.