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The Glaciochemistry of Snowpits from Quelccaya Ice Cap, Peru, 1982

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ABSTRACT

We present glaciochemical data from a pilot study of two snow-pits from Quelccaya ice cap, Peruvian Andes. These are the first samples to be analyzed from Quelccaya for nitrate and sulfate by ion chromatography (IC), for nitrate-plus-nitrite, reactive silicate and reactive iron by colorimetry, and for sodium by atomic absorption spectrophotometry. The 3 m pits used in this study represent a one year record of mass accumulation and the 29 samples collected provide the first glaciochemical data from this area which can be compared with glaciochemical studies from other locations.

Reactive iron, reactive silicate and sodium, and the profiles of >0.63μm microparticles from Thompson and others (1984) are coincident, suggesting that transport and deposition into this area of each species are controlled by similar processes. The common source is probably local, resulting from crustal weathering. In general, the reactive silicate values are lower than those observed in other alpine glacier ice. The highest sulfate and nitrate values were observed in the upper few centimeters of the snow-pit. Most of the sulfate concentrations were less than 3 μM and are similar to values obtained for fresh surface snows from Bolivia (Stallard and Edmond 1981). Since biological gaseous emissions are thought to be the major source of sulfur and nitrogen to the atmosphere over the Amazon basin, the sulfate and nitrate fluctuations may be due to seasonal biological input and/or seasonal shifts in wind direction bringing material to Quelccaya.

With only one exception, the colorimetric nitrate-plus-nitrite data were higher than the IC nitrate data. Unfortunately, the IC analyses were conducted 81 d after the colorimetric analyses. The difference between the two data sets could be attributable to the following: (1) the colorimetric technique may yield erroneously high results as suggested for polar ice by Herron (1982), (2) the IC technique yields erroneously low results due, in part, to the possible exclusion of nitrate concentrations, and/or (3) nitrite was lost via biological removal during the 81 d period before the IC analyses. If the IC data are correct, the mean nitrate value is 0.4μM (n = 29). This value is similar to those reported from pre-industrial aged polar ice (Herron 1982). If the colorimetric mean value (1.1 μM) is correct, it is similar to colorimetrically determined values from other high-elevation alpine ice (Lyons and Mayewski 1983).

INTRODUCTION

The chemistry of polar ice and snow has long been employed as a paleo-atmospheric surrogate (Murozumi and others 1969, Herron 1982, Boutron and Patterson 1983). Only recently have studies of high-altitude temperate and tropical alpine glaciers been undertaken to determine if these types of permanent ice/snow fields provide detailed records of past atmospheric conditions (Lyons and Mayewski 1983, Haebler and others 1983, Thompson and others 1984, Mayewski and others 1984). We present glaciochemical data from samples collected in two 3-m snow pits from Quelccaya ice cap, Peru. Although these samples represent only one year of precipitation accumulation, these are the first glaciochemical data from a South American ice field. These data suggest that chemical records reflecting changes in atmospheric chemistry, and therefore atmospheric circulation and climate dynamics, may be retrieved from certain high-elevation glaciers. Such glaciers must experience the physical environment and local climatic conditions essential to the preservation of annual stratigraphic and geochemical records.

The Quelccaya ice cap (5670 m) and the summit sampling location, along with complementary studies on its modern climate, have been discussed in detail previously (Hastenrath 1978, Thompson and others 1979, 1984, Thompson 1980, Mosley-Thompson 1982). Therefore this information will not be repeated here.

METHODOLOGY

Samples were collected in July 1982, using pre-cleaned plexiglass scrapers and distilled-deionized washed polyethylene bottles (30 ml), and immediately inserted into polyethylene bags. Groups of bagged bottles were then placed in another plastic bag for transport. Personnel wore polyethylene gloves and particle masks.

Sodium was analyzed by flame atomic absorption spectrometry using a Perkin-Elmer model 2280. Cesium chloride solution was added to the 2 ml sample for a final concentration of 2% to control ionization. Reactive silicate was determined colorimetrically using 5 ml samples on an AutoAnalyzer II (Gilbert and Loder 1977) while reactive iron was analyzed colorimetrically (Stookey 1970) using low-volume 10 cm cells. For the iron analysis 5 ml aliquots were added to acid-washed test tubes containing 0.03 ml reducing agent, 0.20 ml Ferrozine solution and 0.25 ml buffer solution. Reactive silicate and reactive iron are defined as the amount of silicate and iron reacting colorimetrically after an addition of Baker Ultrex nitric acid (Mayewski and Lyons 1982). The above analyses were made in the laboratories of the Department of Earth Sciences at the University of New Hampshire.

Sulfate and nitrate were determined simultaneously on a Dionex 10 ion chromatograph (IC) at 0.3 μS
concentration using an ion chromatography column with an elution time of 7.5 m, the eluent consisting of 0.003 mol NaHCO₃ and 0.002 mol Na₂CO₃. Samples were injected with a Hamilton Teflon tipped gas-tight syringe into a 1 ml loop. The analysis was performed in the Class 100 clean laboratory at the Mellon Institute, Pittsburgh, Pennsylvania. In addition, nitrate-plus-nitrite was analyzed in an AutoAnalyzer II (Glibert and Loder 1977).

Analytical error (±1 standard deviation) was estimated from the standard deviation in replicate runs of standards and samples. These are listed in Table I. Bottle blanks were created by filling washed sample bottles with Milli-Q in the laboratory. These bottles were then processed as samples and underwent identical handling and analytical procedures. Blank concentration means are also listed in Table I.

| TABLE I. ANALYTICAL ERRORS, LISTED FOR STANDARDS, SAMPLES AND BLANKS |
|-----------------------------|-----------------------------|-----------------------------|
| Analytical error (µM)       | Standards (µM)              | Samples (µM)                | Blanks (µM)                |
| Na                          | 0.03                        | 0.09                        | 0.13                       |
| Si                          | 0.02                        | 0.03                        | 0.04                       |
| Fe                          | 0.001                       | 0.01                        | 0.02                       |
| SO₄                         | 0.02                        | 0.04                        | 0.06                       |
| NO₃                         | 0.01                        | 0.01                        | 0.01                       |
| NO₃+NO₂                     | 0.03                        |                             | 0.03                       |

RESULTS AND DISCUSSION

Glaciochemical results are plotted with depth in Figures 1 and 2. Only reactive silicate, reactive iron, and sodium were measured in both pits; therefore we will only discuss the results of pit #1 in detail. As mentioned above, although these data only represent a year's accumulation, some general statements can be made regarding chemical distribution with depth and its relationship with climatic events.

Reactive silicate, reactive iron, and sodium profiles are similar to that of the >0.63 µm microparticle profile in both pits (e.g., compare Figure 1 in this paper with figure 3 from Thompson and others 1984). Therefore we assume that these three chemical species have a common primary source from crustal weathering. This deposition is at a maximum during the dry austral winter (Thompson and others 1979, 1984), due to a combination of (1) a dominant wind direction from the west and north-west, transporting material from the high, dry Altiplano, (2) slightly higher mean wind speeds during this season, and (3) the seasonal difference in snow mass accumulation. Thus we suggest that higher concentrations of crustal material are deposited during the dry season when they are not diluted by snow accumulation. This seasonal microparticle (and one would expect reactive silicate, reactive iron and sodium) signal is preserved on Quelccaya to bedrock (Thompson and others 1984). During the dry, more windy season, the predominant wind is from the west and north-west, so some of the sodium deposited at this time may be marine in origin.

If the six values >1 µM for reactive silicate and the six values >2 µM for reactive iron are included, the mean values from snow pit #1 (n = 29) are 1.71 and 1.79 µM, respectively. The six highest reactive silicate and iron values are coincident and represent June to August, and (3) the seasonal difference in snow mass accumulation. Thus we suggest that higher concentrations of crustal debris are deposited during the dry season when the microparticle concentrations are also the highest. If those six samples are disregarded, the means decrease dramatically to 0.39 and 0.46 µM, respectively. Stallard and Edmond (1981) reported values of 0.3 µM (austral summer) and 0.6 µM (austral winter) for surface snows at Chacaltaya Observatory, Bolivia (5222 m). These sparse data from the Bolivian Andes suggest higher crustal debris accumulation during the dry winter season. The values are lower than those observed by us for other alpine glaciers (Butler and others 1980, Mayewski and Lyons 1982, Mayewski and others 1984), indicating that Quelccaya ice cap receives less crustal weathering
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The sulfate values obtained in this study are low (<3 µM) but are higher than those reported for polar snow (Herron 1982). They compare well with those of Stallard and Edmond (1981) and also are within the range of the mean precipitation values of 5.1 µM for the Amazon basin (Stallard and Edmond 1981) and of 1.6 µM for the Venezuelan Amazonas (Galloway and others 1982). These data indicate, at least in a preliminary sense, that the influx of sulfate into the area is different to the other chemical species under investigation.

Recent studies have indicated that tropical rain forests of the Amazon basin are a major source of atmospheric nitrogen and sulfur (Lawson and Winchester 1979, Stallard and Edmond 1981). A variation in this biogenic source term may therefore alter the concentrations of both nitrogen and sulfur in the Quelccaya precipitation. The time and amount of clear cutting and burning of tropical forest may also affect the nitrogen and sulfur precipitation chemistry in this area (Galloway and others 1982).

The IC nitrate data in all but one case for the Quelccaya data were lower than the colorimetrically determined nitrate-plus-nitrite values (Fig.2). Based on the precision of these analyses (Table I) this discrepancy is real. Obviously this is not a trivial problem. Most of the previous precipitation data have been analyzed for nitrate by the colorimetric technique. Recently more laboratories have switched to IC instrumentation and thus it is critical to determine if data sets generated by the two techniques are compatible. Unfortunately the IC analyses were undertaken 81 d after the nitrate-plus-nitrite analyses. The samples arrived at the

![Fig. 2. Concentrations in µM of sulfate, nitrate-plus-nitrite and nitrate plotted against depth in snow-pit #1, Quelccaya ice cap.](image)

![Fig. 3. Microparticle data (>0.63 µm) plotted against depth in snow-pit #1, Quelccaya ice cap.](image)
laboratory in an unfrozen state and were immediately frozen (-20°C). Upon thawing, the nitrate-plus-nitrite analysis was the first to be undertaken. After this analysis was completed, the samples were again refrozen and finally thawed again and analyzed 81 d later for nitrate by means of IC. The difference between the two data sets could be due to one of three possibilities: (1) the colorimetric technique yields erroneously high results, or (2) the IC technique yields erroneously low results. (3) loss of nitrate occurs during the interval between the two different analyses. Herron (1982) has suggested that his observed differences between nitrate data from Dye 3, Greenland and South Pole, Antarctica and those of other investigators reflect real differences between these two techniques. Using IC, ion chromatography, Herron’s data were consistently lower than the other studies which used cadmium reduction colorimetry. It is possible that either the colorimetric technique, as suggested by Herron (1982), yields higher than “true” values, or that the IC techniques yield lower than “true” values for nitrate.

During IC runs nitrate standards were not analyzed. On a limited number of IC samples a small peak, probably nitrite, was observed, but in most cases this peak was obscured by the much larger chloride peak. Harding and Miller (1982), employing IC instrumentation, have analyzed precipitation samples from Hawaii for both nitrate and nitrite. The concentrations were similar. To our knowledge these are the first data indicating that nitrite is an important component of tropical/subtropical precipitation. It is tempting to interpret the difference between the two techniques or whether this is an analytical artefact or a problem of sample handling is unknown at present, and (6) further glaciochemical studies on the Quelccaya ice cap may provide an important paleoclimatic record.

CONCLUSIONS

The major conclusions of this study are as follows:

1. reactive silicate, reactive iron and sodium profiles are coincident with the >0.63 μm microparticle profiles indicating a common source of weathered or regolith material.

2. the above-mentioned chemical species reach their highest concentrations in the dry season (the austral winter) indicating dependency on wind direction and/or snow accumulation rate.

3. nitrate and sulfate concentrations in the Quelccaya snow-pit are highest in the surface and are similar to those reported for precipitation around the Amazon basin.

4. the source of the N and S in Quelccaya precipitation may be primarily biogenic input from the Amazon basin.

5. nitrate values determined by ion chromatography are lower than nitrate-plus-nitrite values determined by automated colorimetry; whether this is an analytical artefact or a problem of sample handling is unknown at present, and (6) further glaciochemical studies on the Quelccaya ice cap may provide an important paleoclimatic record.

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