

# WEATHERING AND MAJOR-ION CHEMISTRY IN THE HERBERT, EAGLE, AND MENDENHALL GLACIAL MELTWATERS

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## INTRODUCTION

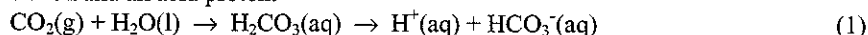
Although extremely low temperatures tend to reduce chemical weathering rates, other factors are enhanced in a wet-based glacial environment. These include large amount of reactive surface area of fine-grained rock flour, the presence of microparticles on the surfaces of freshly comminuted grains, and the high flushing rates of dilute, poorly-buffered waters through these environments—all of which serve to increase rates of chemical weathering (Sharp et al., 1995a).

This chemical weathering may contribute, especially during periods of glaciation, to the reduction of global CO<sub>2</sub> levels (Raymo and Ruddiman, 1992). Studies measuring the solute flux from temperate glacial basins have shown that chemical denudation rates exceed the continental average (Sharp et al., 1995a). Of the total solute flux a fraction is derived from the weathering of silicates, primarily through acid hydrolysis reactions (Tranter et al., 1993). This type of silicate weathering involves the consumption of atmospheric CO<sub>2</sub>, a primary greenhouse gas. Thus the drawdown of atmospheric CO<sub>2</sub> by chemical weathering in glacial environments is of particular interest in evaluating glaciation as a feedback mechanism for climate change (Raymo and Ruddiman, 1992).

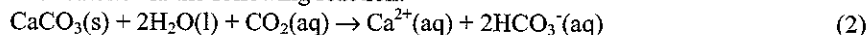
This study uses the solute characteristics of meteoric and meltwater samples within the drainage basins of the Herbert, Eagle, and Mendenhall glaciers to assess chemical weathering rates.

## SOURCES OF SOLUTE:

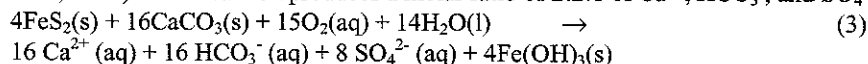
Natural waters acquire solutes predominantly by the chemical weathering of minerals. Two types of reaction have been indicated as being particularly relevant to the glacial environment (Sharp et al., 1995a). Carbonate hydrolysis is the reaction whereby carbonate minerals dissolve in the presence of acid protons (H<sup>+</sup>). In dilute natural waters, dissolved CO<sub>2</sub> forms carbonic acid which then dissociates into a bicarbonate ion and an acid proton:



Thus, dissolved CO<sub>2</sub> can be the proton donor for a hydrolysis reaction (Raiswell, 1984), leading to the dissolution of calcite via the following reaction:



This process, called a carbonation reaction (Sharp et al., 1995a), releases a 2:1 molar ratio of HCO<sub>3</sub><sup>-</sup> to Ca<sup>2+</sup> and consumes dissolved CO<sub>2</sub> until saturation with respect to calcite is achieved. Carbonate dissolution can also occur as a coupled reaction with sulfide oxidation, where the sulfide oxidation acts as a proton source (Tranter et al., 1993). This reaction produces a molar ratio of 2:2:1 of Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, respectively:



Carbonation reactions may be limited in subglacial environments by the amount of CO<sub>2</sub> initially dissolved in the water, since the reaction consumes dissolved CO<sub>2</sub> quickly and subglacial waters become depleted as they are removed from contact with the air. Thus the combined sulfide oxidation/carbonate dissolution (SO/CD) reaction may control weathering, as it does not require an external proton source (Tranter et al., 1997). Carbonate hydrolysis as well as the coupled SO/CD reactions are rapid, and exert a strong influence on solute composition of waters. Indeed, even trace amounts of carbonates in bedrock have been shown to dominate the solute load of glacial meltwaters (Blum et al., 1998).

Another contributor to the solute load in natural waters is the wet and dry deposition of aerosols (Drever, 1997). Due to the proximity of the ocean, sea-spray aerosols are a likely contributor of Cl<sup>-</sup> and Na<sup>+</sup>, as well as other minor ions. Cl<sup>-</sup> is a conservative species (Sharp et al., 1995b) and all Cl<sup>-</sup> in our waters is assumed to be from sea-spray input.

## METHODS

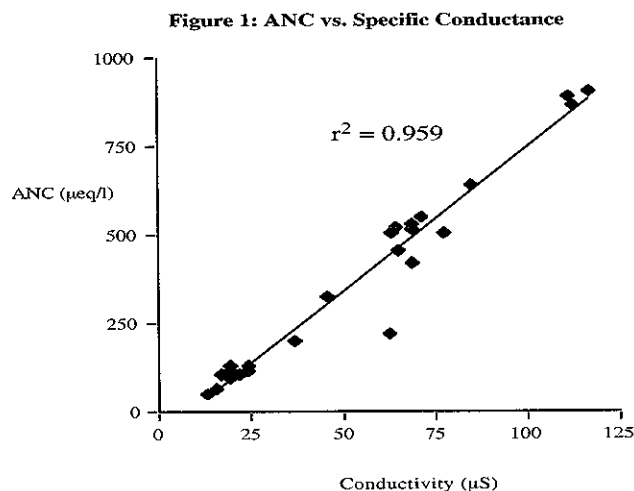
### FIELD METHODS:

Water samples were taken from both meteoric (non-glacial) and meltwater streams after field measurements of temperature and pH were made. Meltwater samples were taken from subglacial outlets and represent the bulk meltwater composition. Ice, rainwater, and rock samples were also collected from all three glacial environments. Water samples were filtered within 36 hours, and titrated for Acid-Neutralizing Capacity (ANC) within 4 days, using the Gran titration method.

### LABORATORY METHODS:

Filtered, acidified aliquots were analyzed on a Leeman Labs Inductively-Coupled Plasma Spectrometer (ICP-AES) for cation and silica content (Ca, Mg, Sr, Ba, Fe, and Si), with a precision of  $\pm 4\%$ . Filtered, unacidified samples were analyzed for anions (F, Cl,  $\text{SO}_4$ ,  $\text{PO}_4$ ,  $\text{NO}_3$ ) on a Dionex Ion Chromatograph (IC) with a precision of  $\pm 3\%$ . Conductivity was measured on all samples using a Corning conductivity meter. Filtered, acidified samples were also run on a Dionex IC for K, Na, and  $\text{NH}_4$ , with a precision of  $\pm 5\%$ .

Charge balances were calculated and, for nearly all samples with conductivities above  $10\mu\text{S}$ , the balances were within 15%. Representative chemistries of each water type were input to the geochemical modeling program SOLMINEQ to determine the saturation state of certain minerals. Selected aliquots were sent to the University of Michigan stable isotope laboratory for  $\delta^{18}\text{O}$  analysis.



## RESULTS

### Overview:

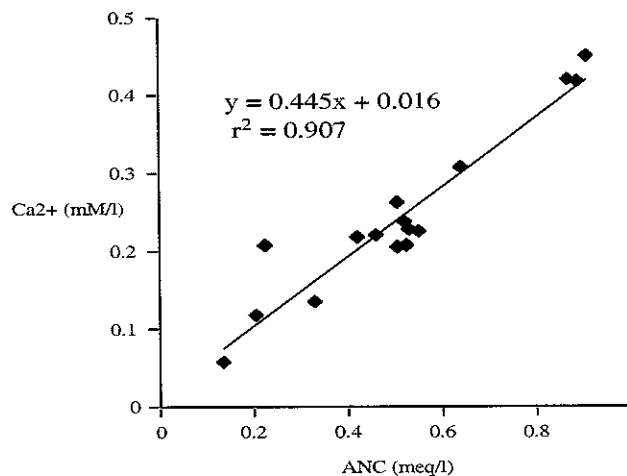
A scatter-plot of conductivity vs. ANC (Figure 1) shows a separation between meltwaters (bottom-left cluster) and meteorics (higher values). It also suggests that the major anion for both water types is bicarbonate ( $\text{HCO}_3^-$ ), because at the pH levels in these streams

(generally 6-8), the carbonate ion ( $\text{CO}_3^{2-}$ ) is a negligible fraction.

### METEORIC WATERS:

It is clear that the SO/CD coupled reactions are not the major solute-generating process in meteoric waters because  $\text{SO}_4^{2-}$  shows a relatively poor correlation with total solute load. Additionally, sulfate levels are much lower than the 2:1  $\text{HCO}_3^-$ :  $\text{SO}_4^{2-}$  molar ratio produced by SO/CD. And most convincingly, there appears to be no definite connection between  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ , so the dominant weathering reaction must affect  $\text{Ca}^{2+}$  but not  $\text{SO}_4^{2-}$ .

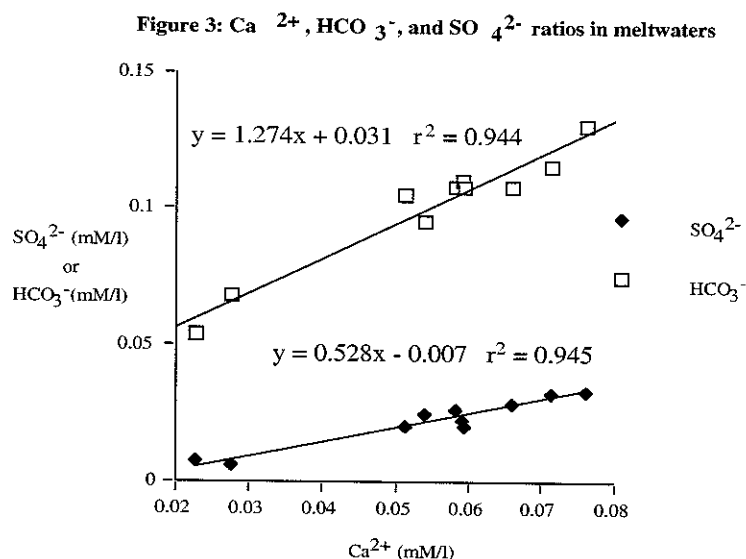
**Figure 2:  $\text{Ca}^{2+}$  vs.  $\text{HCO}_3^-$  in meteorics.**



A scatter-plot comparison of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  in meteoric samples shows a very close 2:1 molar ratio (Figure 2). This suggests that the carbonation reaction shown in equation (1) controls these solutes. In the meteoric environment, water is in constant contact with the atmosphere, which maintains dissolved  $\text{CO}_2$  concentrations. In addition, sulfides present in the meteoric environment will develop a coating of oxides, inhibiting the coupled SO/CD reactions.

### MELTWATERS:

The combined SO/CD reactions provide a major control on meltwater solute concentrations. This can be illustrated by a conceptual mass-balance:  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  are observed in a very close 2:1 molar ratio (Figure 3), and a scatter-plot of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  appears to describe a good 3:4 molar ratio (also Figure 3). Combining these gives approximate molar ratios of 3:6:8 of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , and  $\text{HCO}_3^-$ , respectively.



$\text{SO}_4^{2-}$  is a relatively conservative species in glacial environments (Sharp et al., 1995b), since it has only two major sources: snowpack melting (see Sharp et al., 1995a) and SO/CD coupled reactions. The melting of snowpack (as opposed to ice) is theorized to be the major source of water for subglacial waters (Lamb et al., 1995), so 1 molar unit of  $\text{SO}_4^{2-}$  is designated as snowpack sulfate input. Removal of this input brings the ratio down to 2:6:8 ( $\text{SO}_4^{2-}$  :  $\text{Ca}^{2+}$  :  $\text{HCO}_3^-$ ). The rest of the  $\text{SO}_4^{2-}$  in this model comes from combined SO/CD reactions, which release a

ratio of 1:2:2 of these same ions. Thus all  $\text{SO}_4^{2-}$  is removed, as well as proportionate amounts of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ . The remaining  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$ , in a 2:4 ratio, is accounted for by carbonation reactions. Carbonation reactions are favored above possible silicate dissolution (e.g. anorthite also releases  $\text{Ca}^{2+}$  and creates  $\text{HCO}_3^-$ ) because carbonate dissolution occurs orders of magnitude faster than silicate weathering (Drever, 1997).

### MINERAL EQUILIBRIA:

Representative samples of both meteoric and meltwaters were input to the computer model SOLMINEQ to determine saturation values of minerals. While the waters generally remain unsaturated with respect to calcite, the calcite saturation indices are consistently and significantly higher than those of most other dissolved phases. This supports the emphasis placed on carbonate weathering as the dominant solute-acquiring process in these waters.

Quartz, however, consistently displayed saturation values equal to or higher than calcite. These high quartz saturation values suggest that, despite the dominance of carbonate dissolution products in the solute load, significant silicate weathering is occurring in these glacial systems. This is apparent in the dissolved silica levels in both water types, since any non-trace amount of silica indicates that silicate weathering must be occurring; that is, aerosol and snowpack input cannot explain dissolved silica. In meteoric waters, silica makes up an average of 7.6% of the total solute load, and in meltwaters an average of 4.8%.

While normalized silica levels are higher in meteoric waters than in meltwaters, the reverse is seen for the  $K^+$  ion. Meteoric waters display an average of 2% of all solutes as  $K^+$ , where meltwaters show 5%. This increased amount of  $K^+$ , especially in light of the lower silica levels in meltwaters, suggests that subglacial biotite weathering is an important process. Glacial grinding promotes the release of  $K^+$  from inter-layer sites to solution in biotite grains, and this has been demonstrated to be an effective source for solutes in the glacial environment (Anderson et al., 1997).

## **OXYGEN ISOTOPES:**

Meteoric water samples show  $\delta^{18}O$  (VSMOW) values from  $-14.02$  to  $-14.47\text{‰}$ , and meltwaters range from  $-15.82$  to  $-16.32$ . A bulk rainwater sample was measured at  $-10.42\text{‰}$ . As this is mid-summer rain, the inferred annual range in precipitation values is from approximately  $-10\text{‰}$  (summer rain) to  $-16\text{‰}$  (winter snow). These precipitation values are consistent with those seen in similar locations around the world (IAEA/WMO, 1998).

The snow that falls on the icefield and eventually forms the glaciers is deposited primarily in winter months, and elevation effects may cause further depletion in  $\delta^{18}O$  values. Thus, snowpack and glacial ice are assumed to lie at approximately  $-16\text{‰}$   $\delta^{18}O$ —that is, they should be similar to the range seen in meltwaters. Meteoric waters are fed by snowmelt draining off the mountains as well as by rainfall runoff and infiltration. If the melting snow (approx.  $-16\text{‰}$ ) mixes with even a small amount of heavier spring or summer rains (as heavy as  $-10\text{‰}$ ), a composite value would result. This is a likely scenario for the meteoric water samples, which display values of  $-14.02$  to  $-14.47$  parts per mil.

## **CONCLUSIONS**

The major solute-generating processes differ between meteoric and subglacial meltwaters. Meteoric waters, with abundant dissolved  $CO_2$ , are dominated by carbonate dissolution. In contrast, meltwaters are removed from contact with the atmosphere, and gain a significant amount of their solutes via the coupled sulfide oxidation/carbonate dissolution reactions. Trace amounts of reactive carbonates and sulfides in the bedrock are responsible for the majority of solutes in these waters.

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# SEDIMENTOLOGICAL DESCRIPTION AND PROCESS INTERPRETATION OF GLACIOGENIC LANDFORMS AT THE HERBERT GLACIER ICE FRONT

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## INTRODUCTION

Recent rapid recession of the Herbert Glacier, an outlet glacier of the Juneau Icefield, has revealed a striking set of glacial, sub-glacial, and proglacial landforms and sediments. The Herbert Glacier has receded 3.5 km in the last 235 years since its Little Ice Age maximum stand (Lawrence, 1950), and for the past 15 years has been receding at a rate of 20 m per year. This recent recession has uncovered a small basin approximately 300 m north/south and 350 m east/west located at the current (July 2000) ice front.

Multiple kame terraces ring the walls of the ice marginal basin and are graded to several past meltwater outlets. These terraces, and most other deposits in the basin, including moraines, other ice contact stratified drift, and the sediment melting out from under the ice, are composed entirely of rounded granitic clasts. In remarkable contrast to these subglacial clasts are very few, angular, iron-stained metamorphic rocks that are seen in supraglacial transport. Large (>2 m diameter) well-rounded boulders are scattered throughout the basin on kame terraces, in moraines, and mixed with till. There is also a 20 m stratigraphic section exposed in the steep northern basin wall. This section is composed of two tills and a suite of stratified drift units. The lower till is highly weathered and contains large subangular clasts of tonalite, while the upper till is unweathered and composed of smaller (< 30 cm) subrounded to rounded clasts of tonalite.

The principle goals of this project are to examine the dynamics responsible for rounding the clasts in the basin, especially the larger boulders, and to map and describe the origin of the multiple kame terraces. Multiple hypotheses have been informally suggested as explanations for the rounding of the large boulders, most of which could be used to explain the rounding of the smaller clasts as well. The boulders could come pre-rounded as corestones. They could be rounded by direct ice transport. They could be rounded by subglacial fluvial transport at the bottom of moulins (Connor, 2000) or in a network of subglacial fluvial channels. They could be rounded in subaerial fluvial process in either normal flow regimes or catastrophic jökulhlaup events. They could also be rounded in a subglacial deforming till (Fleisher, 2000). Each of these hypothesis will be examined for validity.

## METHODS

A GIS surface expression map of the Herbert Glacier ice front and surroundings was created in ArcView using GPS data (Figure 1). GPS data points were collected in the field at the contacts between different surface features including bedrock, ice, stagnant ice, river channel, braid plain, moraine, and kame terraces. Features were differentiated based on clast lithology, size and shape, outcrop pattern, and general appearance. These data were then transferred into ArcView, and from them a map of ice, bedrock, river channel, and geomorphic features, was created. To provide a third dimension to the map, topographic profiles of the basin were also created.

A plot comparing the seven kame terrace slopes was produced by a combination of GPS and altimeter/barometer data (Figure 2). This plot was also used to compare the slopes of multiple terraces grading to a single outlet.

Quantification of the rounding, lithology and size of clasts on the kame terraces was done by seven pebble counts. For each pebble count, a 30 m tape was placed on the tread of a kame terrace following the trend down its slope and the size, lithology, and degree of rounding of each rock at every 0.5 m was tabulated. Rocks that spanned 0.5 m intervals were counted as one rock and not tabulated twice. Total sample size was 274 rocks.