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# CHEMICAL WEATHERING OF BASALT IN SOUTHWEST ICELAND: EFFECTS OF RUNOFF, AGE OF ROCKS AND VEGETATIVE/GLACIAL COVER

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**ABSTRACT. Compared to the global average, the chemical weathering rates of basalt in southwest Iceland are high and rather variable. This can be attributed to soluble rock type (basalt) and mechanical weathering, variation in runoff and age of rocks, and variable vegetative/glacial cover. The average temperature of the catchments in this study is near constant, 5°C. Chemical weathering of the basalt is incongruent. Some of the primary minerals do not dissolve, and secondary minerals form, resulting in the fact that fluxes of all elements increase with runoff, and there is an enormous variation in the relative mobility of elements in the basalt during weathering. The relative mobility, in decreasing order, is: S > F > Na > K ≫ Ca > Si > Mg > P > Sr ⋙ Mn > Al > Ti > Fe. Relative to Na, close to 90 percent of Mg and Ca in the original rocks is left behind at the weathering site. The runoff dependence of fluxes and the variation in relative mobility is less in old rocks than in young ones. In old rocks the number of saturated minerals with respect to soil solutions has decreased because of lesser amount of soluble basaltic glass and an increased vegetative cover on old rocks. The saturation state of basaltic minerals is the most important variable for the dissolution and precipitation rate of minerals during weathering in southwest Iceland and is dictated by the pH of the weathering solutions.**

**The overall rate of chemical denudation rate in southwest Iceland is independent of vegetative cover. However, fluxes of Ca, Mg, and Sr increase with increasing vegetative cover at constant runoff, whereas fluxes of Na and K decrease. With a continuous vegetative cover the pH of the soil solutions tends to be low (<7), and glass, olivine, pyroxene, and plagioclase are unstable, but the solutions are decreasingly saturated or more undersaturated with respect to zeolites and smectite, thus increasing the relative mobility and fluxes of Ca, Mg, and Sr. Since the weathering of Ca-Mg silicate rocks is the principal process by which $CO_2$ is removed from the atmosphere on a geological time scale (Berner, 1992), the spread of vascular plants on the continents during the mid-Paleozoic may have resulted in a drop in $CO_2$, not necessarily because of greatly enhanced bulk chemical weathering, as suggested by Trendall (1966) and Berner (1993), but rather due to the enhanced relative mobility and fluxes of Ca and Mg.**

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Glacial cover slows down the overall chemical denudation rates in southwest Iceland. It increases the probability of high pH weathering solutions by excluding direct and indirect routes for the $CO_2$ from the atmosphere to the weathering site and by continuously exposing fresh rocks to the incoming solutions. A high pH (8-10) makes the primary Ca silicates stable and the Mg silicates stable or less unstable, and the high pH increases the probability of deposition of zeolites and smectites. Thus, the relative mobility and fluxes of Ca and Mg slow down during glacial cover and therefore retard the permanent long-term consumption of atmospheric $CO_2$. This process supports the theory of a negative feedback mechanism for the long-term stabilization of the Earth's surface temperature (Walker, Hays, and Kasting, 1981).

Transient consumption of atmospheric $CO_2$ by chemical weathering in Iceland is greater than $CO_2$ degassing from the Icelandic mantle plume. However, long-term consumption by weathering of Ca-Mg silicates and precipitation of Ca-Mg carbonates in the ocean is smaller than the $CO_2$ degassing.

The relative mobility of the least mobile elements during weathering in southwest Iceland is similar to that observed elsewhere in the world under remarkably variable climatic conditions. Thus we agree with Nesbitt and Wilson (1992) and Taylor and others (1992) that laterites and bauxites are not necessarily representative of a tropical climate, but rather the ratio of mechanical versus chemical denudation rates.

Icelandic precipitation shows a normal distribution around a mean pH of 5.4. Na/Cl, K/Cl, Mg/Cl, and Sr/Cl ratios in the precipitation are close to oceanic ratios, indicating that they are solely of marine origin. The concentrations of Ca, $SO_4$, $NO_3$, and $NH_4$ are higher than predicted by an unfractionated marine contribution. The pH of spring-fed rivers in southwest Iceland is high, and they are relatively poor in total dissolved inorganic carbon, calcium, and magnesium. The pH of other rivers ranges from 7.15 to 7.94, which is typical for waters with access to atmospheric $CO_2$ during or after water-rock interaction. The water in the main channels of the rivers has enough time for significant heat exchange with its surroundings and significant gas exchange with the atmosphere, but the water-rock interactions are insignificant.

The airborne dissolved or soluble solids contribution to the total dissolved solids in rivers in southwest Iceland (only carbon dissolved in rain is considered) ranges from 14 to 38 percent for those catchment areas closest to the coast. Most of the airborne contribution is of marine source and the airborne contribution is, in descending order; Cl, $NO_3$, and $NH_4$ ($\approx$100 percent) > Sr (44 percent) $\geq$ $SO_4$ (42 percent) > Na (33 percent) > Mg (23 percent) $\geq$ K (21 percent) > Ca, PO4 (13 percent) $\gg$ $SiO_2$, F, Al, Fe, Mn, Ti (0 percent). The dissolved carbon in the rivers is primarily, directly, or indirectly derived from the atmosphere. The average total dissolved inorganic N content of Icelandic precipitation is 124 μg/l N, but the discharge weighted average of the total inorganic N concentration of Icelandic rivers is 62 μg/l N. Thus there is a nitrogen sink in Icelandic catchment areas, caused by primary production of progressive vegetation and biota.

## INTRODUCTION

Chemical weathering of the Mg–Ca silicates is the primary process in removing $CO_2$ from the atmosphere on a geological time scale. Weathering of Mg-Ca silicates on land results in the transport of Mg and Ca by rivers to the ocean, where it eventually precipitates as carbonates, making the ocean capable of absorbing more $CO_2$ from the atmosphere and bicarbonate from rivers (Urey, 1952; Holland, 1978; Berner, 1992). Regions dominated by exposed reactive Mg-Ca silicate rocks, high rainfall, and high relief are the most important long term $CO_2$ sinks on land.

Iceland provides an opportunity to study the weathering of Mg-Ca silicates under uniform lithology, at a constant average temperature, variable rainfall and rock age, high relief, and variable glacial/vegetative cover. More than 90 percent of the island is of basaltic composition. The primary Mg-Ca silicates of the basalt being weathered are: olivine, pyroxene, plagioclase, basaltic glass, and interstitial glass of rhyolitic composition. However, in order to understand the transport of Mg and Ca from the weathering site to the ocean, it is also necessary to consider the formation of Mg-Ca silicate weathering products, such as smectites, zeolites, and serpentine, that constrain the transport of Mg and Ca.

The objective of this paper is to define and interpret the chemistry of rivers in southwest Iceland and to establish the source of dissolved constituents, the relative mobility of the elements, the rate of chemical denudation, the effect of runoff, age, and glacial/vegetative cover on the chemical weathering of basalt and the implication of the findings.

Chemical weathering rates are complex functions of runoff and lithology (Garrels and Mackenzie, 1971; Meybeck, 1979; Bricker and Rice, 1989; Bluth and Kump, 1994), temperature (Brady, 1991; Velbel, 1993, Gwiazda and Broecker, 1994; White and Blum, 1995), organic activity and therefore vegetative cover (Cawley, Burruss, and Holland, 1969; Volk, 1987; Schwartzman and Volk, 1989; Berner, 1992; Cochran and Berner, 1992; Drever 1994; Brady and Carroll, 1994), tectonics and therefore exposure and elevation (Stallard and Edmond, 1983; Raymo and Ruddiman, 1992; Drever and Zobrist, 1992; Edmond and others, 1995), and glacial cover and the abundance of mechanically strained glacier sediments (Gíslason, Arnórsson, and Ármannsson, 1994; Kump and Alley, 1995; Meybeck, 1995; Sharp and others, 1995).

Numerous studies have been carried out on the weathering of basalt on land (Sigvaldason, 1959; Craig and Loughnan, 1964; Tardy, 1969; Cawley, Burruss, and Holland, 1969; Hay and Jones, 1972; Jakobsson, 1978; Chesworth, Dejou, and Larroque 1981; Colman, 1982; Furnes, 1984; Gíslason and Eugster, 1987b; Eggleton, Foudoulis, and Farkevisser, 1987; Smith, Milnes, and Eggleton, 1987; Crovisier, ms; Noack and others 1990; Veldkamp and Jongmans, 1990; White and Hochella, 1992; Crovisier and others, 1992; Cochran and Berner 1992; Nesbitt and Wilson, 1992; Taylor and others, 1992; Gíslason and Arnórsson, 1993; Bluth and Kump, 1994; Benedetti and others, 1994; Daux and others, 1994; Dorn and Brady, 1995) that define the changes in rock chemistry

and mineralogy during weathering, the chemistry of the water involved in the weathering process, the relative mobility of the elements, chemical fluxes, and the effect of vegetation on weathering rates. Experimental studies on weathering and/or alteration of basalt and basaltic glass have underscored the importance of pH, water composition, temperature, glass content, and the presence of bacteria on the rate of weathering (Hoppe, 1940; Furnes, 1975; Gíslason and Eugster, 1987a; Crovisier, ms; Guy and Schott, 1989; Gíslason, Veblen, and Livi, 1993; Berger and others, 1994; and Thorséth, Furnes, and Tumyr, 1995).

Studies of the chemistry of surface and groundwaters in Iceland have increased in number during the last two decades. Most of the data on river water composition are from the southern and western parts of the country (Ármannsson 1970, 1971; Ármannsson and others, 1973; Rist, 1974, 1986; Sigbjarnarson, 1972). The data base set up by Rist, Ármannsson, and coworkers is extensive, reporting the monitoring of chemistry, suspended load, and discharge of 20 rivers in south and west Iceland on a monthly basis for up to 2 yrs. Cawley, Burruss, and Holland (1969) studied the carbonate concentration and the partial pressure of $CO_2$ in the Skjálfandafljót River in northern Iceland. They concluded that the harsh climate in central Iceland does not result in abnormally low rates of chemical weathering, and they found the chemical weathering rates to be two to three times higher in areas with plant cover than in barren areas. With the aid of deuterium isotopes, Árnason (1976) defined the flow paths and the age of ground waters in Iceland. The chemistry of several lakes and of the Laxá River in northeast Iceland has been studied by Ólafsson (1979, 1980, 1992), Stefánsson (1950), Stefánsson and Jóhannesson (1987), Sveinbjörnsdóttir and Johnsen (1992), and Petersen, Gíslason, and Vought (1995). The effects of geothermal and volcanic activity and glacier burst on river water chemistry have been described by Sigvaldason (1963, 1965), Steinthórsson and Óskarsson (1983), Björnsson and Kristmannsdóttir (1984), Ágústsdóttir and others (1992), Brantley, Ágústsdóttir, and Rowe (1993), Ágústsdóttir and Brantley (1994), and Lawler, Björnsson, and Dolan (1996). The solute acquisition in glacier melt waters from the Fjallsjökull in southeast Iceland has been studied by Raiswell and Thomas (1984). Airo (1982) analyzed surface and spring waters in the rift zone south of the Langjökull Glacier. Sigurdsson (1990) studied the chemistry of groundwaters of glacier origin in Iceland. The processes governing the chemistry of precipitation, surface, ground, and geothermal waters in the rift zone north of the Vatnajökull Glacier were defined and interpreted with the aid of laboratory experiments (Gíslason, ms; Gíslason and Rettig, 1986; Gíslason and Eugster 1987a, b; Gíslason, Veblen, and Livi, 1993). The chemistry of rivers in Iceland and the rate of chemical denudation have been interpreted by Gíslason and Arnórsson (1988, 1993) and Gíslason, Arnórsson, and Ármannsson (1990). The rate of water-air interactions in rivers has been described and interpreted (Gíslason, 1989) as well as the contamination of surface waters by the Hekla volcanic eruption of 1991 (Gíslason and others, 1992).

## CLIMATE, GEOLOGY, HYDROLOGY, AND VEGETATION

The climate in Iceland is oceanic boreal with rather cool summers and relatively warm winters. It is characterized by alternating invasions of polar air from the north and warm or transitional air masses from the Atlantic (Eythórsson and Sigtryggsson, 1971). The mean temperature of the inhabited part of the country, the coastal areas, and the lowlands is around 4°C, and the annual precipitation ranges from less than 400 mm to more than 4000 mm (Eythórsson and Sigtryggsson, 1971; Einarsson, 1991). The central region of Iceland consists of a 500 to 700 m high plateau, stretching 300 km west to east and about 100 km from north to south. Numerous snowcapped mountains and glaciers protrude from this plateau up to 1500 to 2000 m above sealevel. Mountain ranges radiate in all directions from the central plateau toward the coast, separating the inhabited valleys and dividing the coastal lowlands (fig. 1). The size of the island is about 103,000 km$^2$. This is about 0.1 percent of the global land area drained to the oceans (Meybeck, 1988). A little less than 24,000 km$^2$ are vegetated, wasteland accounts for just over 64,000 km$^2$, glaciers take up about 12,000 km$^2$, and lakes somewhat less than 3000 km$^2$ (The Statistical Bureau of Iceland, 1984). Iceland was mostly covered with ice during the Pleistocene, but the ice caps reached their present size about 8000 yrs ago (Einarsson, 1985).

Iceland is built of volcanic rocks which are predominantly (80-85 percent) of basaltic composition, the remainder being intermediate and silicic volcanics and clastic sediments of volcanic origin (fig. 1; Saemundsson, 1979). The oldest rocks exposed are about 13 my (Moorbath, Sigurdsson, and Goodwin, 1968; McDougall and others, 1977). Recent and Upper Quaternary volcanics are largely confined to the active volcanic zones (fig. 1). Generally the age of the rocks increases with distance from the volcanic zones as a result of crustal accretion (Óskarsson, Sigvaldason, and Steinthórsson, 1982).

Permeability, both primary and tectonic, is higher within the young volcanic zones than in older rocks outside them. The post-glacial lavas of the young volcanic zones have extremely high permeability, $1–10^{-2}$ cm$^3$/cm$^2$ sec (Sigurdsson and Ingimarsson, 1990) and have for that reason no surface streams. Compaction and sealing by secondary mineralization reduces the permeability as the rocks drift out of the volcanic zones. The permeability of the Quaternary and Tertiary formations lies in the range of $5 \times 10^{-5}$ to $10^{-7}$ cm$^3$/cm$^2$ sec (Sigurdsson and Ingimarsson, 1990). As a result, runoff dominates in the Quaternary and Tertiary formations. On the other hand, a large part of the precipitation that falls on ice-free land in the volcanic zones infiltrates and may discharge directly as groundwater into the ocean or emerge as springs to form spring-fed streams and rivers.

The total annual discharge of the rivers in Iceland is 170 km$^3$ (Rist, 1956), about 0.45 percent of the global river discharge to the ocean (Baumgartner and Reichel, 1975). The total annual discharge in Iceland translates to $1.65 \times 10^6$ m$^3$/km$^2$/yr or about 55 l/sec km$^2$ runoff compared to the exorheic world average drainage of 11.8 l/sec km$^2$ (Rist,

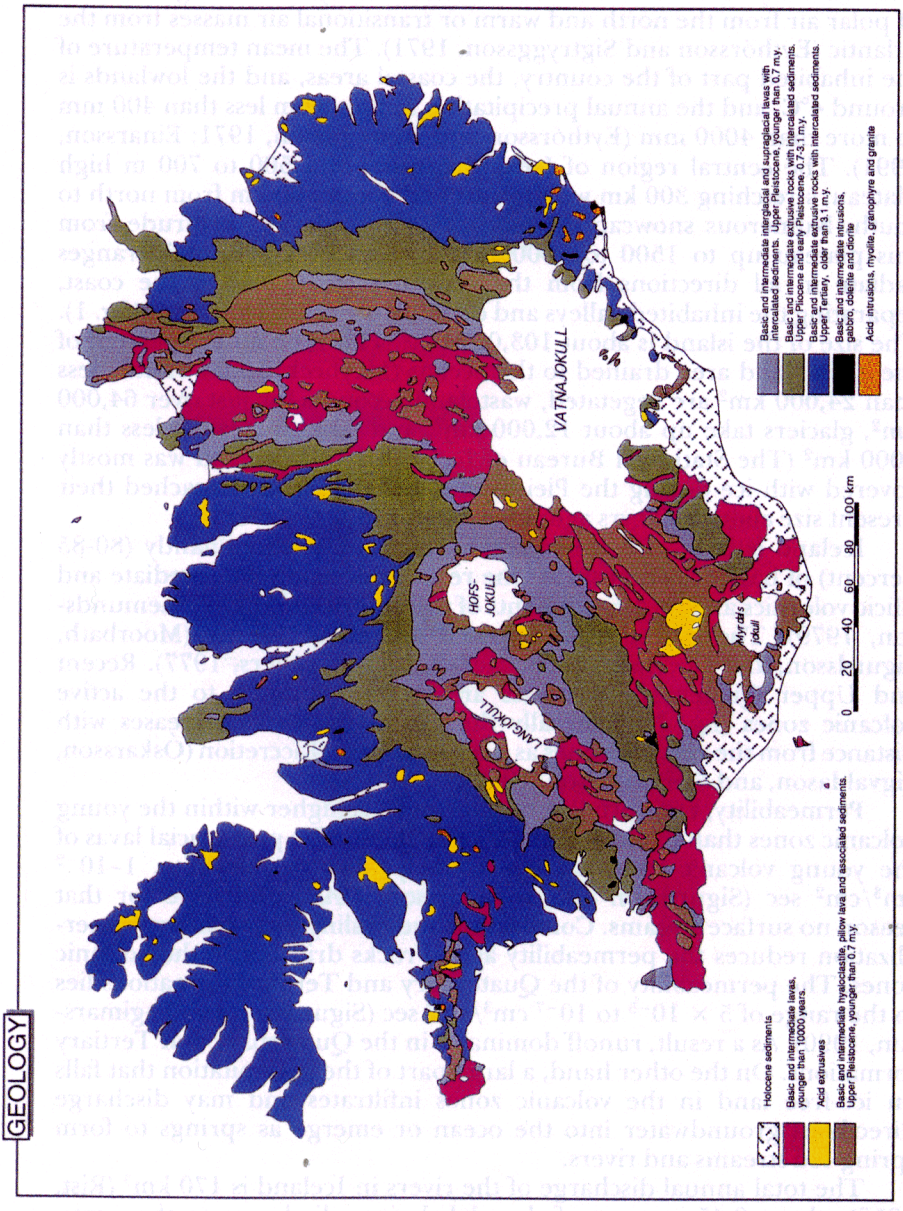



Fig. 1. Geological map of Iceland. Modified from Jóhannesson and Saemundsson (1989). Published with the permission (LMI 104-94) of the Iceland Geodetic Survey.

1956; Meybeck, 1988). The annual transport of suspended load by Icelandic rivers is about 0.02 $km^3$ to 0.025 $km^3$ which is about 0.3 percent of the total amount of suspended matter transported to the oceans annually (Maybeck, 1988). This flux by the Icelandic rivers translates to about 500 $t/km^2/yr$ (Tómasson, 1986; Steinthórsson, 1987) which is considerably greater than the average mechanical denudation rate for the world of 178 $t/km^2/yr$ (Meybeck, 1988). The rivers in Iceland have been classified as: spring-fed (s-rivers), direct runoff (d-rivers), glacier-fed rivers (g-rivers) (Kjartansson, 1945), rivers draining lakes (l-rivers; Rist, 1956), and mixtures thereof.

Owing to last glaciation, the isolation of the island in the Atlantic, and the recent cold climate, there are only about 470 species of vascular plants in Iceland (The Statistical Bureau of Iceland, 1984). Of these, 37 are Pteridophytes, 287 are Diocotyledons, and 145 Monocotyledons. By far the largest families belonging to the Monocotyledons are Sedges (Cyperaceae, 53 species) and Grasses (Poaceae, Gramineae; 46 species). The largest families of Diocotyledons are Daisies (Asteraceae, Compositae; 37 species) and Pinks (Cary-ophyllaceae; 28 species). Only one Gymnosperm is a native of Iceland. There are about 500 species of mosses in Iceland, at least 500 species of lichens have been found as well as 1100 to 1200 species of Fungi.

The upper limit of continuous vegetative cover is at an average altitude of 700 m above sealevel, but scattered individuals of hardy arctic alpine species of vascular plants grow there, along with lichens and mosses (The Statistical Bureau of Iceland, 1984). A near continuous carpet of mosses, consisting mostly of *Racomitrium languinosum* and *Racomirtium canescens,* may cover lava flows at all elevations. This moss is gradually replaced by dwarf shrubs and grasses and later birch, on old lava flows in the lowlands. Only small patches of wood and scrubland exist in sheltered places in lowland valleys in Iceland. The treeline stands at less than 300 m above sealevel. The only tree of importance is birch (*Betula pubescens*).

Moss heaths are the most extensive plant communities in the Icelandic highlands, but they are by far the least productive. The mean annual yield of Icelandic plant communities in the lowlands (below 400 m above sealevel) is 8.4 t/km2/yr of dry matter, but it is 6.7 t/km2/yr in the highlands (Thorsteinsson, 1980). The annual yield in previously heavily grazed areas in the lowlands can be as low as 6.9 t/km2/yr (Gísladóttir, 1995).

## DATA BASE AND DATA HANDLING

The chemistry of precipitation in southwest Iceland has been monitored by the Icelandic Meteorological Office since 1958 (The Icelandic Meteorological Office, 1958-1981). The samples are integrated monthly samples from 1 to 3 meteorological stations. Data on the chemistry of precipitation from northeast Iceland are available for the summers of 1982 and 1983 as well as for the 1982 winter precipitation on the northwestern part of the Vatnajökull glacier (Gíslason and Rettig, 1986).

This data base is used to define the chemistry of precipitation in Iceland. The analytical results from the above sources were accepted and incorporated into the present study when the difference between the equivalent sums of positively and negatively charged species is less than 25 percent. The number of acceptable samples is 338. To this data base we have added 36 chemical analyses of snow sampled across Iceland in February and March 1992, from north to south, from coast to coast, west, east and, across the Hofsjökull glacier (fig. 1). The snow was melted in the laboratory; part of the sample was used to measure pH and Cl by electrodes, and the rest filtered, acidified, and then stored until analyzed by the ICP method described below.

Ármannsson and others (1973) and Rist (1974 and 1986) monitored the major element and nutrient composition of 19 rivers in southwest Iceland, collecting monthly samples for up to 23 months for individual rivers in 1972, 1973, and 1974 (fig. 2). The averages of their data have been used for the present study (table 1). The river types are spring-fed

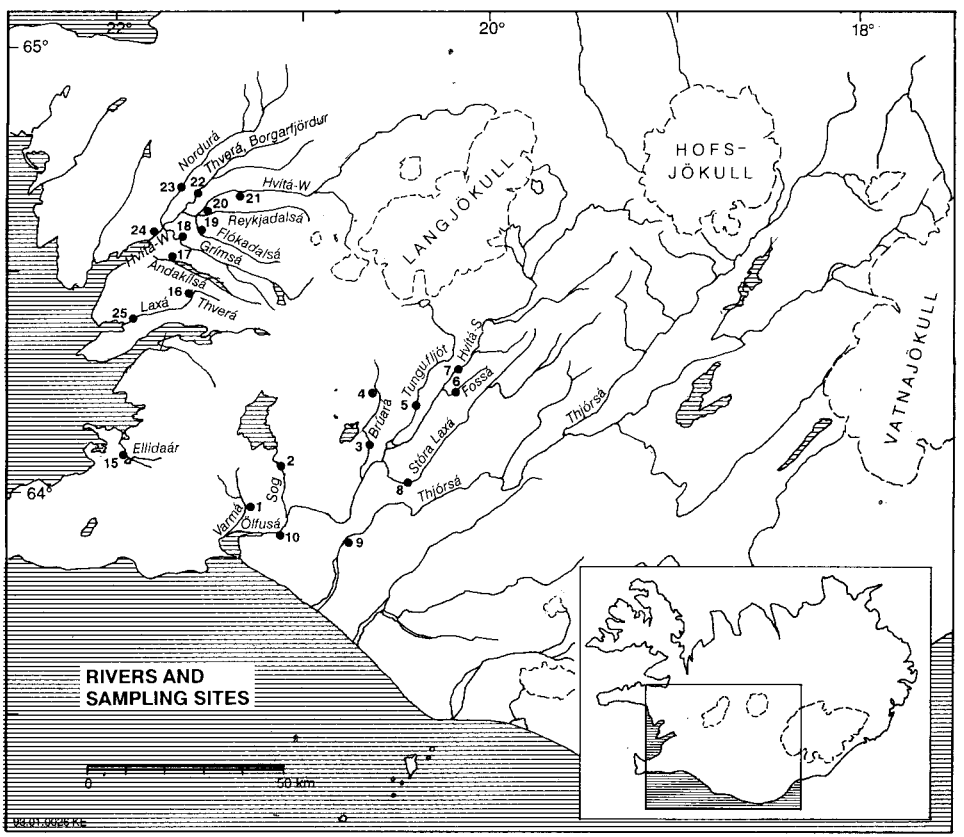



Fig. 2. Map of the rivers under study showing the sampling sites (table 1).

rivers (s-rivers), direct runoff rivers (d-rivers), rivers draining lakes, and rivers of mixed origin. Additionally, we collected 11 samples from the same rivers at the same sampling sites (table 1; fig. 2) for the analysis of major and some trace elements (Al, Fe, Mn, Ti, and Sr). The total area of the 19 catchments included in this study is close to 16977 km$^2$ which is more than 16 percent of the total surface area of Iceland. Of these 16977 km$^2$, about 1990 km$^2$ or about 12 percent are covered with glaciers (figs. 2 and 3).

The samples collected as part of the present study were filtered through 0.1 micron millepore filters into low density polyethylene bottles. One aliquot was acidified with 1 ml of suprapure® concentrated nitric acid to 190 ml sample and used for ICP (Inductively Coupled Plasma Emission Spectrometry) analysis. One filtered but otherwise untreated aliquot was collected for determination of chloride and fluoride by ion sensitive electrodes. The pH and total carbonate concentration of the samples were measured at the sample site at the temperature (±3°C)

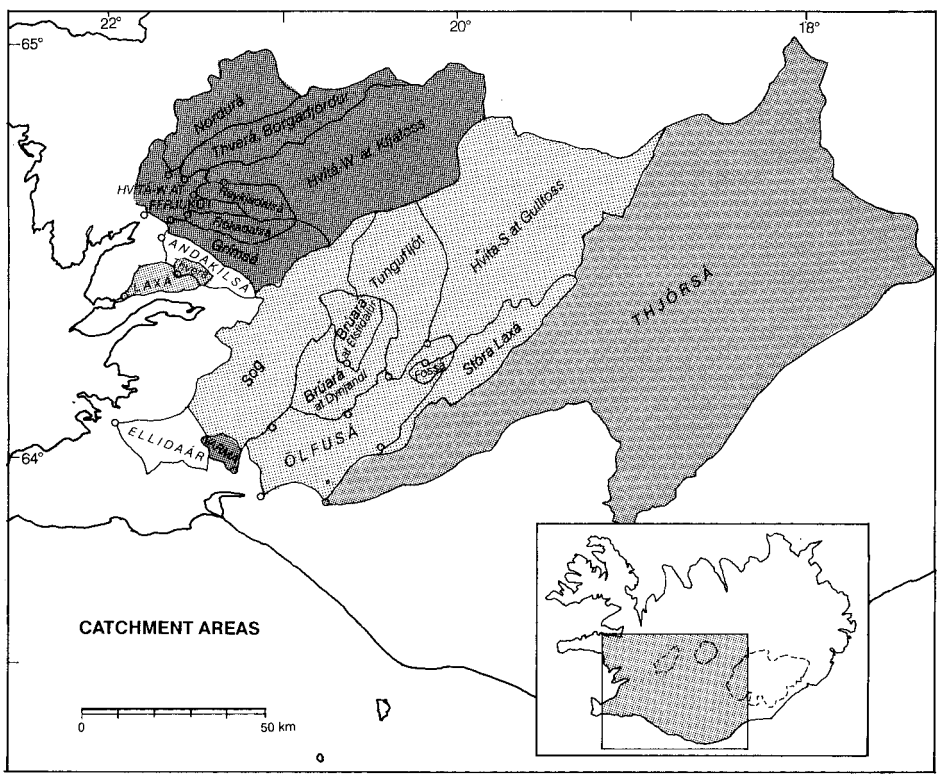



Fig. 3. Map of the areal extent of the catchment areas under study. Catchment areas of main rivers are labelled with upper case letters. The catchment areas of the main rivers are differentiated by shade.

TABLE 1

*Average composition(1) of individual rivers in southwest Iceland, discharge weighted average of the main rivers in southwest Iceland, and the unpolluted average for the world*

| | MAIN RIVER<br>*Tributary* | Location number(2) | River type | Temp °C | Disch. m3/sec | pH/T /°C | SiO2 mg/l | Na mg/l | K mg/l | Ca mg/l | Mg mg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|
| southern Iceland | THJÓRSÁ(5) | 9 | d+g+s | 5.2 | 399.5 | 7.51 | 14.4 | 10.52 | 0.56 | 4.56 | 1.81 |
| | ÖLFUSÁ | 10 | s+d+g | 5.1 | 439.8 | 7.38 | 14.1 | 8.47 | 0.53 | 3.77 | 1.40 |
| | *Stóra Laxá* | 8 | d | 5.0 | 20.3 | 7.34 | 16.9 | 7.34 | 0.59 | 3.78 | 1.47 |
| | *Fossá* | 6 | d | 6.4 | 1.7 | 7.50 | 22.8 | 7.85 | 0.76 | 5.20 | 2.44 |
| | *Hvítá-s, Gullfoss* | 7 | d+g+l+s | 4.3 | 132.9 | 7.43 | 14.0 | 7.94 | 0.53 | 3.68 | 1.27 |
| | *Tungufljót* | 5 | s+g | 4.7 | 47.3 | 7.29 | 14.7 | 6.39 | 0.43 | 2.47 | 0.86 |
| | *Brúará, Dynjandi* | 4 | s+l | 4.2 | 73.9 | 7.64 | 14.6 | 8.49 | 0.39 | 3.16 | 0.89 |
| | *Brúará, Efstidalur* | 3 | s | 3.3 | 41.2 | 8.77 | 14.6 | 7.45 | 0.36 | 2.46 | 0.45 |
| | *Sog* | 2 | s+l | 4.6 | 116.3 | 7.41 | 11.4 | 8.97 | 0.64 | 3.80 | 1.38 |
| | VARMÁ | 1 | d+s | 11.4 | 2.2 | 7.94 | 45.9 | 23.03 | 8.79 | 14.57 | 4.17 |
| | ELLIDAÁR | 15 | l+s+d | 4.1 | 7.0 | 7.48 | 11.9 | 9.68 | 0.39 | 3.99 | 1.41 |
| western Iceland | LAXÁ, VOGATUNGA | 25 | d+l | 5.5 | 7.8 | 7.24 | 8.4 | 6.78 | 0.30 | 4.11 | 1.55 |
| | *Thverá, Dragháls* | 16 | d+l | 4.3 | 5.5 | 7.16 | 8.4 | 5.85 | 0.26 | 2.67 | 1.33 |
| | ANDAKÍLSÁ | 17 | l+d | 4.8 | | 7.15 | 7.1 | 6.95 | 0.30 | 2.49 | 1.34 |
| | HVÍTÁ-W, FERJUKOT | 24 | d+s+g | 3.7 | 189.1 | 7.40 | 12.1 | 7.43 | 0.44 | 3.39 | 1.45 |
| | *Grímsá* | 18 | d | 3.9 | 21.6 | 7.28 | 11.7 | 8.08 | 0.36 | 3.44 | 1.69 |
| | *Flókadalsá* | 19 | d | 3.7 | 8.3 | 7.38 | 13.7 | 8.29 | 0.41 | 3.69 | 1.73 |
| | *Reykjadalsá* | 20 | d+s | 5.2 | 10.5 | 7.54 | 24.2 | 16.06 | 0.75 | 5.89 | 3.84 |
| | *Hvíta-W, Kljáfoss* | 21 | s+g | 2.9 | 94.5 | 7.86 | 11.9 | 6.68 | 0.40 | 2.88 | 0.97 |
| | *Thverá, Borgarfjördur* | 22 | d | 4.3 | 25.3 | 7.30 | 11.3 | 8.78 | 0.63 | 4.68 | 2.82 |
| | *Nordurá, Stekkur* | 23 | d | 4.1 | 35.2 | 7.26 | 9.9 | 6.32 | 0.34 | 3.68 | 1.56 |
| single samples(6) | THJÓRSÁ | 9 | d+g+s | 16.0 | | 7.80/18.0 | 11.2 | 6.78 | 0.33 | 4.39 | 1.32 |
| | ÖLFUSÁ | 10 | s+d+g | 15.0 | | 7.13/20.4 | 12.2 | 8.04 | 0.38 | 3.87 | 1.35 |
| | *Fossá* | 6 | d | 11.4 | | 8.0/12.0 | 23.1 | 8.99 | 0.78 | 6.47 | 2.85 |
| | *Hvítá-S, Gullfoss* | 7 | d+g+l+s | 12.3 | | 7.68/19.7 | 9.8 | 4.62 | 0.29 | 3.01 | 0.90 |
| | *Tungufljót* | 5 | s+g | 7.0 | | 8.17/8.2 | 16.5 | 7.05 | 0.38 | 2.76 | 0.80 |
| | *Brúará, Dynjandi* | 4 | s+l | 8.3 | | 8.82/8.7 | 13.6 | 8.55 | 0.28 | 3.61 | 0.91 |
| | *Brúará, Efstidalur* | 3 | s | 4.0 | | 9.38/6.4 | 13.9 | 7.27 | 0.24 | 2.67 | 0.46 |
| | *Sog* | 2 | s+l | 10.7 | | 8.32/10.9 | 10.9 | 8.38 | 0.46 | 4.15 | 1.38 |
| | HVÍTÁ-W, FERJUKOT | 24 | d+s+g | 7.4 | | 8.14/8.5 | 11.6 | 7.29 | 0.30 | 3.49 | 1.29 |
| | *Hvíta-W, Kljáfoss* | 21 | s+g | 6.3 | | 8.74/6.8 | 12.8 | 6.83 | 0.29 | 3.08 | 0.90 |
| | *Nordurá, Stekkur* | 23 | d | 10.6 | | 8.17/12.6 | 10.1 | 7.45 | 0.28 | 4.36 | 1.76 |
| | SOUTHWEST ICELAND(7) | | | 4.9 | | 7.43 | 13.8 | 9.04 | 0.52 | 3.99 | 1.56 |
| | WORLD AVERAGE(8) | | | | | | 10.4 | 5.15 | 1.30 | 13.40 | 3.35 |

(1)The simple average of individual rivers in South Iceland, including the Varmá, calculated from 23 monthly samples, starting in February, 1972, and ending in December, 1973. The simple average for individual rivers in Western Iceland, including the Ellidaár, calculated from 17 monthly samples starting in July, 1973 and ending in December, 1974.

(2)The location number refers to the numbers in figure 2.

(3)TDS, calculated total dissolved solids.

(4)TER, total evaporated residue.

(5)The rivers are listed in the table, starting in the east with the Thjórsá (fig. 2) and ending with the Nordurá in the west (fig. 2). The names of tributaries are written in italics and are left aligned, following their main river. The Brúará was sampled at two sites, at Efstidalur (fig. 2, loc. 3) and downstream at Dynjandi (fig. 2, loc. 4).

TABLE 1
(continued)

| HCO3 mg/l | SO4 mg/l | Cl mg/l | TDS(3) mg/l | TER(4) mg/l | F µg/l | NO3-N µg/l | NO2-N µg/l | NH4-N µg/l | PO4-P µg/l | Al µg/l | Fe µg/l | Mn µg/l | Ti µg/l | Sr µg/l |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 41.6 | 6.38 | 4.58 | 84 | 66 | 155 | 29 | 0.92 | 27 | 18 | | | | | |
| 32.0 | 3.72 | 5.59 | 70 | 53 | 91 | 24 | 0.96 | 39 | 8 | | | | | |
| 30.3 | 3.49 | 5.82 | 70 | 52 | 97 | 16 | 0.91 | 30 | 8 | | | | | |
| 39.9 | 4.24 | 6.45 | 90 | 68 | 133 | 20 | 0.90 | 35 | 10 | | | | | |
| 32.5 | 4.91 | 3.66 | 69 | 54 | 96 | 16 | 0.74 | 32 | 10 | | | | | |
| 25.6 | 3.19 | 3.80 | 57 | 44 | 70 | 40 | 0.83 | 32 | 8 | | | | | |
| 30.3 | 3.62 | 4.98 | 66 | 49 | 61 | 29 | 0.88 | 33 | 7 | | | | | |
| 17.1 | 3.73 | 4.02 | 50 | 43 | 46 | 39 | 0.83 | 27 | 12 | | | | | |
| 32.6 | 3.95 | 6.97 | 70 | 51 | 68 | 8 | 0.77 | 37 | 6 | | | | | |
| 81.6 | 15.93 | 16.97 | 211 | 163 | 176 | 28 | 1.38 | 57 | 13 | | | | | |
| 29.0 | 4.35 | 10.10 | 71 | 56 | 48 | 26 | 1.00 | 45 | 2 | | | | | |
| 25.1 | 3.78 | 7.93 | 58 | 45 | 31 | 25 | 0.84 | 45 | 2 | | | | | |
| 19.9 | 3.25 | 7.18 | 49 | 40 | 35 | 13 | 0.87 | 46 | 2 | | | | | |
| 18.9 | 3.81 | 8.59 | 49 | 40 | 46 | 14 | 0.78 | 52 | 2 | | | | | |
| 29.1 | 3.72 | 5.69 | 63 | 47 | 67 | 30 | 0.93 | 43 | 6 | | | | | |
| 30.1 | 3.57 | 7.13 | 66 | 51 | 56 | 15 | 0.82 | 43 | 3 | | | | | |
| 31.1 | 3.20 | 7.24 | 69 | 55 | 49 | 13 | 1.02 | 36 | 2 | | | | | |
| 51.7 | 8.53 | 12.17 | 123 | 99 | 207 | 41 | 1.41 | 54 | 2 | | | | | |
| 25.5 | 3.59 | 4.35 | 56 | 44 | 57 | 33 | 1.02 | 33 | 10 | | | | | |
| 37.8 | 3.79 | 8.85 | 79 | 60 | 64 | 23 | 0.90 | 51 | 3 | | | | | |
| 25.5 | 3.51 | 6.72 | 58 | 44 | 36 | 30 | 0.84 | 34 | 3 | | | | | |
| 33.0 | 6.10 | 3.90 | 67 | | 755 | | | | 9 | 81 | 62 | 2.5 | 7.1 | 4.4 |
| 33.6 | 3.80 | 7.69 | 71 | | 116 | | | | 12 | 33 | 23 | 5.7 | 2.8 | 6.1 |
| 33.1 | 2.19 | 7.70 | 85 | | 123 | | | | 9 | 4 | 23 | 0.1 | 0.8 | 22.0 |
| 47.1 | 3.83 | 2.97 | 73 | | 146 | | | | 12 | 38 | 22 | 2.4 | 2.4 | 3.3 |
| 24.7 | 1.41 | 4.06 | 58 | | 77 | | | | 17 | 24 | 50 | 3.9 | 1.4 | 3.5 |
| 26.7 | 2.08 | 4.99 | 61 | | 85 | | | | 4 | 45 | 53 | 0.4 | 2.1 | 3.5 |
| 23.4 | 1.84 | 4.01 | 54 | | 69 | | | | 10 | 70 | 9 | n.d. | 1.4 | 1.9 |
| 32.9 | 2.40 | 6.52 | 67 | | 77 | | | | 15 | 15 | 5 | 0.5 | n.d. | 4.2 |
| 25.5 | 2.04 | 5.93 | 57 | | 77 | | | | 13 | 40 | 16 | 1.6 | 1.6 | 4.4 |
| 22.4 | 1.78 | 4.51 | 53 | | 85 | | | | 22 | 62 | 4 | 0.3 | 1.3 | 2.9 |
| 24.7 | 2.37 | 9.00 | 60 | | 44 | | | | 7 | 2 | 9 | n.d. | 0.5 | 7.9 |
| 34.9 | 4.73 | 5.31 | 74 | 57 | 110 | 27 | 0.94 | 35 | 11 | 52 | 37 | 3.7 | 4.2 | 5.1 |
| 52.0 | 8.25 | 5.75 | 100 | | 100 | 100 | 0.91 | 16 | 10 | 50 | 40 | 8.2 | 10.0 | 60.0 |

(6)Single samples from some of the rivers above, including the concentrations of Al, Fe, Mn, Ti, and Sr. The samples from the Thjórsá, Ölfusá, and Hvítá-S, at Gullfoss were taken in July, 1991, but the others in August, 1990.

(7)Discharge weighted average chemical composition of rivers in southwest Iceland calculated from the above averages, excluding tributaries and the Varmá River since it is contaminated with geothermal water. The discharge weighted concentrations of Al, Fe, Mn, Ti, and Sr were calculated from the single grab samples of the Thjórsá, Ölfusá, and Hvítá-W, at Ferjukot.

(8)The "natural" average for the rivers of the world (Meybeck, 1979; 1982; Martin and Meybeck, 1979; Martin and Withfield, 1983).

of the river water. The total carbonate concentration was measured by alkalinity titration from a pH of 8.3 to the actual end point of the alkalinity titration, which ranged from pH 4.75 to 5.00. When dissolved silica had been determined, its contribution to the alkalinity and the total dissolved carbonate concentration was calculated.

The silica concentrations in samples collected during the first 6 months of the monitoring study of Rist (1974) are about half of those in samples collected from the same rivers during the previous year by Ármannsson and others (1973) and of samples analyzed by us. The silica data reported by Rist (1974) for the first 6 months of 1973 are thought to be low due to analytical error and have not been incorporated when calculating the average silica. The chemical analyses of phosphorus for all the rivers sampled on March 23 and April 27, 1972 (Ármannsson and others, 1973) were erroneously reported as nmole/l, rather than μg/kg, and are in error by a factor of 9.497. This correction has been applied to the relevant results in table 1. The measured total evaporated residue (TER) is always lower than the sum of the concentration of the major elements (TDS), indicating loss of carbon during evaporation for the TER measurement. There are no discharge measurements for the rivers Andakílsá (Rist, 1986) or Stóra Laxá (Ármannsson and others, 1973). However, the water depth of the Stóra Laxá was measured when the first 10 samples were taken in 1972. These water depth measurements were used to calculate the discharge of the Stóra Laxá, using unpublished data of the National Energy Authority.

The WATCH program of Arnórsson, Sigurdsson, and Svavarsson (1982) was used to obtain the aqueous speciation for the waters selected for the present study. The data base is that given in their table 5, except for aqueous aluminum hydroxy complexes for which the data of Kuyunko, Malinin, and Khodakovskiy (1983) were used, as discussed by Gíslason and Arnórsson (1993). Thermodynamic data for the solubility of the minerals are from Helgeson and Kirkham (1974), Helgeson and others (1978), Shock and Helgeson (1988, 1989), Tanger and Helgeson (1988), Walther and Helgeson (1977), Johnson and others (1983), Fournier (1977), and Plummer and Busenberg (1982).

The chemical composition of rocks in the catchment areas under study (figs. 2 and 3) comes from various sources, published and unpublished, as referred to in table 2.

The extent of the catchment areas and their glacial cover was estimated on a topographic map (fig. 3; table 3), comparing well with the catchment areas given in Ármannsson and others (1973) and Rist (1974, 1986). The uncertainty is greatest for the spring-fed rivers and catchment areas covered by glaciers. The runoff was calculated from the discharge (table 1) and the catchment areas (table 3). According to Björnsson (1987), about 74 percent of the runoff from the Ellidaár catchment area (figs. 2 and 3) is lost to groundwater flowing out of the basin and therefore does not enter the river. This loss is accounted for in the

TABLE 2

*Composition of rocks in the catchment area of the major rivers: Thjórsá, Ölfusá, and Hvítá-W at Ferjukot*

| Discharge area<br>Oxides, weight % | SiO2 | Al2O3 | TiO2 | Fe2O3 | FeO | MnO | MgO | CaO | Na2O | K2O | P2O5 | H2O | Sr ppm | F ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| THJÓRSÁ, Postglacial basalts(1) | 48.8 | 14.9 | 1.66 | 1.07 | 10.56 | 0.18 | 7.60 | 11.76 | 2.27 | 0.24 | 0.18 | 0.28 | 157 | 120 |
| THJÓRSÁ, Postglacial obsidian(2) | 72.9 | 12.3 | 0.30 | 1.49 | 1.83 | 0.07 | 0.07 | 0.47 | 5.48 | 4.59 | 0.01 | 0.51 | 6 | 2320 |
| ÖLFUSÁ, Postglacial basalts(3) | 47.8 | 15.5 | 1.32 | 1.08 | 10.05 | 0.18 | 8.81 | 12.64 | 1.96 | 0.14 | 0.13 | 0.23 | 158 | 70 |
| *Hvítá-w, Kljáfoss, Postglacial basalts(4)* | 48.1 | 15.6 | 1.41 | 1.07 | 10.14 | 0.19 | 9.94 | 12.44 | 2.14 | 0.16 | 0.14 | 0.36 | 147 | 80 |
| *Nordurá, Stekkur, Tertiary basalts(5)* | 50.0 | 14.5 | 2.82 | 4.49 | 9.29 | 0.23 | 4.54 | 10.28 | 3.02 | 0.47 | 0.36 | | 267 | 235 |
| *Nordurá, Stekkur, Tertiary rhyolites(6)* | 73.8 | 13.8 | 0.25 | 1.97 | 0.92 | 0.05 | 0.18 | 1.16 | 4.88 | 2.92 | 0.04 | | 99 | 146 |

| g/kg | SiO2 | Al | Ti | Fe | Mn | Mg | Ca | Na | K | PO4 | Sr | $F_{(10)}$ | $SO4_{(11)}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| THJÓRSÁ, weigthed average(7) | 492 | 78.7 | 9.81 | 84.2 | 1.38 | 45.1 | 82.7 | 17.2 | 2.61 | 2.37 | 0.154 | 0.157 | 1.1 |
| ÖLFUSÁ, Postglacial basalts | 478 | 81.8 | 7.91 | 81.6 | 1.39 | 53.1 | 90.3 | 14.5 | 1.16 | 1.74 | 0.158 | 0.070 | 1.1 |
| HVÍTÁ-W, FERJUKOT, weighted average(8) | 491 | 79.3 | 12.89 | 95.4 | 1.63 | 42.8 | 80.8 | 19.3 | 2.68 | 2.56 | 0.210 | 0.161 | 1.1 |
| *Hvítá-w, Kljáfoss, Postglacial basalts* | 481 | 82.4 | 8.45 | 86.3 | 1.47 | 59.9 | 88.9 | 15.9 | 1.33 | 1.87 | 0.147 | 0.080 | 1.1 |
| *Nordurá, Stekkur, weighed average(9)* | 505 | 76.5 | 16.60 | 98.1 | 1.75 | 26.8 | 72.1 | 22.7 | 4.33 | 4.73 | 0.263 | 0.233 | |

(1)The average chemical composition of postglacial basalts in the catchment area of the Thjórsá calculated from 36 analyses of rocks in that area (Nordic Volcanological Institute and Science Institute, University of Iceland, unpublished results). Analytical methods are given in Sigvaldason (1974).

(2)The chemical composition of the rhyolitic rocks in the catchment area of the Thjórsá is represented by a postglacial obsidian from the Torfajökull volcanic system (table 2; O'Nions and Grönvold, 1973).

(3)The average chemical composition of postglacial basalts in the catchment area of the Ölfusá and its tributaries calculated from 31 analysis of rocks in that area (Nordic Volcanological Institute and Science Institute, University of Iceland, unpublished results).

(4)The average chemical composition of postglacial basalts in the catchment area of the Hvítá-W at Kljáfoss (figs. 1, 2, and 3, sample spot 21) calculated from 7 analyses of rocks in that area (Nordic Volcanological Institute and Science Institute, University of Iceland, unpublished results).

(5)Calculated from 77 analyses of quartz normative tholeiites ( Jóhannesson, ms) from the catchment area of the Nordurá (figs. 1 and 3).

(6)The average composition of rhyolites in the catchment area of the Nordurá (figs. 1 and 3) calculated from 35 analyses of rocks in that area ( Jóhannesson, ms).

(7)The basalt and rhyolite are weighted according to their areal extent on the 1:250,000 geological map of the region ( Jóhannesson, Jakobsson, and Saemundsson, 1982). The basalt fraction is 0.983.

(8)The average chemical composition of Tertiary basalts in the catchment area of the Hvítá-W at Ferjukot (loc. 24) and its tributaries (table 2; figs. 1, 2, and 3) is calculated from 77 analyses of quartz normative tholeiites ( Jóhannesson, ms) from the catchment area of the Nordurá (figs. 1 and 3). The chemical composition of Quaternary basalts in the catchment area of the Hvítá-W at Ferjukot is represented by the Postglacial basalts in the catchment area of the Hvítá-W at Kljáfoss (figs. 1 and 3). The Quaternary rocks are weighted according to the size of the drainage area of the Hvítá-W by Kljáfoss (1685 $km^2$, figs. 1 and 3), but the Tertiary basalts are weighted according to the size of the catchment area of the Hvítá-W near Ferjukot (figs. 1 and 3) minus its catchment area by Kljáfoss (fig. 3; 3550 $km^2$ − 1685 $km^2$ = 1865 $km^2$).

(9)The weighted average chemical composition of Tertiary basalts and rhyolites in the catchment area of the Nordurá (figs. 1 and 3) is calculated from 112 analyses of rocks in that area ( Jóhannesson, ms). The rock types are weighted according to their areal extent on a geological map of the region (Kjartansson, 1968). The basalt fraction is 0.979.

(10)The average fluorine content of all the rocks except the rhyolite from the Thjórsá catchment area was calculated from the average potassium content of the rocks using the potassium/fluorine ratio of 16.6 suggested for Icelandic basalts by Sigvaldason and Óskarsson (1986).

(11)The average sulfur content of Quaternary basaltic rocks in Iceland (table 2) calculated from the 45 samples of Gunnlaugsson (ms) and Torssander (1989) which have an average value of 366 mg/kg S. The standard deviation is 264, the maximum value is 1250 and the minimum 10 mg/kg. Glassy rocks, especially those quenched at depth, such as pillow lavas, have a higher sulfur contents than thin lava flows (Gunnlaugsson, ms; Torssander, 1989).

TABLE 3

*Catchment areas*

| MAIN RIVER<br>*Tributary* | Area<br>km2 | Glaciers<br>km2 | Runoff<br>l/km2/s | Veget.<br>cover % | "Age"<br>m.y. |
|---|---|---|---|---|---|
| THJÓRSÁ | 7200 | 1010 | 55.5 | 16.8 | 0.6 |
| ÖLFUSÁ | 5760 | 620 | 76.4 | 36.9 | 0.6 |
| *Stóra Laxá* | 433 | | 46.9 | 31.4 | 1.9 |
| *Fossá* | 29 | | 57.3 | 58.5 | 1.9 |
| *Hvítá-S, Gullfoss* | 2000 | 370 | 66.5 | 21.5 | 0.5 |
| *Tungufljót* | 720 | 250 | 65.8 | 19.0 | 0.3 |
| *Brúará, Dynjandi* | 670 | | 110.3 | 54.0 | 0.3 |
| *Brúará, Efstidalur* | 215 | | 191.6 | 36.5 | 0.2 |
| *Sog* | 1050 | 21 | 110.7 | 40.8 | 0.3 |
| VARMÁ | 55 | | 40.3 | 67.9 | 0.3 |
| ELLIDAÁR | 270 | | 100.1 | 57.9 | 0.2 |
| LAXÁ, VOGATUNGA | 142 | | 54.9 | 55.6 | 6.7 |
| *Thverá, Dragháls* | 44 | | 123.9 | 55.3 | 5.2 |
| ANDAKÍLSÁ | 147 | | | 52.3 | 5.2 |
| HVÍTÁ-W, FERJUKOT | 3550 | 360 | 53.3 | 38.4 | 3.7 |
| *Grímsá* | 313 | | 69.0 | 44.7 | 2.9 |
| *Flókadalsá* | 155 | | 53.8 | 43.0 | 2.7 |
| *Reykjadalsá* | 210 | | 49.8 | 43.2 | 4.6 |
| *Hvítá-W, Kljáfoss* | 1685 | 360 | 56.1 | 19.0 | 1.0 |
| *Thverá, Borgarfjördur* | 480 | | 52.8 | 64.8 | 6.6 |
| *Nordurá, Stekkur* | 500 | | 70.5 | 50.9 | 7.7 |
| SOUTHWEST ICELAND(1) | 16922 | 1990 | 62.8 | 29.2 | 1.3 |

(1)The total catchment area for southwest Iceland and the area covered by glaciers is simply the cumulative drainage area of the main rivers, excluding the Varmá and Andakílsá (shown with upper case letters in table 3 and fig. 3). The average runoff, vegetative cover, and age for southwest Iceland (excluding the Varmá and Andakílsá), are weighted according to the size of the catchment areas of the main rivers.

average results for the runoff (table 3) and later in the chemical denudation rate for the Ellidaár river (table 6).

The areal distributions of individual rock formations and vegetative cover were measured for each catchment area. For the rock formations the geological map of Iceland (fig. 1; Jóhannesson and Saemundsson, 1989) was used. The oldest rocks in the catchment areas of Tertiary age in this study are about 13 my old (Jóhannesson, ms). Individual rock formations are divided into age groups and assigned an average age, that is Upper Tertiary, 8 my, Upper Pliocene and Lower Pleistocene, 1.9 my, Upper Pleistocene, 0.36 my, and Postglacial formations 0.005 my. In order to calculate the "weighted average age" of the rocks in each catchment area, the fraction of the total area covered by each formation

was measured and multiplied by its assigned age, and the results are shown in table 3.

A similar method was used for the estimation of vegetative cover of each catchment area. The vegetative cover groups are the ones reported by the National Centre for Educational Materials (1992; fig. 4). Each group was assigned an average vegetative cover of 75, 30, 5 and 0 percent respectively. The results for "weighted average vegetative cover" according to the areal distribution of each group (fig. 4) are shown in table 3.

## COMPOSITIONAL CHARACTERISTICS OF RIVERS IN SOUTHWEST ICELAND

The average chemical compositions, temperature, and discharge of the rivers in figure 2 are shown in table 1. In general, there is some variation in the chemical composition between and within individual rivers. The pH of the water in the s-river Brúará at Efstidalur is highest (8.77), and this water is also low in total dissolved inorganic carbon,

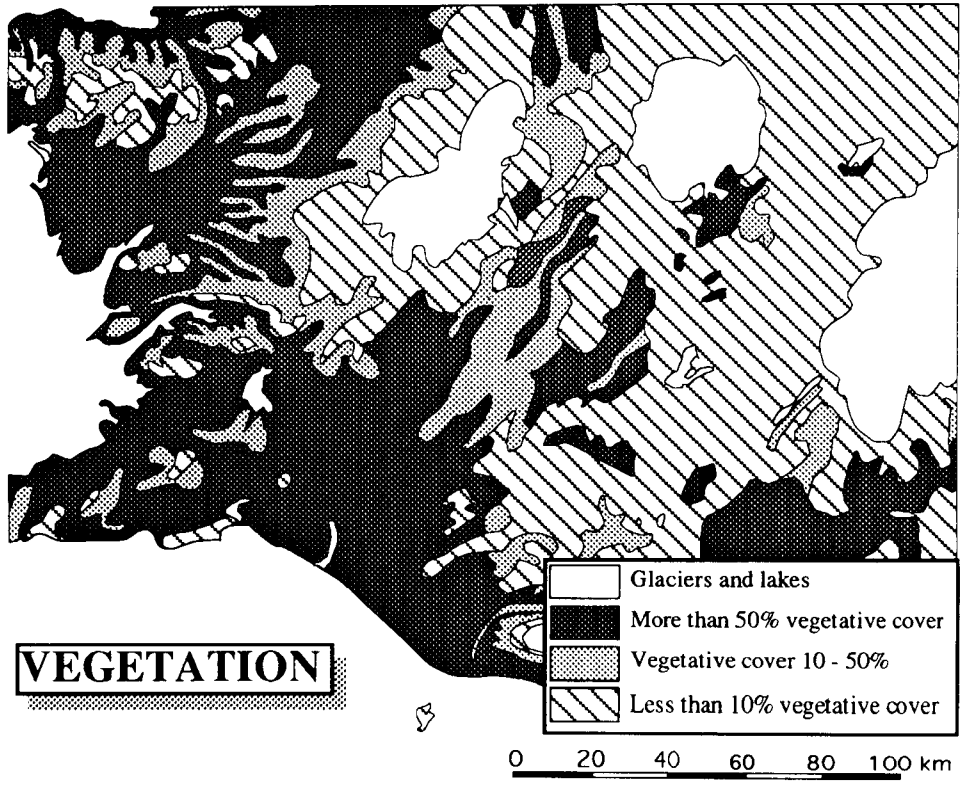



Fig. 4. Vegetation map of southwest Iceland. Modifications from the National Centre for Educational Materials (1992). Published with the permission (LMÍ 104-94) of the Iceland Geodetic Survey.

calcium, and magnesium. The pH is somewhat lower than that typical for groundwaters sealed off from atmospheric $CO_2$ (Gíslason and Eugster, 1987a), indicating some water-air interaction. Downstream at Dynjandi, the Brúará River has nearly doubled its carbon content, and the average pH is down to 7.64, indicating intense water-air interactions, as will be discussed later. The pH of other rivers ranges from 7.15 to 7.94, typical for waters with access to atmospheric $CO_2$ during or after interaction with the rocks (Gíslason and Eugster, 1987a; Gíslason, 1989). The silica concentration ranges from 7 mg/l to 46 mg/l. It is lowest in rivers with high runoff, discharging from old rocks (tables 1 and 3), but highest in the geothermally contaminated rivers Varmá, Reykjadalsá, and Fossá. Geothermal activity affects the river chemistry in Iceland to some extent. The runoff from high-temperature geothermal systems is insignificant, but the total natural runoff from low-temperature systems is 1.8 $m^3$/sec (Saemundsson and Fridleifsson, 1980), which is small compared to the total runoff, 5500 $m^3$/sec, for Iceland (Rist, 1956). However, small rivers are significantly affected, as can be seen in table 1 for the Varmá River, which drains a high-temperature geothermal system, and the rivers Reykjadalsá and Fossá, which drain hot springs. The geothermal activity affects all the major elements and fluorine in the Varmá and Reykjadalsá Rivers, but silica, calcium, sulfur, fluorine, and strontium in the Fossá River. The relatively large rivers, the Thjórsá and the Hvítá River at Gullfoss in southern Iceland (Hvítá-S, Gullfoss; table 1), also drain high-temperature geothermal systems with much less, yet distinct, effects on their chemistry. The total dissolved carbon, sulfur, and fluorine are somewhat elevated in the Thjórsá, and the sulfur concentration is relatively high in the Hvítá-S at Gullfoss (table 1). Magnesium concentration is relatively low in the spring-fed rivers, Tungufljót, Brúará, and the Hvítá River in western Iceland at Kljáfoss (Hvítá-W, Kljáfoss; table 1), chlorine concentration is lowest in rivers with catchment areas far away from the coast and at the highest elevation, and fluorine and phosphorus concentrations are higher in rivers draining young rocks than in those draining old rocks (tables 1, 3).

The concentration of chemical constituents in Icelandic rivers is lower than the world's average with the exception of dissolved silica, sodium, ammonium, and phosphorus.

Seasonal variations in temperature and total evaporated residue (TER) are shown for selected rivers in southern Iceland in figures 5 and 6. The variation in temperature (fig. 5) is considerable in d- and g-rivers, ranging from close to zero to 20°C (Fossá, Tungufljót, and Thjórsá). It is insignificant in s-rivers close to the head springs (Brúará, Efstidalur), but the variations increase downstream (fig. 5, Brúará, Dynjandi). The amount of total evaporated residue (TER) varies seasonally in similar way to temperature. The variation is prominent in g- and d-rivers (fig. 6). The concentration is at a maximum in the wintertime but reaches a minimum in mid- and late summer. At that time their discharge is at maximum, and residual snow and ice being melted is depleted in soluble constituents incorporated in the early melt (Gíslason, 1990). It should be pointed out

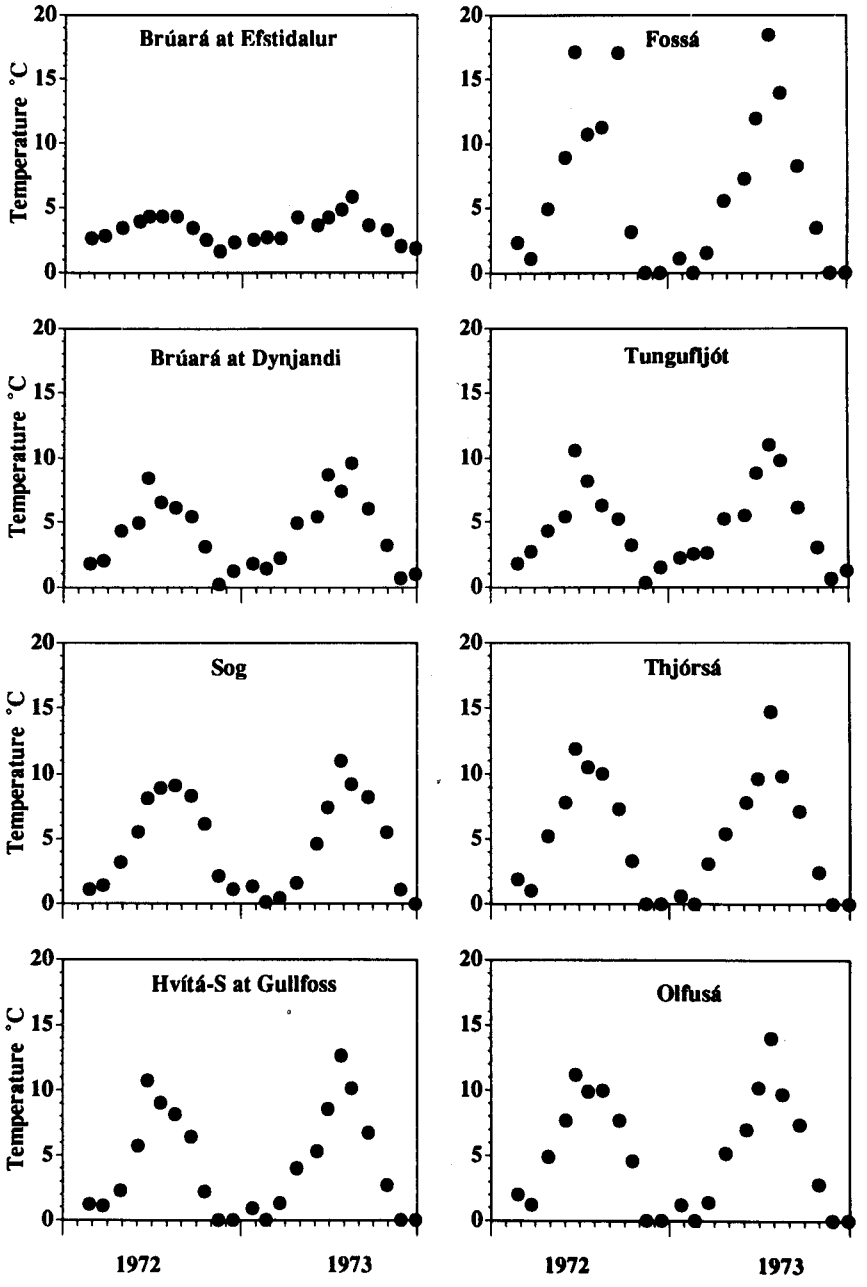



Fig. 5. Variation in river temperature, 1972–1973, in selected rivers in southern Iceland.

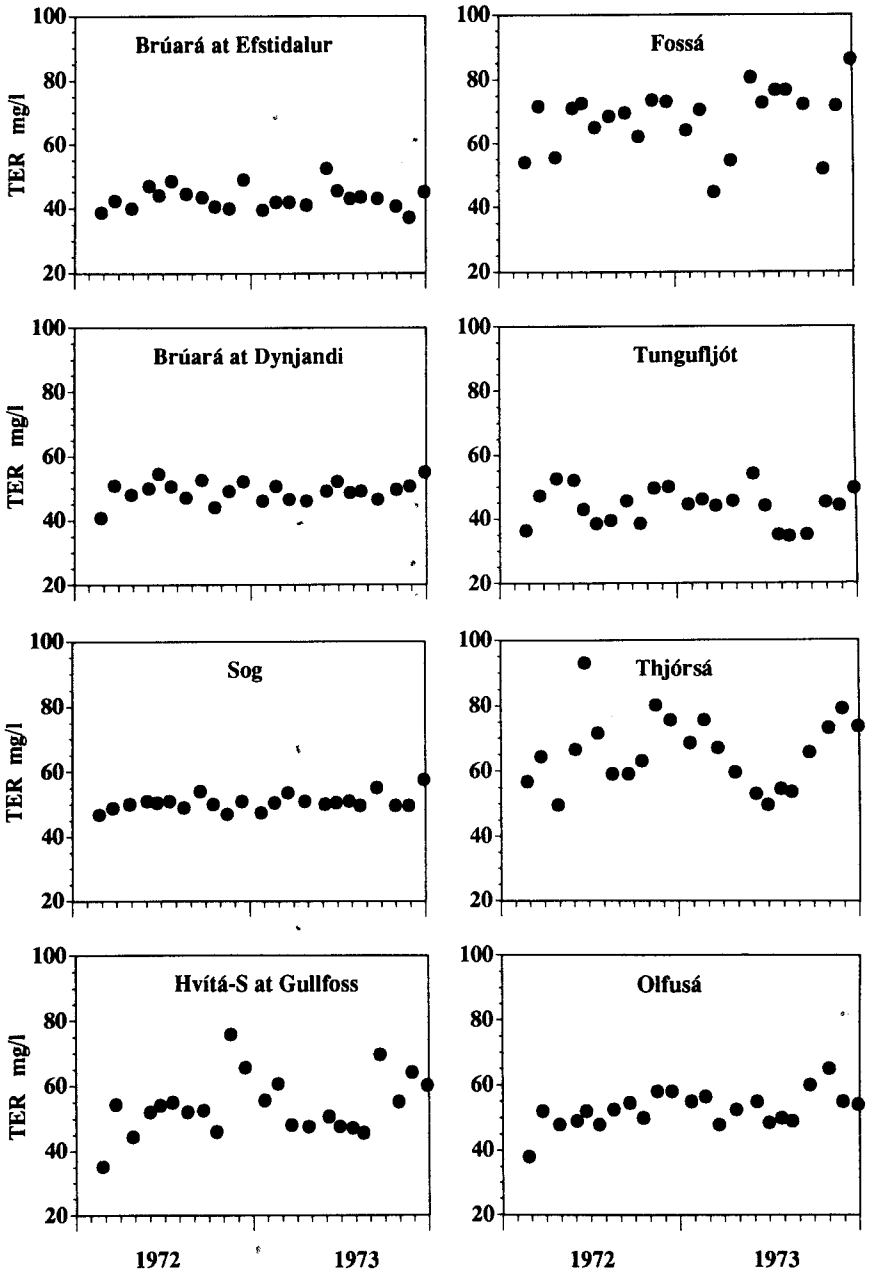



Fig. 6. Variation in total evaporated residue (TER), 1972–1973, in selected rivers in southern Iceland.

that in February and October, 1972, the samples were collected during floods in the d- and s-rivers. Therefore, these samples are exceptionally low in dissolved solids for this part of the year, thus distorting the seasonal variation in total dissolved solids. The decline in the dissolved solid content of the direct runoff rivers in western Iceland starts as early as February. It starts to increase in May when the snow in the catchment areas has melted and reaches its maximum in mid-winter. The dependence of the total evaporated residue (TER) on the amount of discharge will be discussed in later sections.

The seasonal variation in nitrate is shown in figure 7 for some of the rivers in southern Iceland. Dissolved nitrate varies with water temperature (figs. 5 and 7) in all but one of the rivers, the Sog which drains Lake Thingvallavatn (fig. 2). Nitrate is at a minimum in mid- and late summer when photosynthetic consumption dominates but at a maximum in wintertime when respiration and possibly decay of organic material dominate. In the winter there is a lack of light due to the northerly latitude of Iceland and the formation of ice, often snow-covered, on lakes and rivers. The reaction for photosynthesis by algal biomass (Redfield, Ketchum, and Richards, 1963) can be written as shown here,

$$106\ CO_2 + 16\ NO_3^- + HPO_4^- + 122\ H_2O + 18\ H^+ (+ \text{trace elements and energy}) \rightarrow C_{106}H_{263}O_{110}N_{16}P_1 + 138\ O_2$$

Respiration and decay of algal biomass drives the reaction to the left, causing an increase in phosphate, nitrogen, and $CO_2$ in the atomic ratios (P:N:C) 1:16:106 or mass ratios 1:7:41. Photosynthesis has the opposite effect: phosphate, nitrogen, and $CO_2$ are consumed. As shown by Redfield, Ketchum, and Richards (1963), the concentration ratio for nitrate versus phosphate in ocean waters, in marine plankton, continental aquatic plants (7; Vallentyne, 1973) and terrestrial plants (7.6; Likens, Bormann, and Johnsson, 1981) is very close to this stoichiometry. This mass ratio is slightly lower in coastal waters southwest of Iceland (6.2; Stefánsson and Ólafsson, 1991). The seasonal variation in nitrate (fig. 7) cannot be explained by simple dilution by high discharge in the summer. The average $NO_3$ concentration in Icelandic rain is 64 μg/l $NO_3$-N (The Icelandic Meteorological Office, 1958-1981), and s-rivers with stable discharge (Brúará at Efstidalur and Dynjandi) show seasonal variations in nitrate concentration (fig. 7). Nitrate concentrations are always low in the Sog River which drains lake Thingvallavatn. The residence time of water in the lake is 11 months, primary production in the lake is limited by the availability of nitrogen, and a considerable amount of biomass is buried in sediments each year (Ólafsson, 1992; Jónasson, 1992; Jónasson, Adalsteinsson, and Jónsson, 1992). The maximum value for nitrate in the Brúará, a s-river, is around 50 μg/l $NO_3$-N. This value decreases in the summertime at both sample locations in the river (fig. 2) but to a lesser degree at Efstidalur, which is closer to the headspring than Dynjandi (fig. 2). The reason is probably that the water at Efstidalur has had less time

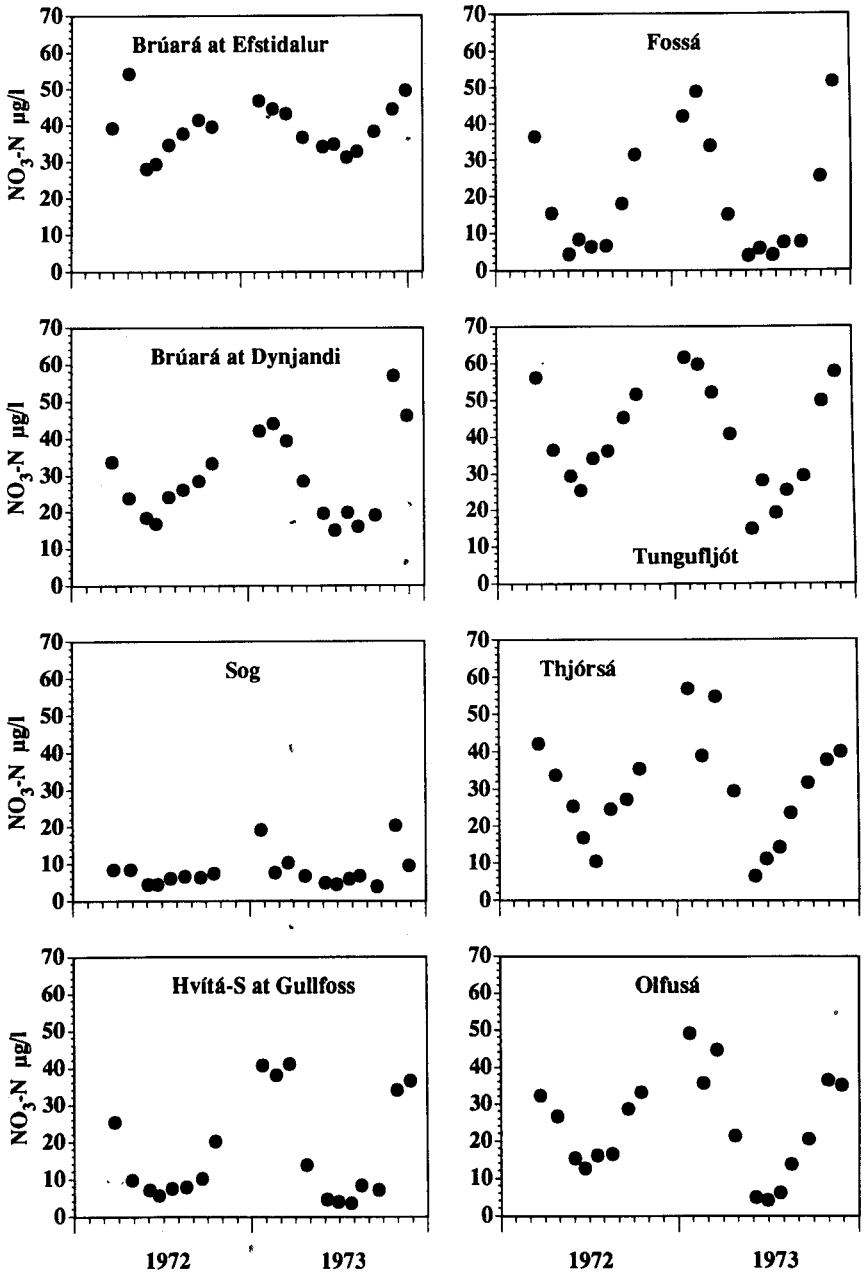



Fig. 7. Variation in nitrate concentration, 1972–1973, in selected rivers in southern Iceland.

for interaction with the biomass than the water at Dynjandi. The same applies to the phosphate content at these two sample locations.

The phosphate concentration is greater close to the source of the Brúará, at Efstidalur than further downstream (Brúará, Dynjandi; table 1). No seasonal variations were observed in the phosphate concentration. If the nutrient chemistry of the river waters were only controlled by the photosynthesis respiration reaction, a similar seasonal variation in the phosphate and the $CO_2$ concentrations as is observed for nitrate would be expected. On an atomic basis this variation is 16 times smaller for phosphorus than nitrogen. The resolution of the analytical method is probably not good enough to record such variations (1-4 μg/l $PO_4$-P), if they exist.

The carbon dioxide variations should be enormous if the above reaction were the only process governing its concentration. However, $CO_2$ can diffuse into and out of the river water, to or from the atmosphere. Nevertheless, some variations similar to the one shown in figure 8 for the Brúará at Dynjandi can be found. As for nitrate, the calculated partial pressure of $CO_2$ is at a minimum in summer.

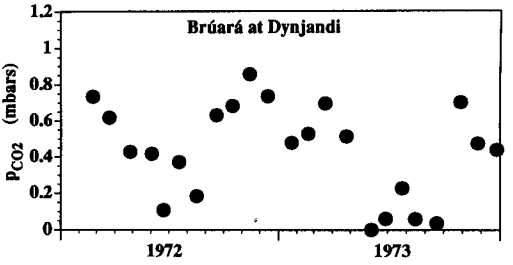



Fig. 8. Variation in calculated partial pressure of $CO_2$, 1972–1973, in the Brúará River at Dynjandi.

The correlation between total evaporated residue (TER) and discharge is shown in figure 9 for d-rivers and rivers of mixed but primarily glacier origin (g-rivers). Normalized discharge, that is, the actual discharge at the time of sampling divided by the average discharge, is reported. The discharge for the enormous flood of February 26, 1974, is excluded from the average discharge for the rivers in western Iceland (Nordurá, Grímsá, Flókadalsá, Thverá, and Hvítá-W at Ferjukot) since it would dominate the average value. In order to get total evaporated residue below 30 mg/l the discharge needs to be more than 3 times the average (fig. 9). There is a sharp initial decrease in TER with increased discharge when the variation from the average discharge is less than twofold. When the discharge becomes greater the correlation function becomes asymptotic to a background value, ranging from 25 to 30 mg/l. This background is probably the TER concentration of the precipitation that gave rise to the flood waters.

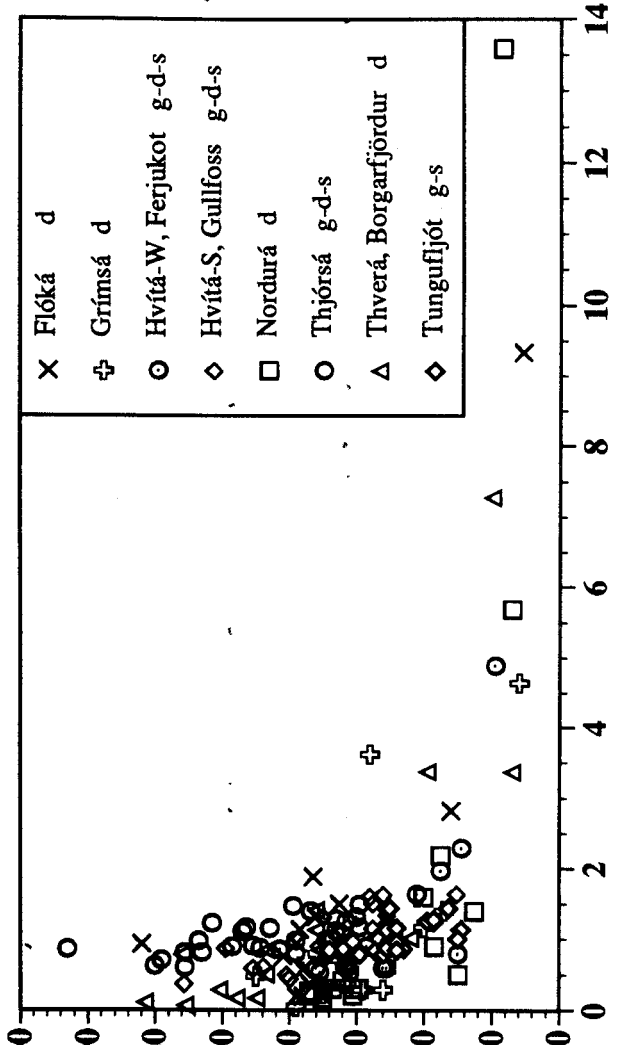



Fig. 9. Total evaporated residue (TER) versus normalized discharge for some rivers in southwest Iceland. River type shown in the legend.

SOURCE OF THE DISSOLVED SOLIDS

The database for the chemistry of precipitation in southwest Iceland and the average chlorine concentration of the river waters can be used to elucidate the source of supply for the dissolved chemical constituents.

*Precipitation.*—Icelandic precipitation shows a near normal distribution around a mean pH of 5.4 (fig. 10) with a standard deviation of 0.46. The mean pH value of Icelandic precipitation is about 0.2 pH units lower than the pH of pure water saturated with air at 25°C. A plot of Cl versus all the major elements in Icelandic precipitation is shown in figures 11A to H. The Cl concentration ranges from 0.27 to 118 mg/l, with a median value of 5.8 mg/l and an average value of 8.9 mg/l. It is at a minimum in July but reaches a maximum in mid-winter. Sigurdsson and Einarsson (1988) have shown that the amount of aerosol is greatest close to the coast and decreases inland and with increased elevation. The meteorological stations from which most of the data originate are located close to sample

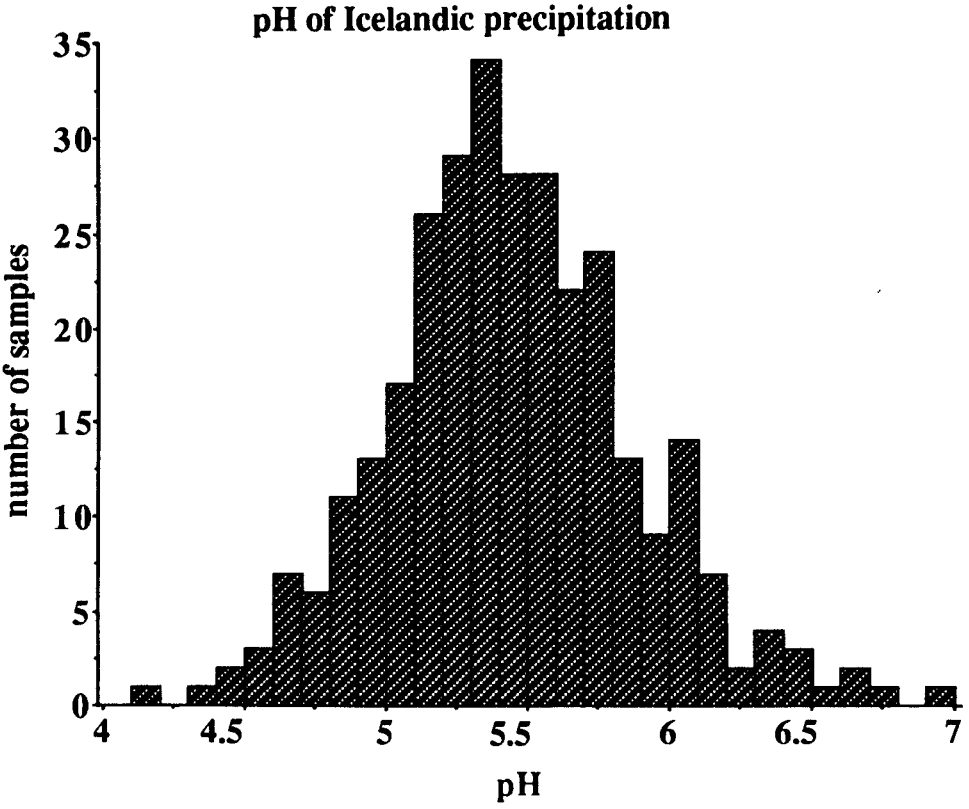
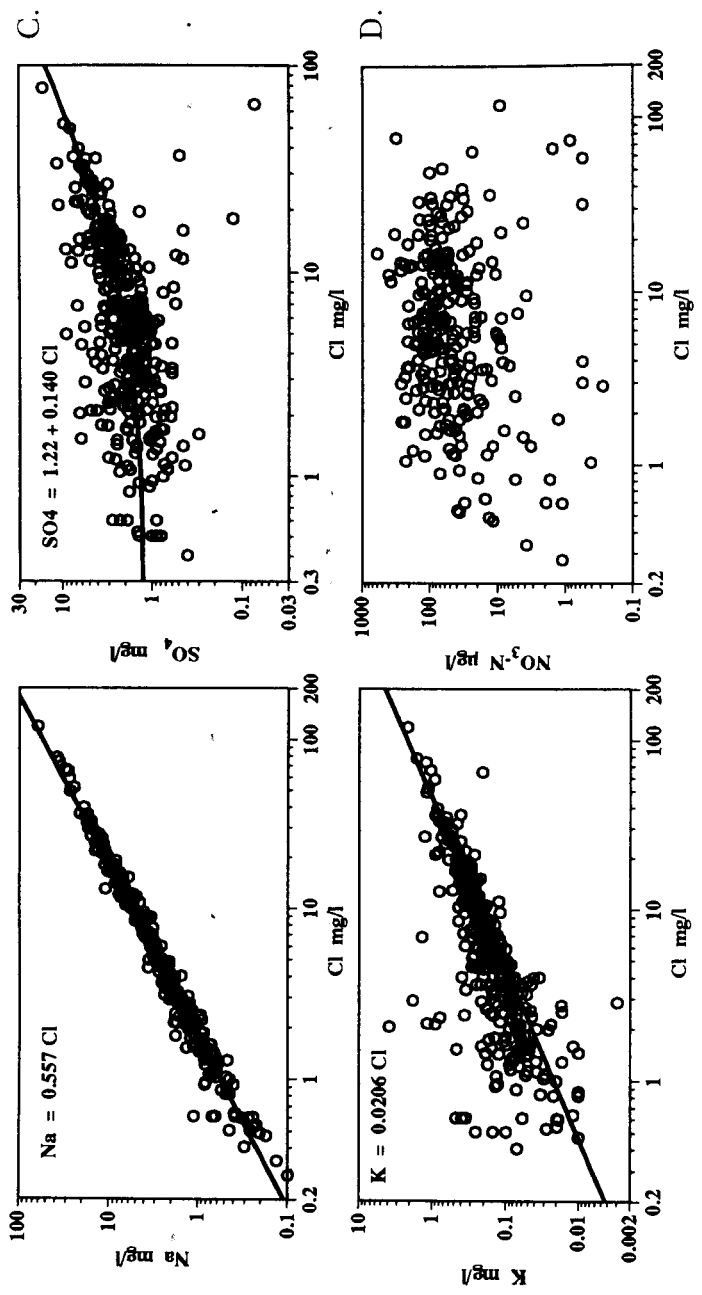



Fig. 10. Frequency diagram for the pH of Icelandic precipitation.


A.
Na = 0.557 Cl
Na mg/l
Cl mg/l
B.
K = 0.0206 Cl
K mg/l
Cl mg/l
C.
SO4 = 1.22 + 0.140 Cl
SO4 mg/l
Cl mg/l
D.
NO3-N µg/l
Cl mg/l

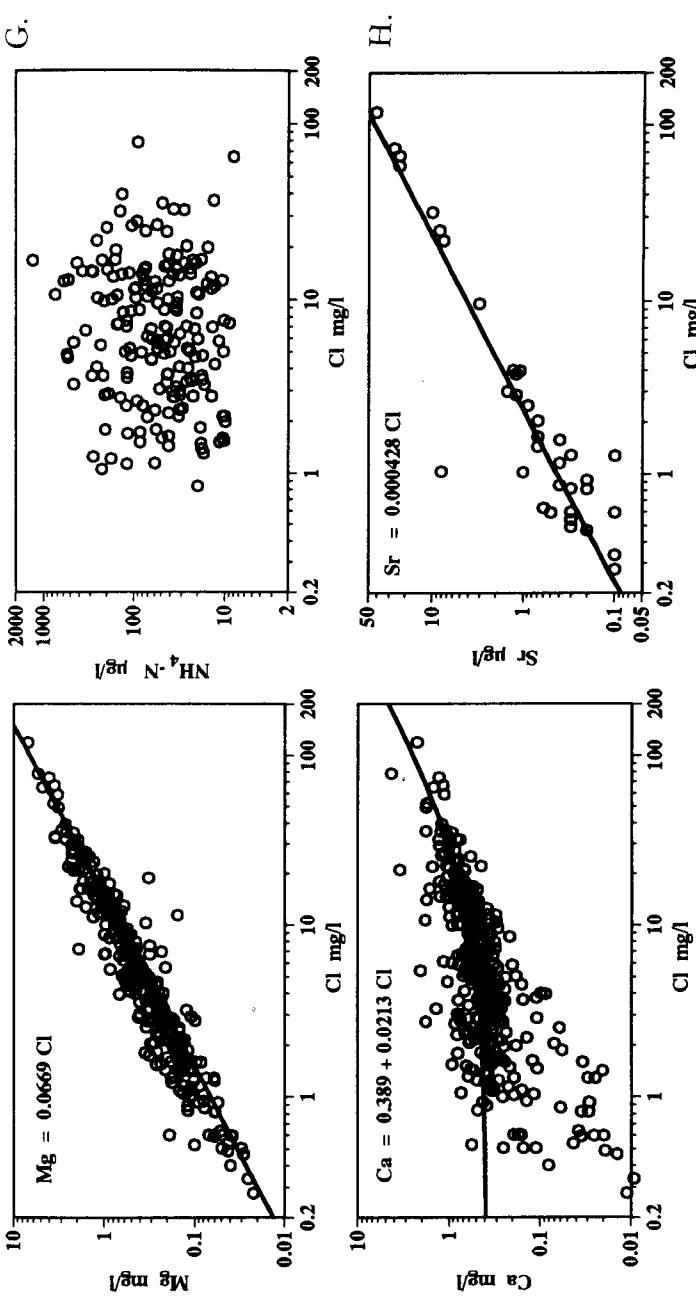



Fig. 11. Plot of measured constituents versus Cl in Icelandic precipitation. The equations and lines on the diagrams represent the ratio of the given constituent versus Cl in mean ocean water as reported by Riley and Chester (1971), but the intercepts of the linear equations in figure 11C and F are the results of a linear regression of the data assuming the slope to be equal to the marine ratios of Riley and Chester (1971).

spots 15, 2, and 3 in figure 2. Most of the river waters originate farther inland; thus riverine Cl concentration is somewhat lower than that of the average precipitation collected at these stations (table 1). No significant difference in the major ion ratios was detected from one meteorological station to another. Na/Cl, K/Cl, Mg/Cl, and Sr/Cl ratios in Icelandic precipitation are close to the oceanic ratios for the same ions (fig. 11A, B, E, and H), indicating that they are solely of marine source. The concentration of Ca and $SO_4$ in Icelandic precipitation is higher than would be predicted from an unfractionated marine contribution. In order to regress linearly the data shown in figures 11C and F, a constant enrichment is assumed, independent of the marine contribution. The non-marine enrichment is represented by the intercept, but the slope of the line is due to the marine contribution. The nitrate and ammonium in Icelandic precipitation are shown in figure 11D and G, respectively. Nitrate and ammonium concentrations in Icelandic precipitation are independent of the Cl concentration, and there is no spatial correlation between sampling sites. Thus the nitrate and ammonium source is non-marine but global with respect to Iceland. The average nitrate and ammonium concentrations in Icelandic precipitation, including samples in which nitrate and ammonium were not detected (0 μg/l), is 64.3 μg/l $NO_3$-N and 59.3 μg/l $NH_4$-N.

*Rock and airborne contribution to river water.*—To calculate the amount of airborne dissolved or soluble solids in the catchment areas of the rivers, it is assumed that all dissolved chlorine in the river water is airborne. Studies of Cl and B in surface waters and cold groundwater in Iceland indeed indicate that only an insignificant portion of Cl present in these waters has been leached from soil and rock (Arnórsson and Andrésdóttir, 1995). The main reason is considered to be the low Cl content of the Icelandic basalts (Sigvaldason and Óskarsson, 1976; Arnórsson and Andrésdóttir, 1995) which is on average somewhat below 200 mg/kg.

Using the Cl concentration of river water (table 1), the airborne contribution of other major solids is obtained from the linear equations shown in figure 11A, B, C, E, F, and H. The total dissolved carbon concentration in precipitation is calculated assuming air saturation of pure water at 0°C, cast in terms of $HCO_3$ (1.66 mg/l). The results are shown in table 4 for individual rivers, and the discharge weighted average for the main rivers in southwest Iceland, excluding the Varmá and Andakílsá. This general approach would lead to overestimation of the airborne supply to the geothermally contaminated Varmá, Reykjadalsá, and Fossá, since some of the Cl in these rivers originates from the rocks. To establish the source for individual chemical constituents in these rivers we used the Cl concentration of the nearest (neighboring) catchment to estimate the airborne contribution. For the Varmá River the Cl concentration of the Ellidaár was used, the Reykjadalsá was corrected by the Cl concentration of the Flókadalsá, and the Fossá by the Cl concentration of the Stóra-Laxá (fig. 3; tables 1 and 4). To calculate the geothermal supply of individual major constituents it is further assumed

that the rock, soil, and air supply during weathering is the same in these catchments as in their neighboring catchment areas. The results of these calculations are shown in table 4.

Most of the dissolved carbon in the Icelandic rivers is derived directly or indirectly (via the soil) from the atmosphere. All the dissolved carbon in the river water, other than that brought in with precipitation (1.66 as mg/l $HCO_3$), is shown as TDS derived from soil and air in table 4. Most of this carbon is derived from soil. However, some carbon as well as sulfur may be derived from rocks or even from a deep source in rivers draining geothermal fields as shown in table 4 for the Varmá, Reykjadalsá, and Fossá.

Silica, F, Al, Fe, Mn, and Ti derive primarily from the dissolution of basalts. If the ratio of these constituents to chlorine in precipitation is the same as in ocean water (Riley and Chester, 1971), their calculated discharge weighted average concentrations in precipitation in southwest Iceland, using a Cl concentration of 5.31 mg/l (table 1), are: $SiO_2$ 0.5 μg/l, F 0.4 μg/l, Al 0.001 μg/l, Fe 0.008 μg/l, Mn 0.005 μg/l, and Ti 0.003 μg/l. In other words, an insignificant fraction of the concentration of these constituents in river water in southwest Iceland is derived from sea water (table 1).

It is difficult to assess the airborn contribution to the phosphorus and nitrogen content of the Icelandic rivers because no data are available on the phosphorus concentration of Icelandic precipitation, their concentration is highly variable in ocean waters, and the atmospheric nitrate and ammonium levels are variable and non-marine (fig. 11D and G). The total dissolved inorganic nitrogen versus dissolved phosphorus in rivers in south and west Iceland is shown in figure 12A and B. The dashed lines in the diagrams represent the average ratio of total dissolved inorganic nitrogen versus phosphorus in "unpolluted rain" (Meybeck, 1982), biomass, and a simple reaction path for an abiotic congruent dissolution of basalt in an average Icelandic precipitation. The average concentration of N ($NO_3$ + $NH_4$) in Icelandic precipitation, 124 μg/l N, is calculated from the data shown in figure 11D and G. The average phosphorus concentration of Icelandic precipitation (1.5 μg/l $PO_4$-P) is then calculated from the N concentration of Icelandic precipitation and the N/P ratio in "unpolluted rain" (Meybeck, 1982). The average total nitrogen content for basalt (30 mg/kg N) is from Wlotzka (1972), and the average phosphorus content (310 mg/kg P) of Icelandic tholeites is calculated from the data of Óskarsson, Sigvaldason, and Steinthórsson (1982). The slope for the photosynthetic reaction shown earlier and the biomass mass ratio in general are close to 7. The Icelandic N and P concentrations of rivers are not as tightly clustered around the biomass stoichiometry (fig. 12A and B) as, for example, those of Icelandic coastal waters (Stefánsson and Ólafsson, 1991). Direct runoff rivers (d-rivers) in western Iceland plot close to the precipitation ratio (fig. 12A), but rivers of spring and glacial origin (s-, g-, l-rivers) are more phosphorus rich (fig. 12B).

TABLE 4

*Source of dissolved solids in rivers in southwest Iceland (percent of the total for each constituent)*

| MAIN RIVER | Cl | Cl | $SiO_2$ | $SiO_2$ | Na | Na | Na | Mg | Mg | Mg | Ca | Ca |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *Tributary* | (1)pr. | (2)ro. geo. | (3)ro. wea. | ro. geo. | pr. | ro. wea. | ro. geo. | pr. | ro. wea. | ro. geo. | pr. | ro. wea. |
| THJÓRSÁ | 100 | | 100 | | 24 | 76 | | 17 | 83 | | 11 | 89 |
| ÖLFUSÁ | 100 | | 100 | | 37 | 63 | | 27 | 73 | | 13 | 87 |
| *Stóra Laxá* | 100 | | 100 | | 44 | 56 | | 26 | 74 | | 14 | 86 |
| *Fossá* | 91 | 9 | 74 | 26 | 41 | 52 | 7 | 16 | 44 | 40 | 10 | 63 |
| *Hvítá-S, Gullfoss* | 100 | | 100 | | 26 | 74 | | 19 | 81 | | 13 | 87 |
| *Tungufljót* | 100 | | 100 | | 33 | 67 | | 29 | 71 | | 19 | 81 |
| *Brúará, Dynjandi* | 100 | | 100 | | 33 | 67 | | 37 | 63 | | 16 | 84 |
| *Brúará, Efstidalur* | 100 | | 100 | | 30 | 70 | | 60 | 40 | | 19 | 81 |
| *Sog* | 100 | | 100 | | 43 | 57 | | 34 | 66 | | 14 | 86 |
| VARMÁ | 60 | 40 | 26 | 74 | 24 | 18 | 58 | 16 | 18 | 66 | 4 | 23 |
| ELLIDAÁR | 100 | | 100 | | 58 | 42 | | 48 | 52 | | 15 | 85 |
| LAXÁ, VOGATUNGA | 100 | | 100 | | 65 | 35 | | 34 | 66 | | 14 | 86 |
| *Thverá, Dragháls* | 100 | | 100 | | 68 | 32 | | 36 | 64 | | 20 | 80 |
| ANDAKÍLSÁ | 100 | | 100 | | 68 | 32 | | 43 | 57 | | 23 | 77 |
| HVÍTÁ-W, FERJUKOT | 100 | | 100 | | 43 | 57 | | 26 | 74 | | 15 | 85 |
| *Grímsá* | 100 | | 100 | | 49 | 51 | | 28 | 72 | | 16 | 84 |
| *Flókadalsá* | 100 | | 100 | | 49 | 51 | | 28 | 72 | | 15 | 85 |
| *Reykjadalsá* | 60 | 40 | 57 | 43 | 35 | 25 | 40 | 18 | 19 | 63 | 10 | 58 |
| *Hvítá-W, Kljáfoss* | 100 | | 100 | | 36 | 64 | | 30 | 70 | | 17 | 83 |
| *Thverá, Borgarfjördur* | 100 | | 100 | | 56 | 44 | | 21 | 79 | | 12 | 88 |
| *Nordurá, Stekkur* | 100 | | 100 | | 59 | 41 | | 29 | 71 | | 14 | 86 |
| SOUTHWEST ICELAND(5) | 100 | | 100 | | 33 | 67 | | 23 | 77 | | 13 | 87 |

(1)Percent Cl in rivers supplied by precipitation.
(2)Percent Cl in rivers supplied by leaching of rocks by geothermal processes.
(3)Percent $SiO_2$ in rivers supplied by weathering of rocks.
(4)Percent $HCO_3$ in rivers supplied by precipitation, soil and air.
(5)The discharge weighted average for the main rivers in southwest Iceland (upper case letters), excluding the Varmá and Andakílsá.

The composition of precipitation, the dissolution of basaltic rocks, photosynthesis, respiration, and decay of biomass (fig. 7), binding of $N_2$ by algae and plants, denitrification in soil, and artificial fertilizing can affect this ratio in river water. The average total dissolved inorganic N ($NO_3$ + $NH_4$) content of Icelandic precipitation is 124 μg/l N, whereas the discharge weighted average total inorganic N ($NO_3$ + $NO_2$ + $NH_4$) concentration of rivers in southwest Iceland is 62 μg/l N (table 1). Thus there is a nitrogen sink in the catchment areas, caused by primary production. Photosynthesis dominates over respiration and decay of organic material. Primary production in waters that plot above the biomass line is P limited, but below the biomass line it is N limited (fig.

TABLE 4
(continued)

| Ca ro. geo. | K pr. | K ro. wea. | K ro. geo. | SO4 pr. | SO4 ro. wea. | SO4 ro. geo. | Sr pr. | Sr ro. | N pr. | PO4 pr. | PO4 ro. | HCO3 (4)pr., soil, air | HCO3 ro. geo. | TDS prec. | TDS ro. | TDS soil air |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 17 | 83 | | 29 | 71 | | 45 | 55 | 100 | 8 | 92 | 100 | | 14 | 39 | 47 |
| | 22 | 78 | | 54 | 46 | | 39 | 61 | 100 | 19 | 81 | 100 | | 19 | 37 | 44 |
| | 20 | 80 | | 58 | 42 | | | | 100 | 18 | 82 | 100 | | 21 | 36 | 43 |
| 27 | 16 | 62 | 22 | 48 | 34 | 18 | 13 | 87 | 100 | 15 | 85 | 76 | 24 | 15 | 53 | 32 |
| | 14 | 86 | | 35 | 65 | | 47 | 53 | 100 | 16 | 84 | 100 | | 14 | 41 | 45 |
| | 18 | 82 | | 55 | 45 | | 47 | 53 | 100 | 19 | 81 | 100 | | 18 | 41 | 42 |
| | 26 | 74 | | 53 | 47 | | 61 | 39 | 100 | 22 | 78 | 100 | | 18 | 38 | 43 |
| | 23 | 77 | | 48 | 52 | | 90 | 10 | 100 | 13 | 88 | 100 | | 21 | 48 | 31 |
| | 22 | 78 | | 56 | 44 | | 71 | 29 | 100 | 24 | 76 | 100 | | 23 | 33 | 44 |
| 73 | 2 | 2 | 96 | 17 | 11 | 73 | | | 100 | 11 | 89 | 36 | 64 | 10 | 77 | 13 |
| | 54 | 46 | | 61 | 39 | | | | 100 | 68 | 32 | 100 | | 30 | 31 | 39 |
| | 55 | 45 | | 62 | 38 | | | | 100 | 61 | 39 | 100 | | | 29 | 40 |
| | 56 | 44 | | 69 | 31 | | | | 100 | 60 | 40 | 100 | | 33 | 29 | 37 |
| | 59 | 41 | | 64 | 36 | | | | 100 | 61 | 39 | 100 | | 38 | 27 | 35 |
| | 27 | 73 | | 54 | 46 | | 55 | 45 | 100 | 27 | 73 | 100 | | 21 | 35 | 43 |
| | 40 | 60 | | 62 | 38 | | | | 100 | 46 | 54 | 100 | | 24 | 33 | 43 |
| | 36 | 64 | | 70 | 30 | | | | 100 | 84 | 16 | 100 | | 24 | 34 | 42 |
| 32 | 28 | 24 | 49 | 31 | 20 | 49 | | | 100 | 74 | 26 | 60 | 40 | 15 | 61 | 24 |
| | 22 | 78 | | 51 | 49 | | 64 | 36 | 100 | 15 | 85 | 100 | | 20 | 38 | 42 |
| | 29 | 71 | | 65 | 35 | | | | 100 | 46 | 54 | 100 | | 24 | 30 | 46 |
| | 41 | 59 | | 62 | 38 | | 36 | 64 | 100 | 53 | 47 | 100 | | 27 | 32 | 41 |
| | 21 | 79 | | 42 | 58 | | 44 | 56 | 100 | 14 | 86 | 100 | | 17 | 38 | 45 |

12A and B). For example, when average Icelandic precipitation of the composition N: 124 and P: 1.5 reacts with the growing biomass (photosynthesis), the N and P concentrations of the water decrease according to the biomass mass ratio 7:1. Eventually, biomass consumes all the dissolved P, leaving behind 114 μg/l N. The lack of P hinders further growth. However, with respect to N and P, dissolution of basalt results primarily in adding P to the water, since the N:P mass ratio of basalt is 1:10.3 (fig. 12A and B). The dissolution of basalt in soil makes further growth possible, followed by a further decline in the N and P concentrations. The large variation in N relative to P for direct runoff rivers in western Iceland can be explained by a balance between production (basalt dissolution) and consumption (photosynthesis) of P (fig. 12A). The waters of the direct runoff rivers are in contact with biomass from the time that precipitation falls on the catchment area. However, the waters of the spring- and glacier-fed rivers have spent most of their time in an

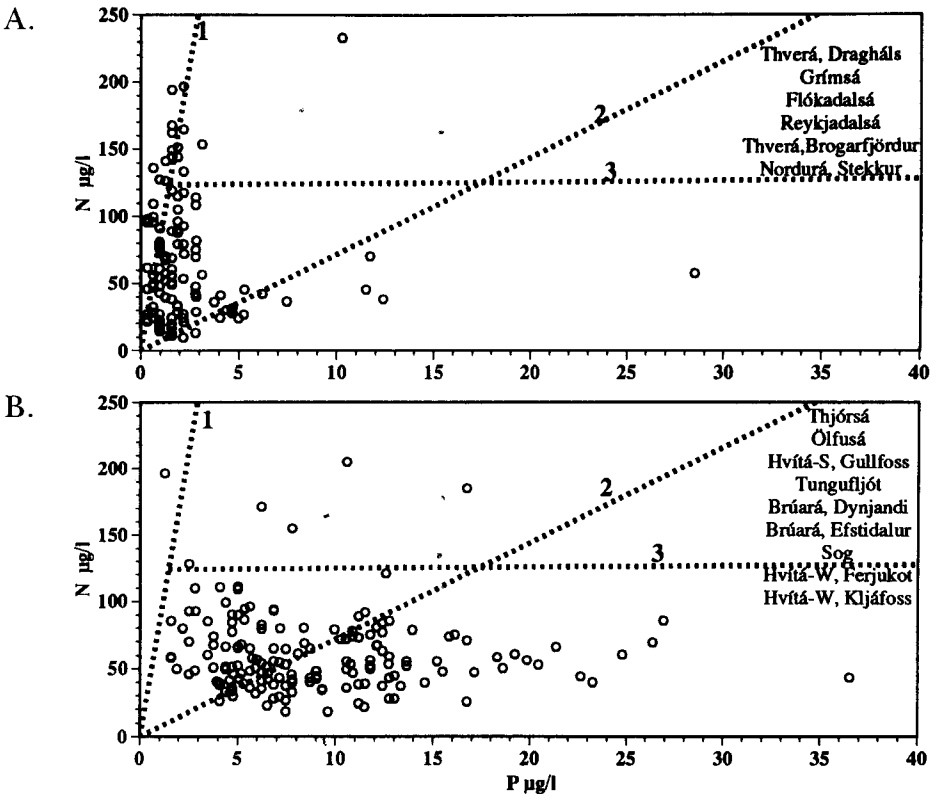



Fig. 12. The total dissolved inorganic nitrogen versus dissolved phosphorus in direct runoff rivers (d-rivers) is shown in (A) and in (B) for rivers of spring and glacial origin (s-, g-, l-rivers). The dashed lines represent the average ratio of total dissolved inorganic nitrogen to phosphorus in (1) "unpolluted rain", (2) biomass, and (3) basaltic rocks.

abiotic world, in and under glaciers and sometimes in deep aquifers. These waters have more rock signature, they are more P rich (fig. 12B) than the waters of the direct runoff rivers in western Iceland (fig. 12A). In these waters there is more production of P (dissolution of basalt) than consumption (photosynthesis). However, it is evident that there is a considerable consumption of N and P in the g- and s-rivers since the N concentration is well below that of the average of the incoming precipitation (fig. 12B). A simple reaction path for an abiotic congruent dissolution of basalt in average Icelandic precipitation is depicted by the basalt line in figure 12A and B.

The airborne contribution to the total dissolved solids in Icelandic rivers ranges from 14 percent, for the catchments that are farthest inland (table 4; fig. 3; Hvítá-S at Gullfoss and Thjórsá) to more than 30 percent for those closest to the coast, such as the catchments of the Andakílsá,

Laxá at Vogatunga, and Ellidaár Rivers (table 4 and fig. 3). The discharge weighted average 17 percent airborne contribution to the total dissolved solids concentration of Icelandic river waters (table 4) is similar to Meybeck's (1979) estimates of an average 15 percent atmospheric contribution to the surface waters of the world but higher than the 1 to 2 percent estimate of Berner and Berner (1987). One would expect an island like Iceland to have relatively more airborne contribution than the continents. Thus the Icelandic data lend credence to Berner and Berner's (1987) estimate for the world.

As shown in table 4 the discharge weighted average airborne or air-derived contribution for the elements in the river waters of southwest Iceland is in declining order: Cl, $HCO_3$, $NO_3$, $NH_4$ ($\approx$ 100 percent) > Sr (44 percent) $\geq$ $SO_4$ (42 percent) > Na (33 percent) > Mg (23 percent) $\geq$ K (21 percent) > PO4 (14 percent) $\geq$ Ca (13 percent) > $SiO_2$, F, Al, Fe, Mn, and Ti (0 percent).

## RELATIVE MOBILITIES

The relative mobility of elements during weathering of basalts can be studied using the chemistry of rivers and rocks in the catchment area of the rivers under study (Tardy, 1969). Alternatively, it can be studied by comparison of the composition of "fresh" and weathered rocks (Craig and Loughnan, 1964). The former approach (river approach) yields, geologically speaking, a near instantaneous look at the relative mobility, whereas the latter (rock approach) gives integrated mobilities, often over millions of years. Furthermore, the river approach defines mobilities over tens to hundreds of kilometers, whereas the rock approach yields mobilities over nanometers to some meters. Attempts have been made to look at the variation in the relative mobility as a function of time or time variables such as a weathering index of rocks or reaction progress as reflected in the weathering state of the rocks (Crovisier and others, 1992; Nesbitt and Wilson, 1992). Alternatively, the river approach can be used to study time variations by defining instantaneous relative mobilities from rocks of variable age.

The relative mobility (Rmobility) is calculated by the water/rock concentration ratio, normalized to sodium, as shown below for Ca

$$\text{Rmobility}_{Ca} = (Ca_{water}/Na_{water})/(Ca_{rock}/Na_{rock})$$

where $Ca_{water}$ and $Na_{water}$ are the concentrations of Ca and Na in a river water, but $Ca_{rock}$ and $Na_{rock}$ are the average concentrations of Ca and Na in unaltered rocks in the catchment area of the river. All water concentrations are corrected for atmospheric contribution (tables 1 and 4). Sodium was chosen as a reference element in this study, as it is the most mobile cation in southwest Iceland, and it is a major element in rocks and water. The mobility of the elements relative to sodium during weathering of basalts in southwest Iceland is shown in table 5, as well as the discharge weighted average for southwest Iceland, and the relative mobility for the experimental weathering of glassy and crystalline basalt at 25°C (Gíslason, ms; Gíslason and Eugster, 1987a). It should be noted that the data

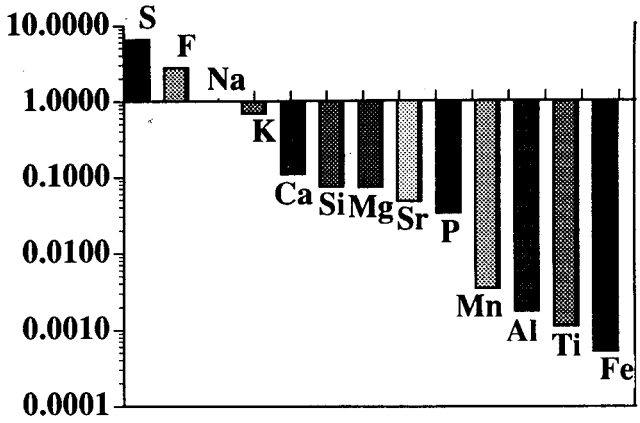



Fig. 13. The weighted average relative mobility of some elements during the present weathering of basalt in southwest Iceland.

on manganese, aluminum, iron, and titanium in the river water and sulfur and fluorine in the rocks are few; thus their order is not as well established as that of the other elements.

The discharge weighted relative mobility is shown in figure 13. Iron is the least mobile element, and Ca and Mg mobilities are only 11 and 7 percent, respectively, of that for Na. In other words, if Na is totally leached from the basalt during weathering in southwest Iceland, 89 percent of the original Ca in the rocks is left behind. The sequence of relative mobility of the elements varies from one discharge area to another (table 5). The relative mobility of Si, Mg, Ca, and Sr increases with age as shown for Ca and Mg in figure 14, but it decreases somewhat with age for K and P. The relative mobility of Al decreases with vegetative cover but increases for Ca and Sr (tables 3 and 5). Thus, the sequence of mobility of the elements in the youngest rocks is different from that of the oldest rocks. For the youngest rocks (Brúará at Efstidalur, 0.2 my) it is $S > F > Na > K \gg Si > P \approx Ca > Mg > Sr > Al > Mn > Ti > Fe$, but for the oldest rocks (Nordurá at Stekkur, 7.7 my) it is $F > Na > Ca \approx Mg \approx K > Si > Sr \gg P \gg Mn > Fe > Ti \geq Al$. The relative mobility of Sr, Mg, Ca, and Si has increased significantly in the old rocks compared to the young ones, but Al has decreased. For example, for Sr and Ca it is only 0.3 and 6 percent, respectively, of that for Na in the youngest rocks, but 17 and 40 percent of that for Na in the oldest rocks.

The discharge weighted average mobility sequence (fig. 13) is similar to the ones calculated from experiments for glassy basalts, that is, $SO_4 > F > Na > K > Ca$, $SiO_2$, Mg, and for crystalline basalts $Na > K > Ca > SiO_2 > Mg$ (table 5). The average relative mobility of Mg, Si, and Ca is considerably less in the natural systems than in the experimental one. This is probably due to the formation of alteration products which

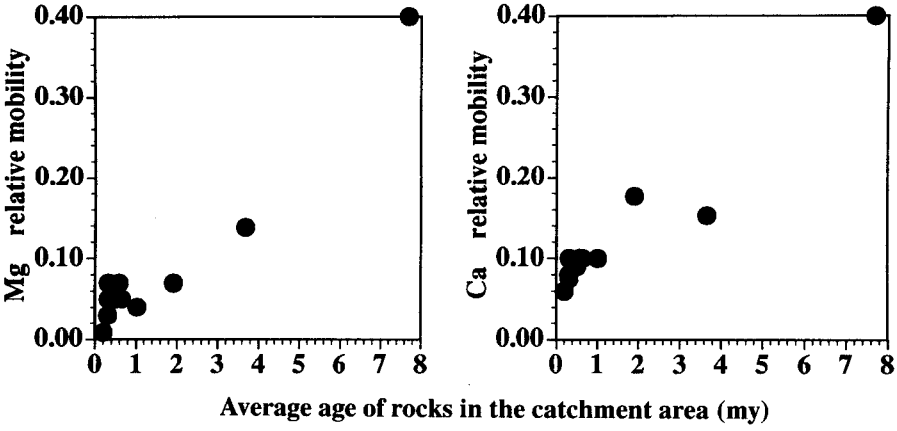



Fig. 14. The relative mobility of calcium and magnesium during the present weathering of basalt in southwest Iceland versus the average age of the rocks in the drainage areas.

consume these components. The high relative mobility of Ca, Mg, Si, and Sr in old as compared to young rocks may indicate less deposition of alteration products, consuming these constituents, and/or increased dissolution of plagioclase. In crystalline basalt, Sr is contained in the plagioclase, the most abundant mineral in the rock. The increase in the relative mobility of Sr could reflect intense dissolution of plagioclase in the old rocks. The pH of the waters draining young rocks is high, causing plagioclase to be stable. The pH has to be lower than 7 for plagioclase to be unstable (Gíslason and Arnórsson, 1993). The pH of waters in old rocks covered with vegetation is low (tables 1 and 3; for example Nordurá at Stekkur, 7.26) and may have been even lower in the soil before entering the river. This is because some of the $CO_2$ has been lost to the atmosphere as discussed later in the chapter on water-air interactions in rivers. The high relative mobility of sulfur in the catchment area of the Thjórsá River can probably be attributed to a contribution from the geothermal system in its catchment area.

Numerous studies have been carried out on the relative mobility of elements during the weathering of basalt (Sigvaldason, 1959; Craig and Loughnan, 1964; Tardy, 1969; Chesworth, Dejou, and Larroque, 1981; Colman, 1982; Eggleton, Foudoulis, and Farkevisser, 1987; Smith, Milnes, and Eggleton, 1987; Noack and others 1990; Veldkamp and Jongmans, 1990; Crovisier and others, 1992; White and Hochella 1992). The present day order of mobilization of elements in alkaline basalt at Belbex, France, as deduced from rocks and river water concentrations, is Na > Ca > Mg > K > Si > Fe > Al (Tardy, 1969, cited by Chesworth, Dejou, and Larroque, 1981). A study in the same area, using rock compositions only, yielded two sequences integrated over time, the early stage of basaltic weathering; Si > K, Na, Mg > Ca > Fe, Al, Ti and a late stage of

basaltic weathering; Si > Ca > K, Na, Mg > Fe, Al, Ti (Chesworth, Dejou, and Larroque 1981). The integrated relative mobilities of elements for alkali basalts in the western United States reported by Colman (1982) are Ca > Na ≫ Mg > Si > Al > K > Ti, whereas Veldkamp and Jongmans (1990) give K > Na > Si > Mg > Ca > Al > Ti for basalts in France. The integrated mobilities during intensive surface weathering of tholeiitic and alkali basalts in eastern Australia reported as percentage loss of the following major elements are: Ca, 85; Mg, 80; Na, 70; K, 50 to 80; P, 55; Si, 45; Mn, 40; Al, 5; Fe, 0; and Ti, 0 (Eggleton, Foudoulis, and Farkevisser, 1987). Crovisier and others (1992) found the relative mobility to be dependent on the reaction progress (the amount of dissolved rocks/per volume of water). At low reaction progress the sequence for basaltic glasses from Iceland is Na > K ≈ Mg ≈ Ca > Si > Ti > Al ≥ Fe, but at high reaction progress it is Na > Ca > K > Mg ≈ Si ≈ Ti > Al > Fe. Nesbitt and Wilson (1992) found Ti to be the least mobile major element in basalts from Australia, followed by Fe and Al.

All these studies, with the exception of Tardy's (1969) and the present study, are rock studies, integrating processes over millions of years. However, when measured, Fe, Ti, and Al are the least mobile elements in all these studies, under remarkably variable conditions, leading to the same end product of chemical weathering of basalt. In light of the "instantaneous" Icelandic data, it is not surprising that the sequence of relative mobility of Na, K, Ca, Mg, and Si varies from one area to another.

TABLE 5

*Relative mobility of elements during weathering of basalt in southwest Iceland, normalized to Na*

| MAIN RIVER *Tributary* | Si | Al | Ti | Fe | Mn | Mg | Ca | Na | K | P | Sr | F | S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| THJÓRSÁ | 0.06 | 0.0022 | 0.0015 | 0.0007 | 0.0018 | 0.070 | 0.10 | 1 | 0.5 | 0.044 | 0.033 | 2.1 | 8.7 |
| ÖLFUSÁ | 0.08 | 0.0011 | 0.0010 | 0.0003 | 0.0042 | 0.050 | 0.10 | 1 | 1.0 | 0.030 | 0.064 | 3.5 | 4.2 |
| *Fossá* | 0.16 | 0.0002 | 0.0003 | 0.0003 | 0.0001 | 0.070 | 0.18 | 1 | 1.8 | 0.050 | 0.415 | 6.5 | 6.6 |
| *Hvítá-s, Gullfoss* | 0.07 | 0.0011 | 0.0007 | 0.0003 | 0.0017 | 0.050 | 0.09 | 1 | 1.0 | 0.036 | 0.027 | 3.4 | 7.1 |
| *Tungufljót* | 0.11 | 0.0010 | 0.0004 | 0.0006 | 0.0030 | 0.070 | 0.08 | 1 | 1.0 | 0.040 | 0.040 | 3.4 | 4.4 |
| *Brúará, Dynjandi* | 0.08 | 0.0010 | 0.0006 | 0.0020 | 0.0003 | 0.030 | 0.08 | 1 | 0.6 | 0.026 | 0.022 | 2.2 | 3.9 |
| *Brúará, Efstidalur* | 0.09 | 0.0020 | 0.0004 | 0.0003 | 0.0008 | 0.009 | 0.06 | 1 | 0.7 | 0.052 | 0.003 | 1.8 | 5 |
| *Sog* | 0.07 | 0.0005 | | 0.0002 | 0.0010 | 0.050 | 0.10 | 1 | 1.0 | 0.025 | 0.022 | 2.8 | 4.6 |
| HVÍTÁ-W, FERJUKOT | 0.10 | 0.0025 | 0.0007 | 0.0008 | 0.0055 | 0.138 | 0.15 | 1 | 0.4 | 0.022 | 0.044 | 2.3 | 7 |
| *Hvítá-w, Kljáfoss* | 0.09 | 0.0030 | 0.0004 | 0.0002 | 0.0008 | 0.040 | 0.10 | 1 | 0.9 | 0.053 | 0.026 | 2.7 | 6 |
| *Nordurá, Stekkur* | 0.20 | 0.0002 | 0.0003 | 0.0008 | 0.0014 | 0.400 | 0.40 | 1 | 0.4 | 0.008 | 0.168 | 1.4 | |
| SOUTHWEST ICELAND(1) | 0.08 | 0.0018 | 0.0011 | 0.0005 | 0.0035 | 0.07 | 0.11 | 1.00 | 0.70 | 0.034 | 0.048 | 2.74 | 6.46 |
| Basaltic glass(2) | 0.60 | | | | | 0.600 | 0.60 | 1 | 0.8 | | | 1.9 | 3.1 |
| Crystalline basalt(2) | 0.20 | | | | | 0.100 | 0.30 | 1 | 0.4 | | | 0.6 | |

(1)Discharge weighted average mobility in the catchment areas of the main rivers in southwest Iceland.
(2)From dissolution rate experiments at 25°C (Gíslason, 1985; Gíslason and Eugster, 1987a)

A simple variation in vegetation, in other words the pH of soil solutions, can have a pronounced effect on the relative mobility of Ca and Mg.

## CHEMICAL DENUDATION RATES

As referred to in the introduction, chemical denudation (weathering) rates are complex functions of runoff, lithology, temperature, organic activity and vegetative cover, tectonics and therefore exposure and elevation, glacial cover, and the abundance of mechanically strained glacier sediments. Similar to relative mobility, chemical denudation rates can be studied by the river approach, yielding on a geological time scale instantaneous fluxes from catchment areas (Garrels and Mackenzie, 1971; Meybeck, 1979). Alternatively the rock approach can be used, resulting in rates integrated over tens to millions of years (Jakobsson and Moore, 1986; Dorn and Brady, 1995). The rock approach yields rates that can be scaled to the specific surface area of minerals and glasses, but river-derived rates are normalized to geographic surface area. Thus, the two are not compatible.

In this section the chemical denudation rate in southwest Iceland will be defined and briefly discussed, using the river approach. $CO_2$ consumption by weathering in Iceland will then be compared with the rate of volcanic $CO_2$ degassing in Iceland. Subsequent sections aim at elucidating the importance of individual processes governing the chemical denudation rates. The conclusions are then summarized and discussed at the end of the paper.

Drever (1994) defined the chemical denudation rate as equivalent to the cation denudation rate, the flux of rock-derived base cations Ca, Mg, Na, and K (units of equivalents/unit area of land surface/unit time). In the absence of anions other than bicarbonate this definition corresponds to the flux of bicarbonate. This definition is similar to the one used by Bluth and Kump (1994) in their study of lithology and climatologic controls of river chemistry. This definition is a good indication of the weathering rates of silicates in general, but it is a poor indicator for the long term net removal of $CO_2$ from the atmosphere, since it is only the weathering of Mg-Ca-silicates that counts for the long time storage. The rates in this study are therefore defined for each element. The chemical denudation rate is defined as the metric tonnes ($10^3$ kg, major elements) or kilos (trace elements) of dissolved solids that are washed off one square kilometer of land per year ($t/km^2/yr$). The following parameters are used to assess this rate: (1) the average estimated chemical composition of precipitation in the catchment area as described above (fig. 11) and the calculated contribution from rock dissolution (table 4); (2) the average concentration of chemical constituents not derived from precipitation in river water (table 1); (3) the average discharge at the sampling location (fig. 2, table 1); (4) the size of the catchment area upstream from the sampling spot (fig. 3, table 3). The chemical denudation rate so calculated is shown in table 6. The weighted average for southwest Iceland, based on the area of the main rivers and excluding the geothermally contami-

TABLE 6

*Chemical weathering rate for individual catchments in southwest Iceland and area weighted average for southwest Iceland*

| MAIN RIVER<br>*Tributary* | SiO2<br>(3)t/<br>km2/y | Na<br>t/<br>km2/y | K<br>t/<br>km2/y | Ca<br>t/<br>km2/y | Mg<br>t/<br>km2/y | HCO3<br>t/<br>km2/y | SO4<br>t/<br>km2/y | TDS(1)<br>t/<br>km2/y | TCDR(2)<br>t/<br>km2/y | F<br>kg/<br>km2/y | NO3-N<br>kg/<br>km2/y | NH4-N<br>kg/<br>km2/y | PO4-P<br>kg/<br>km2/y | Al<br>kg/<br>km2/y | Fe<br>kg/<br>km2/y | Mn<br>kg/<br>km2/y | Ti<br>kg/<br>km2/y | Sr<br>kg/<br>km2/y |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| THJÓRSÁ | 25.3 | 13.9 | 0.82 | 7.1 | 2.6 | 69.9 | 7.9 | 128 | 58 | 272 | -61 | -63 | 29 | 141 | 108 | 4 | 12 | 8 |
| ÖLFUSÁ | 34.1 | 12.9 | 0.99 | 7.9 | 2.5 | 73.0 | 4.1 | 135 | 62 | 220 | -97 | -57 | 15 | 78 | 56 | 14 | 7 | 15 |
| *Stóra Laxá* | 25.0 | 6.06 | 0.7 | 4.8 | 1.6 | 42.3 | 2 | 83 | 40 | 143 | -70 | -49 | 10 | | | | | |
| *Fossá(4)* | 41.1 | 8.3 | 1.15 | 8.5 | 3.7 | 69.0 | 4.0 | 136 | 84 | 240 | -81 | -50 | 15 | 7 | 42 | 0 | 1 | 40 |
| *Hvítá-S, Gullfoss* | 29.4 | 12.4 | 0.96 | 6.7 | 2.2 | 64.7 | 6.7 | 123 | 58 | 201 | -101 | -65 | 17 | 80 | 46 | 5 | 5 | 7 |
| *Tungufljót* | 30.5 | 8.9 | 0.73 | 4.1 | 1.3 | 49.7 | 3.0 | 98 | 48 | 145 | -51 | -64 | 14 | 50 | 104 | 8 | 3 | 7 |
| *Brúará, Dynjandi* | 50.8 | 19.9 | 0.99 | 9.3 | 1.9 | 99.7 | 5.9 | 189 | 89 | 213 | -123 | -105 | 19 | 157 | 184 | 1 | 7 | 12 |
| *Brúará, Efstidalur* | 88.2 | 31.5 | 1.70 | 12.0 | 1.1 | 93.3 | 11.8 | 240 | 146 | 280 | -152 | -216 | 64 | 423 | 54 | 0 | 8 | 11 |
| *Sog* | 39.9 | 17.8 | 1.73 | 11.4 | 3.2 | 108.1 | 6.1 | 188 | 80 | 237 | -197 | -90 | 18 | 52 | 16 | 2 | 0 | 15 |
| VARMÁ(4) | 58.3 | 22.1 | 10.90 | 17.7 | 4.4 | 101.4 | 16.9 | 232 | 204 | 223 | -46 | -6 | 15 | | | | | |
| ELLIDAÁR | 37.6 | 12.8 | 0.56 | 10.7 | 2.3 | 86.3 | 5.4 | 156 | 69 | 152 | -120 | -56 | 2 | | | | | |
| LAXÁ, VOGATUNGA | 14.5 | 4.1 | 0.23 | 6.2 | 1.8 | 40.5 | 2.5 | 70 | 29 | 53 | -68 | -32 | 2 | | | | | |
| *Thverá, Dragháls* | 32.7 | 7.2 | 0.45 | 8.3 | 3.3 | 71.2 | 4.0 | 127 | 56 | 138 | -199 | -67 | 4 | | | | | |
| ANDAKÍLSÁ | | | | | | | | | | | | | | | | | | |
| HVÍTÁ-W, FERJUKOT | 20.4 | 7.2 | 0.54 | 4.8 | 1.8 | 46.1 | 2.9 | 84 | 38 | 112 | -57 | -33 | 7 | 67 | 27 | 3 | 3 | 7 |
| *Grímsá* | 25.5 | 8.9 | 0.47 | 6.3 | 2.7 | 61.9 | 2.9 | 109 | 47 | 121 | -108 | -44 | 4 | | | | | |
| *Flókadalsá* | 23.2 | 7.2 | 0.44 | 5.3 | 2.1 | 49.9 | 1.6 | 90 | 40 | 83 | -86 | -46 | 0 | | | | | |
| *Reykjadalsá(4)* | 38.0 | 16.4 | 0.86 | 8.3 | 5.0 | 78.7 | 9.3 | 157 | 117 | 325 | -36 | -14 | 1 | | | | | |
| *Hvítá-W, Kljáfoss* | 21.0 | 7.5 | 0.55 | 4.2 | 1.2 | 42.2 | 3.1 | 80 | 38 | 101 | -55 | -53 | 15 | | | | | |
| *Thverá, Borgarfjördur* | 18.9 | 6.4 | 0.74 | 6.8 | 3.7 | 60.1 | 2.2 | 99 | 39 | 107 | -68 | -20 | 3 | | | | | |
| *Nordurá, Stekkur* | 22.1 | 5.7 | 0.44 | 7.0 | 2.5 | 52.9 | 3.0 | 94 | 41 | 80 | -77 | -64 | 3 | 5 | 20 | 0 | 1 | 18 |
| SOUTHWEST ICELAND(5) | 27.3 | 12.1 | 0.81 | 6.9 | 2.4 | 66.0 | 5.5 | 121 | 55 | 217 | -73 | -54 | 19 | 101 | 71 | 7 | 8 | 10 |

(1)Total chemical flux including atmospheric and soil derived carbon.
(2)Total chemical denudation rate (TCDR) of rocks not including carbon.
(3)Metric ton.
(4)Fluxes resulting from both weathering and geothermal processes.
(5)Area weighted average for southwest Iceland using the main rivers but excluding the Andakílsá and Varmá.

nated Varmá and the Andakílsá River (no discharge measurement), is shown at the bottom.

The weighted average total chemical denudation rate (TCDR, sum of major fluxes excluding carbonate) and the rate for individual elements or major chemical species are shown graphically in figure 15. The fluxes for $NO_3$ and $NH_4$ are negative since there is a net consumption of these nutrients within the catchments.

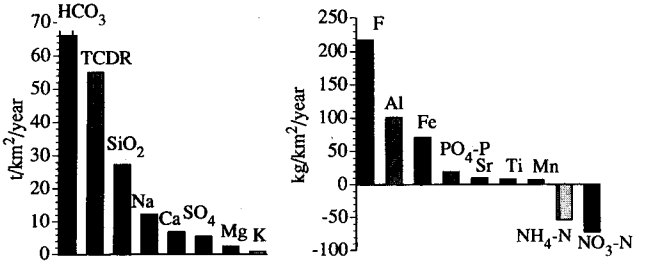



Fig. 15. The area weighted average total chemical denudation rate (TCDR, calculated from the sum of individual chemical major fluxes excluding the bicarbonate flux) and the area weighted average for individual elements or major chemical species in southwest Iceland.

The dependence of total chemical denudation rate (TCDR) on temperature, runoff, the "average age" of rocks, the vegetative cover, and the glacier cover is shown in figure 16A to F. The relationship between runoff and age is shown figure 16D. The geothermally admixed Fossá, Varmá, and Reykjadalsá Rivers are depicted by open circles in figure 16A but will not be discussed further.

Excluding the geothermally affected rivers, the average temperature variation between individual rivers in southwest Iceland is small, only 2.6°C. Thus, when comparing individual catchments, temperature can hardly be considered a variable in this study. This is reflected in the fact that the second coldest catchment, of the Brúará at Efstidalur (3.3°C), has the fastest total chemical denudation rate (TCDR), whereas the warmest catchment, of the Laxá at Vogatunga (5.5°C), has the slowest rate (fig. 16A; tables 1 and 6).

The total chemical denudation rate increases with increasing runoff similar to that found in studies all over the world (Meybeck, 1979; Bluth and Kump, 1994). The total chemical denudation rate decreases with increasing age of the rocks (fig. 16B and C). A considerable part of the rocks younger than 1 my are glassy (hyaloclastites), but glassy basalt dissolves about 10 times faster than crystalline basalt (Gíslason and Eugster, 1987a). In old rocks, glass is less common and if present is often altered. As shown in figure 16D, runoff in southwest Iceland is highly variable in catchments with rocks of an average age less than 1 my, but in "older catchments" it is similar (53-70 l/km²/s) with one exception, the Thverá at Dragháls (age 5.2 my, runoff 123 l/km²/s, TCDR 56 t/km²/yr).

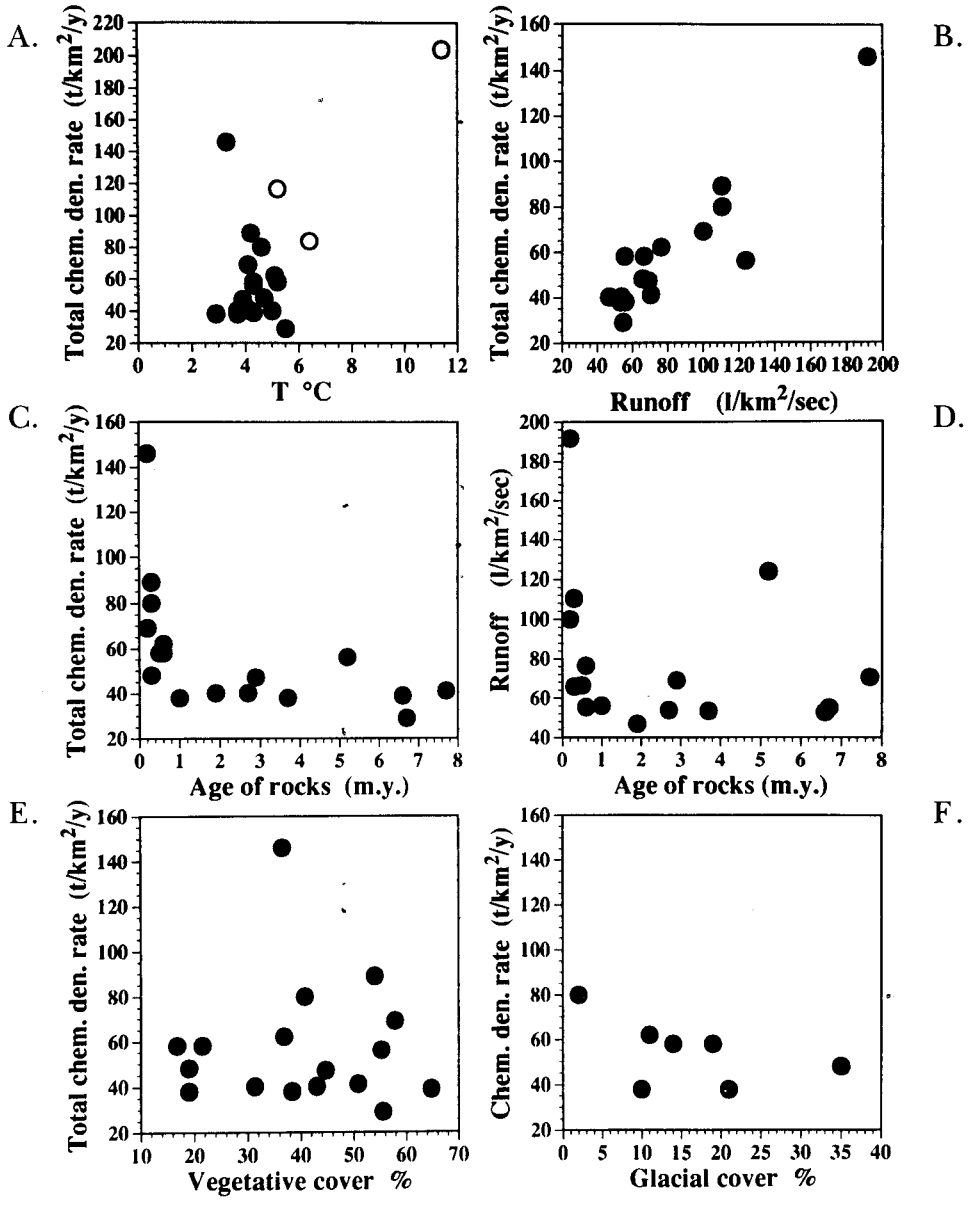



Fig. 16. The dependence of total chemical denudation rate on (A) temperature, including geothermally admixed rivers (open circles), (B) runoff, (C) the "average age" of rocks, (E) the vegetative cover, and (F) the glacial cover. The relationship between runoff and age is shown in (D).

At this high runoff, the Thverá at Dragháls weathers relatively slowly (fig. 16B), but in its "old age" area it weathers relatively rapidly (fig. 16C). This finding suggests that there is not as strong a runoff dependence in old rocks as in young ones. The cause will be discussed in detail in the following sections.

There is no general relationship between the total chemical denudation rate and vegetative cover (table 6 and fig. 16E). Thus, vegetation seems to be a secondary variable for TCDR.

As shown in figure 16F, glacier cover of catchment areas slows down the total chemical denudation rate. The data are scarce, and the uncertainty in the estimation of the extent of the glaciated part of the discharge area of the rivers is large (table 3). In this study, measurement of the extent of the glacial cover is based on the surface topography of the glaciers. Of the partially glaciated river catchments, the chemical denudation rate is lowest for the Hvítá-W River both at Ferjukot and at Kljáfoss. These rivers drain the oldest rocks, 1.0 and 3.7 my respectively. This rate is, on the other hand, highest for the Sog, which drains young rocks (0.3 my) and has a high runoff (111 kg/km$^2$/s). The runoff for other glaciated river basins in figure 16F is similar, ranging from 55 to 76 kg/km$^2$/s (table 3), showing a decrease with increasing glacier cover.

In general there is an increase in the chemical denudation rate for all major elements with increasing runoff, nitrate and ammonium fluxes are increasingly negative, and phosphate fluxes are mostly independent of runoff, but the greater the phosphate flux the more negative are the nitrate and ammonium fluxes (table 6).

The chemical denudation rates for Si, Na, K (fig. 17A, B, C), F, Al, P, Fe, Ti, and Mn decrease with increasing age of rocks as does the total chemical denudation rate shown in figure 16C. Conversely, the chemical denudation rates for Ca, Mg, and Sr increase (fig. 17D, E, F), and the fluxes of nitrate and ammonium are less negative with increasing age of rocks in catchments that are "older" than 1 my.

Where the variation in the primary variables, runoff and age of rocks, is small (older than 1 my, runoff 53 to 70 kg/km$^2$/sec), the denudation rate for Ca, Mg (fig. 17G, H) and Si, increases with increased vegetative cover. It decreases with increased vegetation for Na (fig. 17I), K, and F but the total chemical denudation rate (TCDR) is independent of vegetation. Phosphate fluxes decrease with increased vegetation, but nitrate and ammonium fluxes are less negative with increasing vegetative cover.

All major and minor elemental fluxes decrease with increasing glacier cover with the exception of Fe and Mn, as shown in figure 17J, K, L for Ca, Mg, and Fe. The Fe and Mn fluxes increase with increasing glacier cover.

When comparing the Icelandic chemical denudation rates with the denudation rates of other parts of the world, it is crucial to elucidate how the various authors correct for the atmospherically derived bicarbonate in the river water, since the bicarbonate flux is the largest of the

A
B
C
D
E
F
SiO2 (t/km2/y)
Na (t/km2/y)
K (t/km2/y)
Ca (t/km2/y)
Mg (t/km2/y)
Sr (kg/km2/y)
Average age of rocks (m.y.)

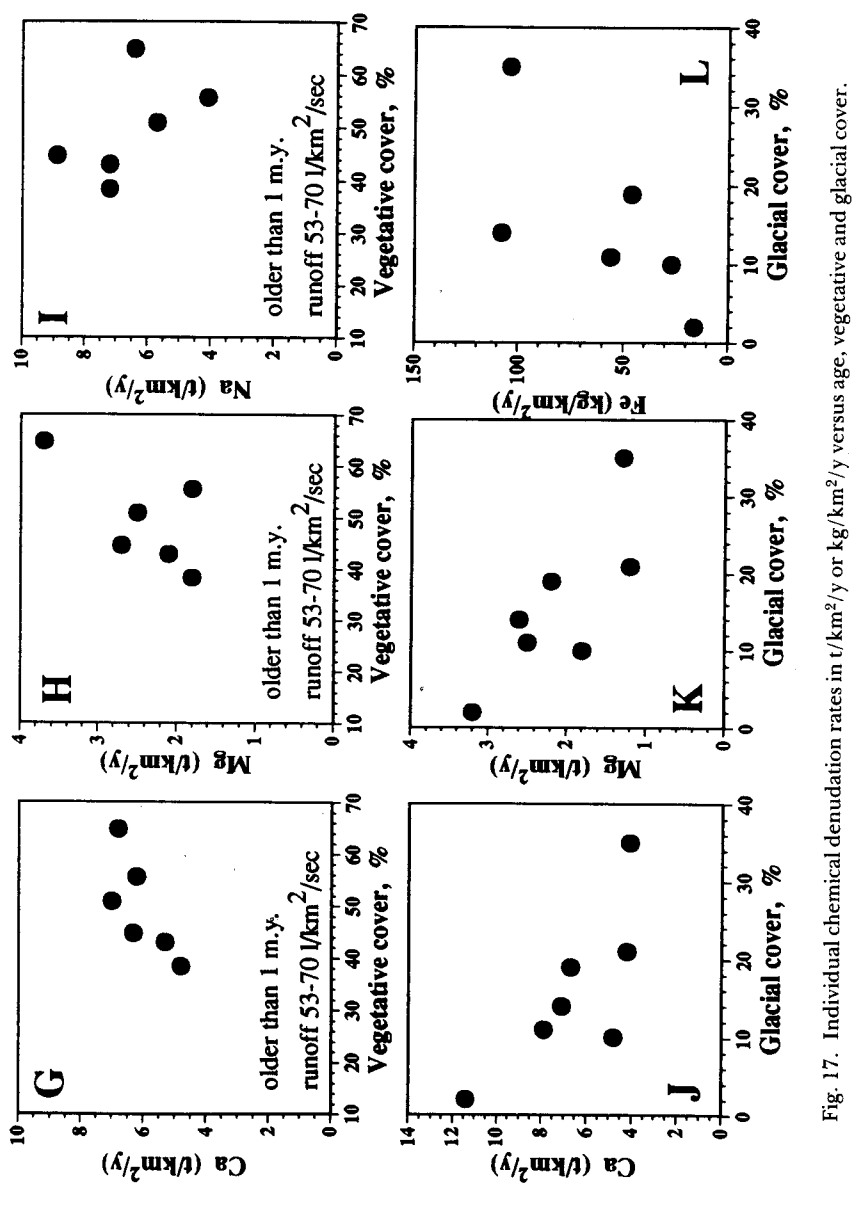



Fig. 17. Individual chemical denudation rates in t/km$^2$/y or kg/km$^2$/y versus age, vegetative and glacial cover.

individual chemical fluxes (fig. 15, table 6). The weighted average total flux (TDS, sum of individual major elemental fluxes) for southwest Iceland is 121 t/km$^2$/yr of which 66 t/km$^2$/yr is bicarbonate, mostly derived, directly or indirectly, from the atmosphere.

Garrels and Mackenzie (1971) calculated the chemical denudation rates for the continents to range from 2 t/km$^2$/yr for Australia to 42 t/km$^2$/yr for Europe. The denudation rate for southwest Iceland, using compatible calculations where most of the bicarbonate in the river water is assigned to the chemical weathering of rocks, is 120 t/km$^2$/yr. This rate is extremely rapid compared to the average for the continents. Meybeck (1979) went much further than Garrels and Mackenzie (1971) in terms of correcting for atmospherically derived $CO_2$. He concluded that the products of continental chemical denudation represent only 65 percent of the material naturally carried by rivers to the ocean. The remaining part derives from oceanic aerosols (5 percent) and atmospheric $CO_2$ (30 percent). The most important contribution to continental chemical denudation is from carbonate rocks (45 percent) (Meybeck, 1987). Volcanic rocks such as basalt do not contain much carbon. Thus, most bicarbonate in Icelandic rivers is derived indirectly from the atmosphere. About 5 percent is brought in with precipitation, the rest comes from the decomposition of organic material in soil and the continuous absorption of $CO_2$ from the atmosphere when the pH of soil and groundwater increases due to water-rock interaction. The calculated total chemical denudation rate (TCDR) for southwest Iceland excluding bicarbonate is 55 t/km$^2$/yr (table 6). Taking this conservative approach to the Icelandic data we can compare it with the chemical denudation rates of the various morphoclimatic types of the world (Meybeck, 1979). The chemical denudation rate is at a maximum in the mountainous regions of the humid temperate and humid tropical zones, 80 t/km$^2$/yr and 67 t/km$^2$/yr, respectively (Meybeck, 1979). These are the only morphoclimatic zones that have higher average total chemical denudation rates than the conservative 55 t/km$^2$/yr for southwest Iceland.

The difference in rock-derived natural and experimental chemical weathering rates and the rate derived from river studies can be used to estimate the difference in geographic surface area and the active surface area of rocks in contact with water. The calculation for the Ölfusá catchment (T: 5.1°C, pH: 7.38) yields $2.7 \times 10^{-1}$ mm/y, assuming the geographic surface area to be equal to the active surface area in contact with basaltic glass of the composition given in table 2 and density of 2.8 g/cm$^3$. Similar calculations for experimental weathering (Gíslason and Eugster, 1987a) at the same temperature (5°C) but at a higher pH (9.4) yield $2.6 \times 10^{-4}$ mm/y. And the measurements of the rate of growth of palagonite on the ocean floor south of Iceland (T: $\approx$5°C, pH: $\approx$8.2) (Jakobsson and Moore, 1986) give $2 \times 10^{-5}$, mm/y. If this discrepancy is largely due to the surface area estimate, the geographic surface area is about $10^3$ to $10^4$ smaller than the effective surface area of rocks in contact with water.

The relatively high rate of chemical denudation in Iceland, its dependence on runoff and age of rocks, and the increased flux of Ca and Mg with vegetative cover at a fixed runoff and age of rocks are interpreted in the sections following the next one.

## PERMANENT AND TRANSIENT UPTAKE OF $CO_2$ FROM THE ATMOSPHERE BY CHEMICAL WEATHERING OF ICELANDIC ROCKS COMPARED WITH $CO_2$ DEGASSING FROM THE ICELANDIC MANTLE PLUME

Global rates of $CO_2$ uptake by surficial processes must be essentially balanced, on a million year time scale, by global rates of degassing to avoid environmentally unacceptable fluctuations in atmospheric $CO_2$ (Holland, 1978; Berner, Lasaga, and Garrels, 1983; Berner, 1990). $CO_2$ degassing occurs, for example, at mid-ocean ridges, sites of mid-plate volcanism, and subduction zone metamorphism and volcanism, and because of loss of volatile carbon containing gases during the burial of sedimentary organic matter (Berner, 1990).

The global features of Iceland's geology are the product of the Icelandic Mantle Plume and crustal accretion at the European and North American lithosphere plate boundary. This "double feature" results in an anomalous high lava production rate, 3.4 $km^3$ per century, along the Mid-Atlantic ridge (Jakobsson, 1972). Thus one would expect $CO_2$ degassing to be at the global maximum at such locations on a mid-ocean ridge. It is therefore of interest to compare the production (degassing) and consumption rate (weathering) of $CO_2$ at such a spot.

The $CO_2$ degassing from Iceland ($103 \times 10^3$ $km^2$) has been estimated to be 70 to 39 kg/s (Arnórsson and Gíslason, 1994). This translates to $1.59 \times 10^3$ to $0.886 \times 10^3$ moles $CO_2$/s. As shown earlier, chemical weathering rates in Iceland are primarily a function of runoff and age of the rocks. The runoff and age of the catchment area for the Hvítá-W River at Ferjukot is close to the average for Iceland (fig. 3; table 3). The surface area normalized fluxes for this catchment area (table 6) can therefore be used to assess the uptake of $CO_2$ by weathering in Iceland. Total or transient uptake is calculated from the bicarbonate flux in table 6 (table 7). We refer to this as transient uptake, since $CO_2$ uptake resulting in the weathering of Na and K silicates would in the long run, in the absence of weathering of Ca and Mg silicates, lead to the $CO_2$ supersaturation of the ocean with respect to the atmosphere. Furthermore, the stoichiometry of the Ca and Mg silicate weathering alone is two moles of $CO_2$ for each mole of Ca or Mg released. Permanent uptake is the $CO_2$ consumption associated with the weathering of Ca and Mg silicates and their precipitation as carbonates in the ocean. The net stoichiometry of the weathering and carbonate precipitation is one mole of $CO_2$ for each mole of Ca or Mg released by weathering. The net transient $CO_2$ flux for Iceland is negative (table 7). That is, more $CO_2$ is consumed during weathering and transported by rivers to the ocean than is released to the atmosphere from Icelandic volcanoes and geothermal systems. However, the net permanent $CO_2$ flux is positive (table 7). In other words, more

TABLE 7

*Total CO2 degassing from the Icelandic mantle plume compared to total permanent and total transient uptake of CO2 from the atmosphere by chemical weathering of Icelandic rocks*

| Total CO2 degassing | Total transient CO2 uptake (HCO3) | Permanent CO2 uptake (Ca) | Permanent CO2 uptake (Mg) | Total permanent CO2 uptake (Ca and Mg) | Net transient CO2 flux | Net permanent CO2 flux |
|---|---|---|---|---|---|---|
| moles CO2/s | moles CO2/s | moles CO2/s | moles CO2/s | moles CO2/s | moles CO2/s | moles CO2/s |
| 1590(1) | 2468 | 395 | 241 | 636 | -878 | 954 |
| 886(2) | 2468 | 395 | 241 | 636 | -1582 | 250 |

(1)The higher estimated value for the total $CO_2$ degassing from Iceland (Arnórsson and Gíslason, 1994).

(2)The lower estimated value for the total $CO_2$ degassing from Iceland (Arnórsson and Gíslason, 1994).

$CO_2$ is released from the Icelandic Mantle Plume and the segment of the mid-Atlantic ridge in Iceland to the atmosphere than will eventually precipitate in the ocean as Ca and Mg carbonates, as the result of Ca and Mg released during weathering of rocks in Iceland.

## WATER-ROCK AND WATER-AIR INTERACTION IN RIVERS

In the present study, river chemistry is used to ascertain weathering processes that take place in rocks and soil. It is, therefore, of importance to assess how much the chemistry of water is altered in the rivers on their way from the source (spring, glacier, soil, bog, et cetera) to the sampling site in the river. But as described in the introduction, the water in the main river channels has enough time for significant heat exchange with its surroundings before reaching the sampling site.

*Interaction between air and river water.*—The flux of $CO_2$ in and out of river water will affect the pH of the water. Similarly the flux of $O_2$ will alter its redox potential. Changes in the pH and the redox potential of waters will alter the saturation state of the waters with respect to rock forming minerals. But the saturation state determines which minerals dissolve or precipitate, and it may govern the rate of these processes. The saturation state of Icelandic waters is assessed in the following section. It is, therefore, important to define the direction and rate of the $CO_2$ and $O_2$ fluxes and the corresponding change in pH and redox potential.

The $CO_2$ partial pressure ($p_{CO_2}$) of river and spring waters is shown in figure 18. The pH of the waters range from about 7 to 10. With the exception of the samples from Raiswell and Thomas (1984), the partial pressure was calculated by the WATCH program at the temperature of the waters using chemical analyses of the water samples. The $p_{CO_2}$ as calculated for glacier melt water by Raiswell and Thomas (1984) is used directly. The $p_{CO_2}$ in several springs, some spring-fed rivers, and some glacier rivers is lower than that of the atmosphere ($10^{-3.5}$ bars). The $p_{CO_2}$ can be up to 1000 times lower than the atmospheric one. These waters, therefore, tend to absorb $CO_2$ from the atmosphere, causing the pH of

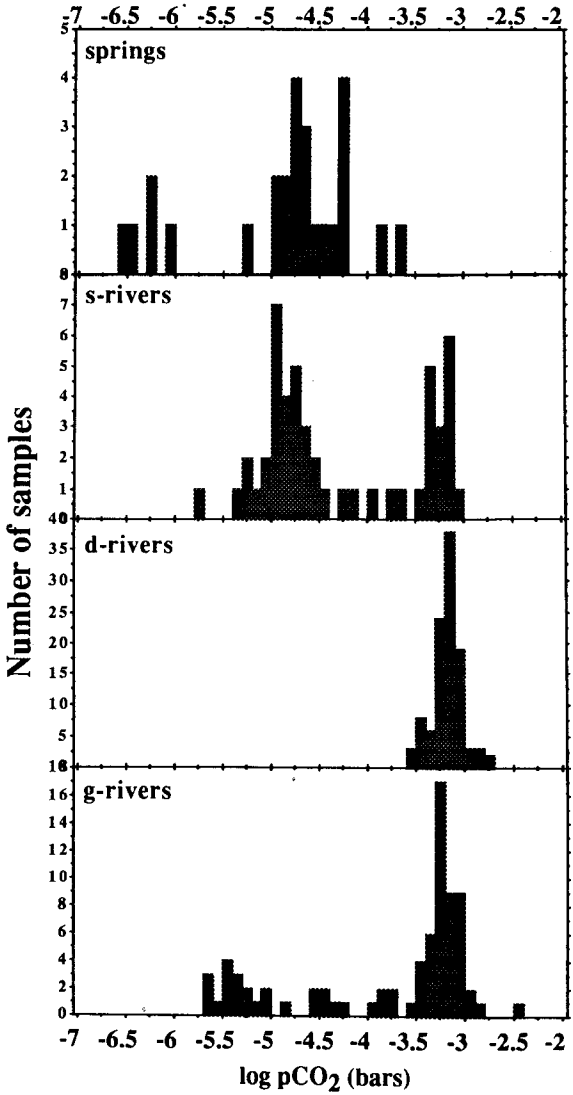



Fig. 18. Frequency plots for the logarithm of the calculated partial pressure of $CO_2$ in springs (Gíslason and Eugster, 1987b; Gíslason, 1989), spring-fed rivers (s-rivers: Gíslason, 1989; Armannsson and others, 1973; Rist, 1974 and 1986), direct-runoff rivers (d-rivers: Armannsson and others 1973; Rist, 1974 and 1986) and glacial-fed rivers (g-rivers: Armannsson and others, 1973; Rist, 1974 and 1986; Raiswell and Thomas, 1984).

the waters to drop. Conversely, the $p_{CO_2}$ of water in most direct runoff rivers and many glacier-fed rivers is higher than that of the atmosphere but never more than ten times higher. Thus, $CO_2$ tends to diffuse out of these rivers into the atmosphere, causing the pH to rise. The rate at

which $CO_2$ diffuses in or out of river water can be assessed by the calculations shown below.

Flow in natural rivers is, almost without exception, fully turbulent (Leopold, Wolman, and Miller, 1964), and dissolved gases are well mixed in the stream water. Thus, one would not expect to find variable diffusion profiles for solids and gases in the water. There is, however, a continuous armouring layer through which gas molecules and dissolved solids are transported by diffusion at the air-water interface (Liss and Slater, 1974). The water molecules at the surface are oriented in such a way that the negative oxygens point out from and the positive hydrogens into the bulk solution (Horne and Courant, 1973). The boundary layer thus formed has a more compact structure than the bulk, but it extends only to the depth of a few molecules (Horne and Courant, 1973). This boundary layer is broken when water foams or "boils" in breaking waves, river rapids, and in and below waterfalls.

The gas exchange between air and water can be described by Fick's first law, according to which molecular diffusion through this water surface film at the air-water interphase is the rate determining step in the exchange process (Liss and Slater 1974, Broecker and Peng 1974), or

$$F = -D\partial C/\partial z \tag{1}$$

where F is the flux of gas through the surface film; D the coefficient of molecular diffusion of gas in the surface film; C the gas concentration in the surface film; and z the thickness of the surface film. Eqn (1) can be simplified to

$$F = -k\Delta C = -k(C_s - C_w) = -k((p_{gas}\, K_H) - C_w) \tag{2}$$

where $\Delta C$ is the concentration difference across the film (thickness $\Delta z$); $C_s$ is the concentration of gas in the top of the film; $C_w$ is the concentration of gas in the water below the film; $p_{gas}$ is the partial pressure of gas in the air above the film; $K_H$ is the Henry's law constant for the gas; and

$$k = D/\Delta z = F/\Delta C \tag{3}$$

k has dimensions of velocity and is called the exchange constant, piston velocity, transfer coefficient, or transfer velocity (Liss, 1983). The transfer velocity has been evaluated for air-sea interactions in natural and experimental systems and has been shown to increase with increased wind velocity (Liss, 1983), and the rate of molecular diffusion (D) increases with temperature. The gas concentration, $C_w$, in eq (2) is dependent on the pH of the water when a gas such as carbon dioxide forms weak acids upon dissolution in water. In the case of carbon dioxide, the $\Delta C$ term in eq (3) can be expressed as a function of pH and the total dissolved carbon, $C_{total}$.

$$\Delta C = (C_s - C_w) = [p_{gas}K_H] - (C_{total}/(1 + K_1/10^{-pH} + K_2K_1/10^{-2PH})) \tag{4}$$

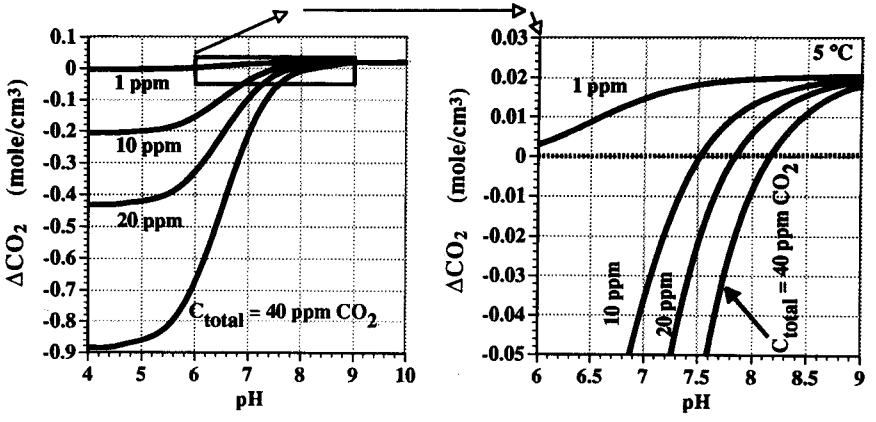



Fig. 19. $\Delta CO_2$ versus pH. $\Delta CO_2$ is the driving force for the $CO_2$ exchange between air and water (eq 4). When $\Delta CO_2$ is positive $CO_2$ diffuses into the water, but when it is negative $CO_2$ diffuses out of the water. (B) is simply an expansion of a part of (A) that is the range for Icelandic rivers.

where $K_1$ and $K_2$ are the first and second dissociation constants for carbonic acid. A solution of eq (4) at 5°C, assuming activity to be equal to molality, is shown in figure 19. When $\Delta CO_2$ is positive, $CO_2$ diffuses into the water, but when it is negative, $CO_2$ diffuses out of the water. It turns out that $\Delta C$, the driving force for the flux, is about equal to $C_s$ at a high pH because the dissolved carbon is in the form of bicarbonate and carbonate. As the pH is lowered, the water reaches a critical pH value, where the $\Delta C$ decreases rapidly because some of the dissolved bicarbonate reacts to form $CO_{2(aq)}$. The pH at which this occurs is strongly dependent on the total amount of dissolved carbon (fig. 19). At a lower pH $\Delta CO_2$ is equal to zero resulting in no exchange, and at still lower pH $\Delta CO_2$ becomes negative, and the flux is reversed, $CO_2$ diffuses out of the water. The $\Delta CO_2$ levels off at a negative value when virtually all dissolved carbon is in the form of $CO_{2(aq)}$ (fig. 19A).

The transfer velocity (k, eq 3) for $CO_2$ in the river Brúará close to its headspring (fig. 2) ranges from about 250 to 350 cm/hr (Gíslason, 1989). These measurements were carried out at relatively high pH values (8.6-9) and a low concentration of total dissolved carbon (10 mg/l as $CO_2$), at which $\Delta CO_2$ is independent of pH (fig. 19B). The lower range for the transfer velocities is comparable to the one suggested by Liss and Merlivat (1986) for seawater in the "breaking wave (bubble) regime," but there are considerable surface waves, ripples, and bubbles in the river. The measurements in the Brúará River were done under calm weather conditions, but the transfer velocity might be increased significantly if a strong wind were blowing upstream (Gíslason, 1989). The calculated "thickness of the surface film" $\Delta z$ ranged from 100 to 150 microns. Laboratory measurements of $\Delta z$ in fresh waters under high agitation give

values around 100 microns but under low agitation around 250 microns (Broecker and Peng, 1974), which is in good agreements with these results.

The flux of $CO_2$ into the Brúará at its source lowered the pH of the water from 9 to 8.6 in 23 min. A continued flux of $CO_2$ caused a further lowering of pH and therefore a diminishing flux. For total carbon of 10 mg/l as $CO_2$, the flux slowed down by a factor of two at pH 7.8 (fig. 19B). Downstream at Dynjandi, the Brúará has nearly doubled its carbon content compared to the sampling spot at Efstidalur (fig. 2; table 1), and the average pH is down to 7.64.

The flux of $CO_2$ out of supersaturated waters can be much more rapid than the one into undersaturated water as described above. This is because the driving force for the flux into the river water, the concentration difference in the surface film, $\Delta C$ (eqs 2 and 4), has an upper limit of 0.02 mole/cm$^3$ (fig. 19A and B), representing the maximum rate for the flux into the water. However, the maximum driving force for the negative flux of $CO_2$ out of the water ($-\Delta C$) is already one order of magnitude larger than the one for the reversed flux at 10 mg/l $CO_2$ (fig. 19A; $-0.2$ mole/cm$^3$). This difference explains the range in $p_{CO_2}$ in figure 18. The $p_{CO_2}$ can be up to 1000 times lower than the $p_{CO_2}$ of the atmosphere, in springs, spring-fed rivers, and glacial-fed rivers, reflecting a relatively slow flux of $CO_2$ into these waters. Conversely, the $p_{CO_2}$ of direct runoff rivers is never more than five times higher, reflecting rapid flux of $CO_2$ out of the waters. Some of the difference in figure 18 could also be due to a difference in hydrology. The overall gas exchange rate is dependent on $\Delta C$, temperature, the depth of the rivers, and the abundance of rapids and waterfalls. The greater the $\Delta C$, the higher the temperature, the shallower the rivers, and the more rapids and waterfalls there are, the faster is the gas exchange.

Icelandic spring waters (0°-5°C) are close to saturation with respect to the $O_2$ of the atmosphere, but indirect evidence suggests that bog waters are sometimes undersaturated. The flux of $O_2$ into, for example, oxygen poor bog waters, can be described by eq (3) and is independent of pH. The maximum driving force, $\Delta C$, when the concentration in the bulk water is close to zero, is 0.35 mole/cm$^3$ at 5°C, more than one order of magnitude greater than the one for $CO_2$ (fig. 19B; 0.02 mole/cm$^3$). Thus, one would expect a relatively rapid flux of $O_2$ into $O_2$-deprived bog water as it comes into contact with the atmosphere.

*Interaction between suspended load and river water.*—The dissolved solids content of river water might be expected to change on its way from the source to the mouth of the river, as a result of dissolution of some of the suspended load, which in the case of glacial rivers is very abundant and fine grained. The extent of this interaction will depend on the transport time, surface area of solids, and the degree of undersaturation between minerals and solution.

Figure 20 shows the total evaporated residue (TER) concentration versus the amount of suspended load in mixed glacier rivers in Iceland.

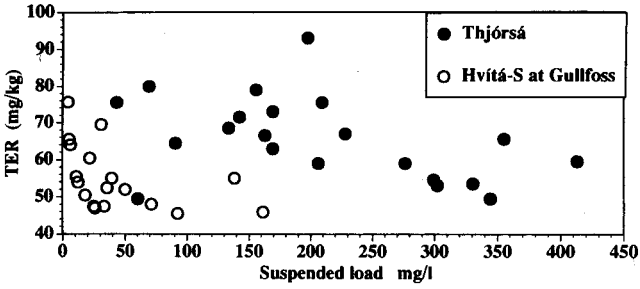



Fig. 20. Total evaporated residue (TER) versus suspended load in samples from the rivers Thjórsá and Hvítá-S at Gullfoss (fig. 2).

There was a decrease in the TER concentration as the suspended load increased. The amount of suspended load increases exponentially with increased discharge (Pálsson and Vigfússon, 1991), and TER concentration decreases with increased discharge as shown for some rivers in figure 9. Some of the decrease in TER concentration in the Thjórsá and Hvítá-S at Gullfoss (fig. 20) can therefore be attributed to dilution by increased discharge. Alternatively, at a low discharge and a low suspended load, the residence time of the water in the river is longer, giving more time for interaction. However, samples studied at the same discharge but with a different suspended load (Rist, 1974) showed no clear increase in TER as the suspended load increases. This observation is consistent with experimental data on the dissolution of basaltic glass and data on the grain size of the suspended matter. This can be demonstrated by the following calculations.

The Thjórsá River in southern Iceland (fig. 2), which is a g-d-s-river, is the longest river in Iceland, 230 km from its source to its mouth (The Statistical Bureau of Iceland, 1984). In August, it takes the meltwater peak 30 hrs to reach Urridafoss Falls, which are about 25 km from the river's mouth (fig. 2; Rist, 1981). Thus, it takes the water about 30 hrs to travel about 200 km, corresponding to an average velocity of about 1.9 m/sec. The residence time of water in the rivers of Iceland is, therefore, at the most one to two days. The average suspended load for the Thjórsá samples is 207 mg per 1 kg of stream water (fig. 20). Pálsson and Vigfússon (1991) have measured the size fractions of these samples. The average amount of each size fraction is as follows: 66 mg of the size $>200$ μm, 81 mg of 200 to 20 μm, 37 mg of 20 to 2 μm, and 23 mg of $<2$ μm. Assuming the particles to be roughly spherical and the average radius of each size group to be 100, 30, 5.5, and 0.5 μm, respectively, the total surface area of the suspended load in contact with 1 kg of water is 604 $cm^2/kg$, taking the average density of the suspended load to be 2.77 $g/cm^3$. Particles much smaller than 1 μm do travel at the speed of the fluid and are therefore not as active as larger particles, travelling at

different velocities, causing solids dissolving from the surface of the particles to be swept away from the surface. In order to calculate the maximum concentration change, it can be assumed that all the particles are basaltic glass, that is, the most soluble phase in the suspended load. The dissolution rate of basaltic glass, at the avs 5°C temperature of the river, can be calculated by the Arrhenius equation using the average activation energy, 32 kJ/mole, given by Gíslason and Eugster (1987a) and adding a corresponding amount of bicarbonate to balance the charge of the cations. Such calculations give an increase in total dissolved solids (TDS) of 0.66 mg/kg. A synthesis of data from natural and experimental systems indicates that BET measurements on fresh surfaces exceed geometric estimates by a mean roughness factor of 7 over a wide range in particle size (White and Peterson, 1990). If the geometric surface area calculated above is multiplied by a mean roughness factor of 7, the concentration increase in the Thjórsá River becomes 3.2 mg/kg. This maximum value is less than 4 percent of the total dissolved solids (table 1). In other words, the water-rock interaction in the main stream of the Thjórsá is probably detectable but not significant and less so in other Icelandic rivers since the Thjórsá is the longest one.

In sum, the water in the main channels of the Icelandic rivers has enough time for significant heat and gas exchange with the atmosphere, whereas water-rock interactions are insignificant. The flux of $CO_2$ and $O_2$ in and out of river water results in changes in the pH and the redox potential of the waters, altering the saturation state of the waters with respect to rock forming minerals. But the saturation state determines which minerals dissolve or precipitate, and it may govern the rate of these processes.

## THE SATURATION STATE ($\Delta G_R$) OF RIVER AND GROUND WATERS RELATIVE TO PRIMARY AND SECONDARY BASALTIC MINERALS

The importance of the saturation state ($\Delta G_r$) is twofold: (1) In general it determines whether minerals tend to precipitate or dissolve in water of a specific composition and temperature. In the case of igneous primary minerals it determines whether they dissolve or not. (2) Within a critical range it determines the rate of dissolution and precipitation.

*Primary minerals.*—Gíslason and Arnórsson (1990, 1993) studied the saturation state of river, ground, and geothermal water in Iceland relative to primary and secondary minerals in basalts. River water and cold groundwater in Iceland are undersaturated with respect to olivine and presumably even more so with basaltic glass (fig. 21). They are generally undersaturated with respect to pyroxene but close to equilibrium with plagioclase. They are more undersaturated with respect to magnesium-rich olivine than iron-rich olivine (fig. 21), and the same applies to orthopyroxenes. The relative saturation state of plagioclase and river and ground water is highly dependent on the composition of the plagioclase (fig. 21). These waters are mostly undersaturated with respect to pure anorthite but supersaturated with respect to high-albite

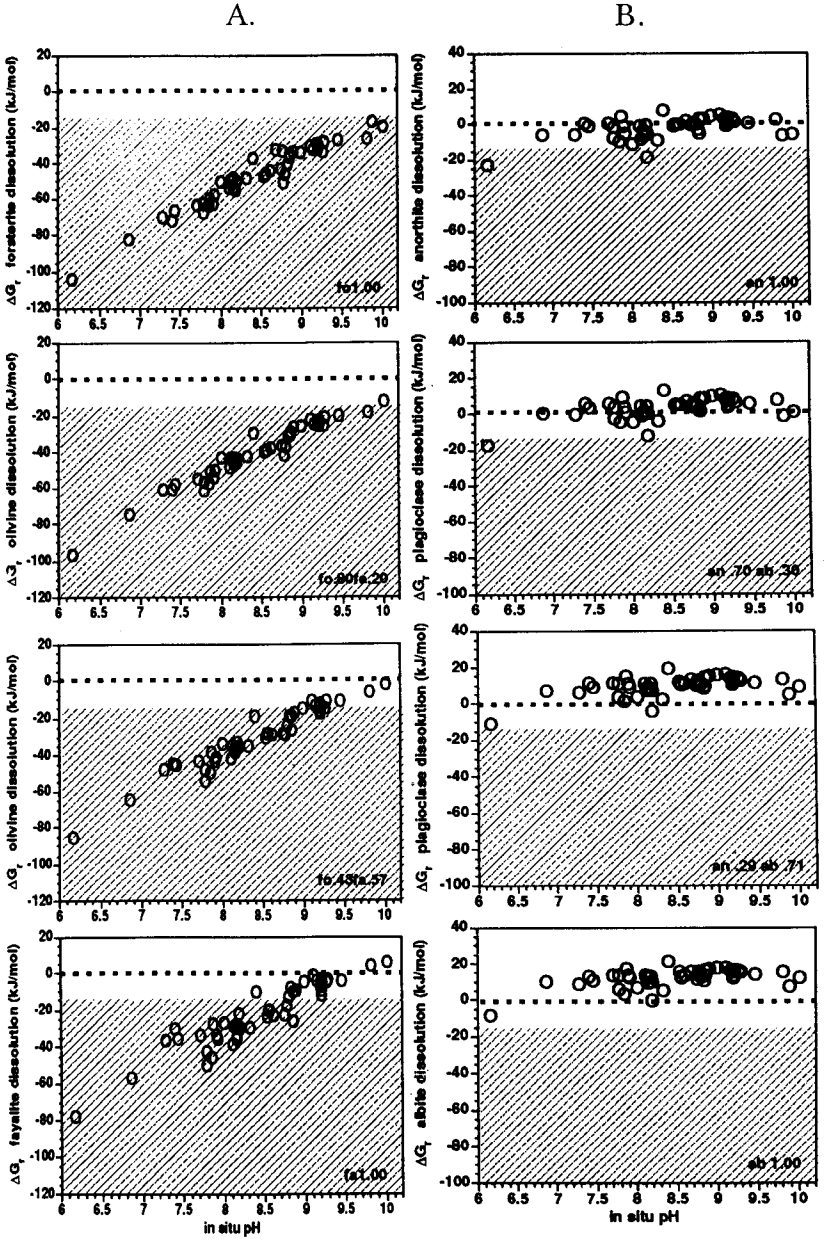



Fig. 21. The pH dependence of the saturation state of olivines (A) and plagioclases (B) in selected cold ground waters and river waters in Iceland, depicted in terms of the Gibbs free energy of the dissolution reactions. The mineral composition is shown in the lower right corner of the diagrams. The dashed lines represent equilibrium conditions, and the shaded area the saturation state independent dissolution rate according to transition state theory (Gíslason and Arnórsson, 1993).

and plagioclase of the composition $An_{0.29}Ab_{0.71}$, which represents a common composition of groundmass plagioclase in Icelandic lavas. Plagioclase, representing the average composition of phenocrysts in basaltic lavas ($An_{0.70}Ab_{0.30}$), is undersaturated in some waters but saturated in others (fig. 21). The saturation state of plagioclase is independent of pH when higher than 7 (Gíslason and Arnórsson, 1993). At a lower pH, Icelandic waters are undersaturated with respect to both types of plagioclase (unpublished data). The pH of waters feeding some of the rivers may have been considerably lower than shown fig. 21 (pH 7-8) due to rapid degassing of $CO_2$ when soil waters come in contact with air, as discussed in the previous section. No data are available to assess the saturation state of the opaque solid solutions magnetite-ulvöspinel and ilmenite-hematite relative to Icelandic ground and river water, but heavy supersaturation with respect to the magnetite and hematite components in these solid solutions is observed for thermal waters in Iceland below 150°C and supersaturation increases with decreasing temperature (Gíslason and Arnórsson, 1990).

These observations are in accord with the results of mineralogical studies on the pattern of weathering susceptibility: that is, olivine > pyroxene > plagioclase > sanidine (Craig and Loughnan, 1964); glass > olivine > pyroxene > amphibole > plagioclase > K-feldspar (Colman, 1982); glass ≈ olivine > plagioclase > pyroxene > opaque minerals (Eggleton, Foudoulis, and Farkevisser, 1987); glass, olivine > laihunite > clinopyroxene > orthopyroxene > plagioclase > K-feldspar > magnetite > apatite > rutile > quartz (Banfield, Jones, and Veblen, 1991) but in some disagreement with Nesbitt and Wilson's (1992) study of Australian basalts, that is, olivine > glass > plagioclase > clinopyroxene > Fe-Ti-oxides.

If the glass and solid solutions dissolve stoichiometrically the following conclusions can be drawn with reference to the above findings. All the major elements of the basaltic rocks are released by the stoichiometric dissolution of basaltic glass. Most of the major elements are also released by the stoichiometric dissolution of interstitial glass in crystalline basalts but Na, K, Si, S, and F probably at elevated rates because their composition is close to that of rhyolite (Meyer and Sigurdsson, 1978). The dissolution of olivine and pyroxene results in the release of Mg, Fe (Mn), Si, and Ca. Some Ca, Na, K, Si, Al, and Sr are released by the dissolution of Ca-rich plagioclase, and if the pH of the reacting waters is below 7, by both Ca-rich and Ca-poor plagioclase. Sr dissolves only from a fully crystalline basalt when the pH is lower than 7, as it is mostly contained in plagioclase. According to the mobility of the elements relative to Na (table 5; fig. 13), more than 99 percent of the original Fe, Ti, Al, and Mn are immobile during the weathering of basalt in southwest Iceland and about 90 percent of the mass of Si, Mg, and Ca. Thus, some weathering minerals that consume at least Fe, Ti, Al, Mn, Mg, Si, and Ca released from glass, olivine, and pyroxene dissolution must form.

*Secondary minerals.*—Great relief and abundant precipitation result in intense physical erosion. Removal of solid weathering material is rapid, and chemical weathering in the soil is incomplete and soils are thin. This will be referred to as the early stage of chemical weathering.

There are few studies on present day weathering products in Iceland. Allophane (X-ray amorphous, Si-Al clay size material), imogolite and poorly-crystalline ferrihydrite are abundant in the clay size fraction of soil in Iceland (Wada and others, 1992). Manganese-rich rock coatings are common on weathered basaltic surfaces in Iceland (Douglas, 1987). According to Douglas (1987) other common weathering products are poorly crystallized iron oxides and hydroxides, smectites, amorphous Si-Al minerals, and perhaps illite or kaolinite. Basaltic glass from Iceland, ranging in age from 2000 yr to 2.2 my has been altered to palagonite (alteration crust formed on the surface of the glass) and clay-like material filling the intergranular spaces of the rock (Crovisier and others, 1992). The chemical composition of the palagonite and that of the intergranular clay-like material are similar. There are two particle populations in the clay-like material: Si-, Mg-, and Ca-rich particles with a smectite structure, and Fe-, Ti-, and Al-rich amorphous particles with a smectite-like morphology. Ca- and sometimes Ca-K-rich zeolites are sometimes found among the alteration products (Crovisier and others, 1992).

At the early stage of weathering of basalt in the vicinity of Abert Lake in Oregon (Banfield, Jones, and Veblen, 1991), glass is replaced by smectite, olivine by smectite and hematite, pyroxenes by smectites, plagioclase by smectite, and in the rare cases where K-feldspar does weather it is replaced by smectite. These smectites are of variable composition. No evidence was found for the weathering of primary Fe-Ti, Ti-, and Fe-oxides. Elsewhere feldspar is found to weather to smectite, but olivine and sometimes pyroxene are replaced by iddingsite (Colman, 1982; Eggleton, Foudoulis, and Farkevisser, 1987). Goethite and hematite have both been positively identified in iddingsite, but the silicate constituent of iddingsite commonly appears to be embryonic in structure and variable in composition (smectite, chlorite, talc, micas; Deer, Howie, and Zussman, 1966; Delvigne and others, 1979; Smith, Milnes, and Eggleton, 1987).

At the late state of weathering Colman (1982) found basalts to contain allophane, amorphous iron oxide-hyroxide, poorly developed clay minerals, and primary opaque minerals. Basalts in stable landforms usually weather down to spheroidal forms (Noack and others 1990), sometimes with unaltered cores which are gradually altered to weathering minerals such as gibbsite, titanomaghemite, small amounts of goethite and kaolinite, and poorly crystallized iron products. The most weathered zone is rich in titanium, iron, and aluminum, as indicated by the mineralogy. This central zone is often capped by a red matrix containing kaolinite, magnetite, goethite, and Mn crust (Noack and others 1990).

It is difficult to assess the saturation state of weathering products with respect to soil and river water since the weathering minerals are

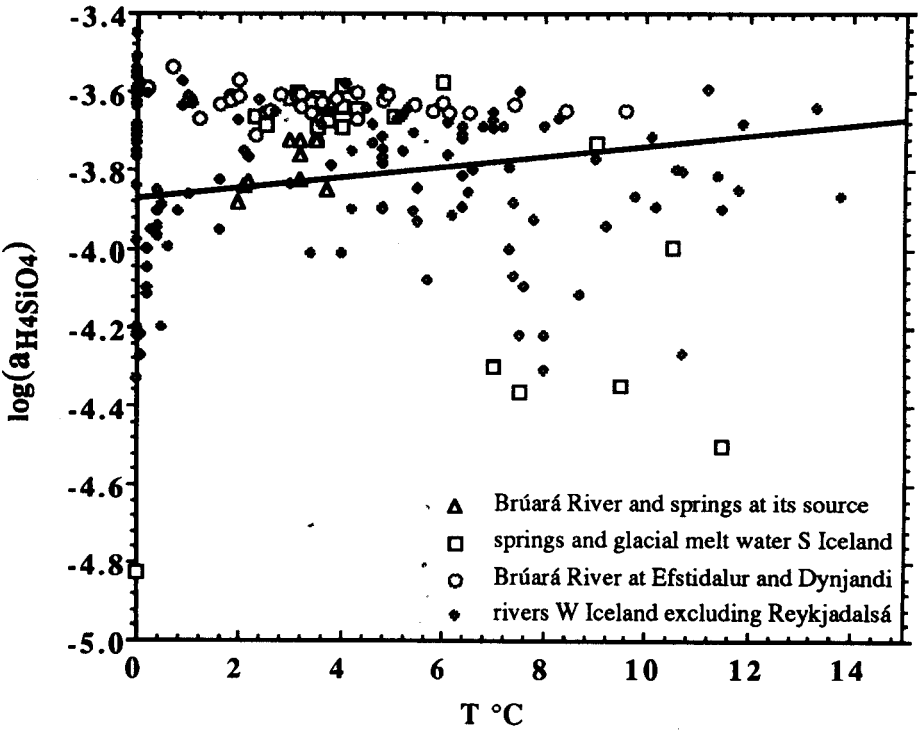



Fig. 22. The activity of the uncharged monomeric silica species in spring glacial melt and river water versus temperature. The original data come from the following sources: The Brúará River and springs at its source (Gíslason, 1989), the Brúará downstream at Efstidalur and Dynjandi (sample spots 3 and 4 in fig. 2; Ármannsson and others, 1973; Rist, 1974), spring and glacier melt waters in south Iceland (Airo, 1982), rivers in west Iceland, excluding the geothermally contaminated Reykjadalsá (Rist, 1986; fig. 2). The curve represents chalcedony solubility (Fournier, 1977).

poorly crystalline, fine grained, and of variable composition, as described in the previous paragraphs. The saturation state and relative stability of weathering minerals are shown in figures 22 to 25.

Glacier melt waters in southern Iceland and some river waters in western Iceland (fig. 22) are undersaturated with respect to chalcedony according to the solubility data given by Fournier (1977), but other waters are supersaturated or close to saturation. The most undersaturated river waters are flood waters. The supersaturation may be caused by the small crystal size of quartz and/or moganite which may put an upper limit on the silica activity in these waters (Heaney and Post, 1992; Gíslason, Veblen, and Livi, 1993; Gíslason and others, 1993). Thus, it is possible that a fine-grained mixture of quartz and moganite consumes a considerable part of the silica released during the dissolution of basaltic glass, olivine, pyroxene, and Ca-rich plagioclase.

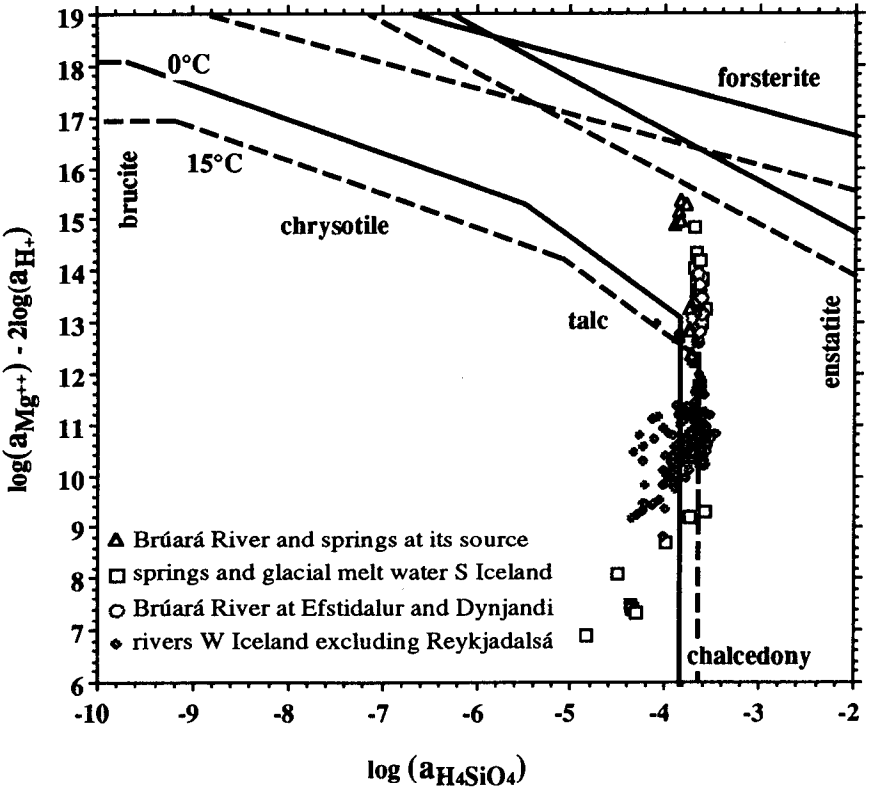



Fig. 23. Congruent dissolution in the Mg-Si-$H_2O$ system. The solubility of the most stable minerals is shown and also the metastable solubility of the magnesium endmembers of the olivine and orthopyroxene solid solutions at 0° and 15°C. Superimposed are the activities of the relevant species in the waters. Water samples the same as in figure 22.

The Mg–Si–$H_2O$ system is shown in figure 23. The Mg endmembers of olivine and orthopyroxene are unstable in these waters, as was also concluded from figure 21. Glacier melt waters are undersaturated with respect to all the minerals shown in the diagram, and some river waters in western Iceland are undersaturated with respect to chalcedony as is discussed above. Spring water at the source of Brúará River is supersaturated with respect to talc and the metastable mineral chrysotile. The degree of supersaturation of the waters of the Brúará relative to chrysotile and talc decreases continuously downstream due to water-air interaction. Most of the water samples collected from the river at Dynjandi (fig. 2; sample spot 3) are undersaturated with respect to talc (fig. 23). The river waters from western Iceland are undersaturated with respect to chrysotile and talc. However, as discussed earlier in the section on water-air interactions, some of the waters were previously either super-

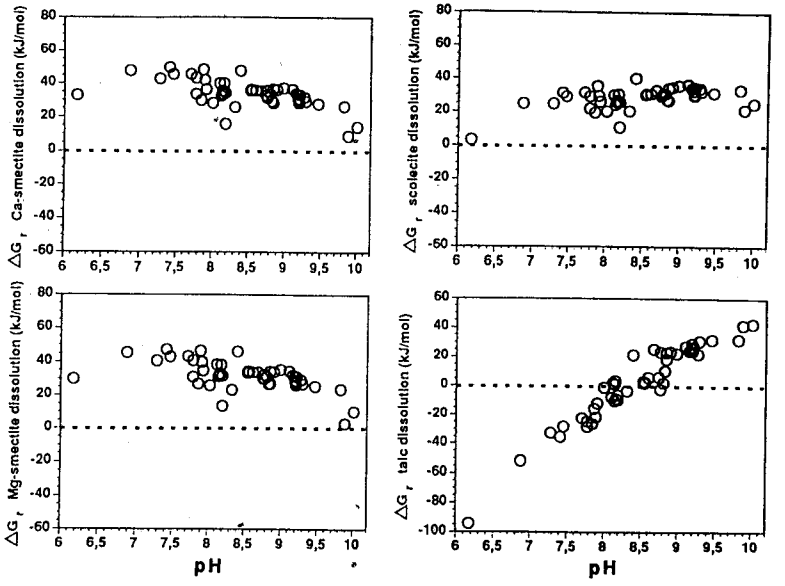



Fig. 24. Saturation state of Ca, and Mg smectites, scolecite, and talc in river and spring waters (Gíslason and Arnórsson, 1993) shown as a function of pH. The dashed lines represent equilibrium conditions; positive $\Delta G_r$ depicts supersaturation but negative $\Delta G_r$ undersaturation.

saturated or more undersaturated with respect to these minerals in the soil or rocks than at the time of sampling.

Glacier melt waters, river waters, and spring waters from southwest Iceland are undersaturated with respect to calcite. Thus, this mineral is not likely to retain calcium in soil and groundwater systems. Icelandic ground and river waters (Gíslason and Arnórsson, 1993) are supersaturated with respect to Ca- and Mg-smectites, Ca-zeolite (scolecite), and talc above a pH of 8.5, as shown in figure 24. The relative stability of common weathering minerals in the Ca-Si-Al-$H_2O$ system is shown in figure 25. Glacier melt waters and river waters from western Iceland plot in the kaolinite field, but spring and river waters with a pH above 9 in the scolecite and Ca-smectite fields. Thus scolecite is more stable than Ca-smectite and kaolinite when in contact with water with a high pH. Kaolinite is more stable than Ca-smectite and kaolinite when in contact with water with a pH lower than 8, but Ca smectite is most stable when in contact with water with an intermediate pH (8-9). However, despite their relative stability, all three can probably form in most of these waters (fig. 24). Thus Ca-smectites and Ca-zeolites are probable candidates for the retention of calcium during weathering of Icelandic basalts.

The above findings can be summarized as follows. At the early stage of weathering, basaltic glass, olivine, pyroxene, and sometimes plagio-

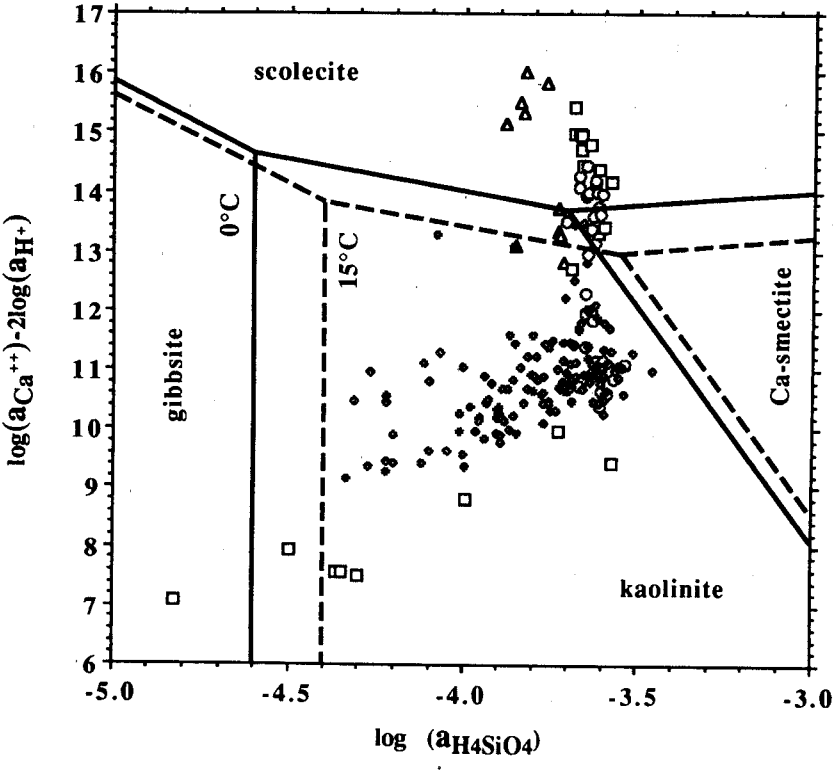



Fig. 25. Relative stability of common weathering minerals in the Ca-Si-Al-$H_2O$ system. The activities of the relevant species in the glacier melt waters, river waters, and spring waters from southwest Iceland are superimposed. The water samples and their legend are the same as in figures 22 and 23.

clase dissolve in Icelandic river and ground waters, releasing elements that are consumed as follows: Ca by smectite and/or Ca-zeolite; Si by a fine-grained mixture of quartz and moganite, smectites, zeolites, kaolinite, and/or in gel-like precursors of these minerals in variable crystalline states, such as allophane and imogolite; Mg by smectite and/or talc. Phosphorus is probably retained in the biomass and adsorbed on clays. Mn and Fe are retained in poorly crystalline oxides and hydroxides and smectites. Aluminum is retained in zeolites, smectites, kaolinite, gibbsite, and/or gel-like precursors of these minerals in variable crystalline states, such as allophane and imogolite. And if titanium is mobile, it is probably retained in some oxides.

## DISSOLUTION RATE OF BASALTIC MINERALS AND GLASS

The solution properties that affect the dissolution and precipitation rates of minerals and glasses and therefore overall chemical denudation

rates are: the temperature, pH, ionic strength, saturation state ($\Delta G_r$), and concentration of individual aqueous species (Guy and Schott, 1989; Oelkers, Schott, and Devidal, 1994; Lasaga and others 1994).

*Temperature.*—On average the dissolution rate of silicates increases by an order of magnitude, from 0° to 25°C (apparent activation energy of 63 kJ/mole; Lasaga and others, 1994). As shown in figure 6, the temperature variation can be as high as 20°C in Icelandic rivers but is probably much less in the rocks being weathered. The average soil temperature at a depth of 100 cm varies from the minimum 1.8°C in April to the maximum 8.4°C in August and September (Eythórsson and Sigtryggsson, 1971). The temperature variation in spring-fed rivers, close to the source, is even smaller, as shown in figure 5 for the Brúará at Efstidalur. The average temperature variation between individual rivers in southwest Iceland is small, 2.6°C (table 1), excluding the geothermally-affected rivers (Fossá, Varmá, and Reykjadalsá). This variation translates to a factor of 1.3 for the dissolution rate of minerals and therefore the chemical denudation rate, if weathering minerals and glass, primary and secondary, are highly undersaturated. However, this is not so in southwest Iceland. The second coldest catchment, the Brúará at Efstidalur (3.3°C), has the fastest total chemical denudation rate (TCDR), whereas the warmest catchment, the Laxá at Vogatunga (5.5°C), has the slowest rate (tables 1 and 6).

*pH.*—The effect of pH on the dissolution rate of minerals and glass far from equilibrium can be described as

$$\text{rate} = k a_H^n \qquad (5)$$

with n having values somewhere between −1 and 1. The pH effect is usually slight ($n \approx 0$) in the region pH 4 to pH 8 (Lasaga and others 1994). As shown in figure 10, the pH of Icelandic precipitation is well within the pH 4 to 8 range. The average pH of all the rivers in this study, except for the spring-fed Brúará River at Efstidalur (table 1), is within the pH 4 to 8 range. However, as discussed in the section on water air-interaction in Icelandic rivers, the pH of spring and glacial waters can be up to and above 10 before contact with the atmosphere. The pH of Icelandic soil waters ranges from 4 to 7 (Jóhannesson, 1960; Helgason, 1981; Fridriksdóttir, ms; Gudmundsson, 1994). Thus the dissolution rate in the high pH range could increase by one to two orders of magnitude according to eq (5) but only if the primary and weathering minerals and glass are highly undersaturated.

*$\Delta G_r$.*—The dependence of the dissolution rate on the saturation state ($\Delta G_r$) is complicated and much more important than predicted by transition state theory (Devidal, Dandurand and Schott, 1992; Nagy and Lasaga, 1992; Burch, Nagy, and Lasaga, 1993; Oelkers, Schott and Devidal, 1994; Lasaga and others, 1994). The $\Delta G_r$ has been shown to suppress dissolution rates as far down as −60 kJ/mole (Oelkers, Schott, and Devidal, 1994). As shown in figure 21 for olivine, undersaturation

decreases with increasing pH in rivers and springs in Iceland, and the same applies for pyroxene (Gíslason and Arnórsson, 1993, 1990). Above a pH of 8, $\Delta G_r$ is less negative than −40 kJ/mole for the most common olivine in the groundmass of Icelandic basalt ($fo_{43}fa_{57}$), and the $\Delta G_r$ is less negative than −20 kJ/mole for orthopyroxene ($en_{38}fs_{62}$) and decreases with increasing pH (Gíslason and Arnórsson, 1993). However, the most abundant plagioclase (groundmass plagioclase, $an_{29}ab_{71}$) in Icelandic basalt is only undersaturated in two of the waters (fig. 21). The decreasing undersaturation for olivine and pyroxene at a high pH cancels out to some extent the proposed increase in the dissolution rate at the high pH suggested in the previous paragraph. However, both the effect of the saturation state and pH on the dissolution rate of basaltic glass below 50°C remain unknown.

*Concentration of individual aqueous species.*—Concerning the effect of the concentration of individual species on the dissolution rate, the concentrations of Al and organic ligands are the most important in the weathering environment. The literature on the effect of organic ligands on the weathering of minerals is confusing. Oxalate has a significant effect on Ca-rich plagioclase and forsterite, but none on oligoclase (Grandstaff, 1986; Amrhein and Suarez, 1988; Mast and Drever, 1987). The amount of dissolved organic carbon (DOC) in Icelandic rivers is insignificant since the major and minor inorganic charged species yield good charge balances. It is only in peat waters that the inorganic charges do not balance because of negatively charged organic species (Fridriksdóttir, ms). In these waters there is a good correlation between the Fe concentration and the magnitude of the missing negative charge (from 0-65 percent of the total positive charge). Thus, the effect of organic ligands on the rate of weathering in general is small in Iceland but is of importance in peat areas.

The logarithm of the dissolution rates of albite and kaolinite are linear functions of the logarithm of the Al concentration in solution over wide ranges of saturation states (Oelkers, Schott, and Devidal, 1994). If the same applies to other Al-silicates, such as intermediate plagioclase, this would be important in the weathering of basalt. However, the variation in Al concentration in Icelandic river waters is small (table 1), and the concentration is mostly below the concentration range explored in experiments. It is only in surface waters contaminated by volcanic eruptions that the high Al concentration could have a significant effect (Gíslason and others, 1992).

In summary, the variation in the chemical denudation rate in southwest Iceland is not the result of temperature differences. The concentration of aqueous Al and organic ligands is too low to have a direct effect on the dissolution and precipitation rate of minerals in southwest Iceland. The expected dissolution rate enhancement at a high pH (8-10) is cancelled out to some extent by the small undersaturation ($-\Delta G_r$) or supersaturation ($+\Delta G_r$) at a high pH. The state of undersaturation ($-\Delta G_r$) dictates the dissolution rate for plagioclase at all explored

pH levels (6-10) and the ones for olivine and pyroxenes above a pH of 8. Furthermore, the observed state of supersaturation ($+\Delta G_r$) with respect to weathering minerals controls the rate of precipitation of these minerals. The dominant effect of the saturation state ($\pm\Delta G_r$) is reflected in the dependence of the chemical denudation rate on runoff in southwest Iceland (fig. 16B) and elsewhere (Meybeck, 1979; Bluth and Kump, 1994; White and Blum, 1995).

## SUMMARY AND CONCLUSIONS

*Chemical denudation, the age of rocks, relative mobility of elements, and runoff.*—The abundance of basaltic glass is much greater in the younger than in the older rocks in southwest Iceland. This is because basaltic eruptions under glaciers produce glassy rocks (hyaloclastites) while basaltic eruptions on glacier free land result in lava flows, mostly crystalline but with a glassy top and base. Glassy rocks dissolve about 10 times faster in meteoric water than crystalline basalt (Gíslason and Eugster, 1987a). This fact explains to some degree the dependence of the chemical denudation rates on rock age in southwest Iceland (figs. 16C and 17A-C). The presence of unaltered soluble basaltic glass in young rocks could lead to the stabilization of igneous minerals (Gíslason and Arnórsson, 1990, 1993). For example, release of Ca, Mg, Na, Fe, Al, and Si from the glass could reduce the degree of undersaturation with respect to olivine and may even cause the water to become supersaturated with respect to plagioclase and pyroxene (fig. 21). Where glass is not present for dissolution, either because it was absent from the beginning or previously altered, as in the relatively old Tertiary rocks of southwest Iceland, the rock dissolution pattern is different. Under these circumstances the water is at greater olivine and pyroxene undersaturation, and plagioclase is less supersaturated or more undersaturated.

In young catchment areas basaltic glass is often unaltered and plentiful. Under these conditions, Na and K are much more mobile than Ca, Mg, and Si. This is probably because of the stabilization of the igneous plagioclase and pyroxene and the formation of alteration minerals such as Ca, Mg-smectites, serpentine minerals, and Ca-zeolites. In the relatively old Tertiary rocks, basaltic glass, if present, is heavily altered. In this environment the relative mobility of Sr, Ca, Mg, and Si is much greater (table 5) than in the youngest rocks. This is because of increased igneous plagioclase dissolution and less stability of alteration minerals consuming Ca, Mg, and Si.

The dependence of chemical denudation rate on runoff is much lower in older rocks than in younger ones (fig. 16B, C, and D), and Na and K are even independent of runoff in the old catchments (fig. 17B and C). In the older rocks there is less glass and more vegetation, resulting in an increased number of minerals being undersaturated.

*Laterite formation and climate.*—The relative mobility of the least mobile elements during weathering in Iceland is similar to that observed elsewhere in the world under remarkably variable climatic conditions.

The least mobile or conservative elements are Fe, Ti, Al, and Mn, and they are $10^3$ to $10^4$ times less mobile than Na. Thus, one would expect a similar end product of chemical weathering in Iceland as, for example, in Hawaii, namely iron-rich bauxite containing the minerals gibbsite, goethite, and some halloysite and hematite (Bates, 1962) or their precursors. However, Iceland has not yet reached this stage. It has only been about 10,000 yrs since the whole island was glaciated, setting the chemical weathering clock to zero. The ratio of mechanical versus total present chemical weathering in Iceland is 9 ($500\ t\ km^{-2}y^{-1}/55\ t\ km^{-2}y^{-1}$), that is, higher than the overall 4.7 for the world (Garrels and Mackenzie, 1971). This ratio can vary considerably in Iceland as it does worldwide. Where the ratio is low, one would eventually expect to see the actual results of chemical weathering. Thus we agree with Nesbitt and Wilson (1992) and Taylor and others (1992) that laterites and bauxites are not necessarily representative of a "tropical climate" but rather the ratio of mechanical versus chemical denudation rates.

*Vegetation and chemical weathering.*—The vegetative cover of Icelandic catchment areas is not a primary variable for the overall rate of chemical denudation, perhaps because the vegetation slows down mechanical denudation rates by stabilizing soil, thus decreasing the exposure of fresh rocks to the incoming solutions (Drever, 1994). Bluth and Kump (1994) concluded that the overall chemical denudation rate is determined by a balance between physical and chemical weathering; thus a wet climate or the presence of abundant vegetation cannot guarantee high rates of chemical denudation unless accompanied by high rates of physical removal. Similarly Drever (1994) suggested that plants can greatly increase weathering rates in areas of high physical erosion by binding fine particles. However, over a long period of time plants may decrease chemical weathering rates by binding secondary products and isolating unweathered minerals from meteoric water.

In southwest Iceland the vegetative cover is important because it diminishes the selective weathering of the primary minerals and therefore the variation in the relative mobility of the elements during the weathering of basalts. With a continuous vegetative cover the pH of the soil solutions tends to be low ($<7$), and glass, olivine, pyroxene, and plagioclase are unstable; however, the solutions are decreasingly saturated or more undersaturated with respect to zeolites and smectite, thus increasing the relative mobility and fluxes of Ca and Mg. Since the weathering of Ca-Mg silicate rocks is the principal process by which $CO_2$ is removed from the atmosphere on a geological time scale (Berner, 1992), the spread of vascular plants on the continents during the mid-Paleozoic may have resulted in a drop in $CO_2$, not necessarily because of greatly enhanced bulk chemical weathering, as suggested by Trendall (1966) and Berner (1993), but rather due to the enhanced relative mobility and flux of Ca and Mg.

We agree with Drever (1994) to some extent that the "direct kinetic effect" of plants on the dissolution rates of rock-forming minerals is small.

However, this study contradicts his assumption that Mg-Ca-silicates are highly undersaturated in the weathering environment. The Icelandic ground and river waters are more dilute than the world's average (table 1). However, plagioclase, the most abundant mineral in the basalts, is never highly undersaturated in the Icelandic river waters. Here, vegetation can play a key role in leading to undersaturation by lowering the pH of the soil solutions well below 7. Furthermore, Drever (1994) ignores the effect of plants on the formation of secondary minerals in the soil. The solubility and therefore saturation state of Ca and Mg smectites is highly dependent on pH. By lowering the pH, plants can make these minerals undersaturated. In southwest Iceland the relative mobility of Ca and Mg is only 10 percent of that of Na despite the fact that Ca-rich plagioclase is undersaturated but Na-rich plagioclase not, and Mg-rich olivine and pyroxene are always undersaturated. Furthermore, dissolving basaltic glass contains nearly three times more Mg or Ca than Na on a molar basis. Thus, the difference in relative mobility can only be explained by extensive formation of weathering minerals that consume Mg and Ca.

*Glaciers and chemical weathering.*—Direct studies of chemical weathering rates in glacial catchments (Reynolds and Johnson, 1972; Collins, 1983; Metcalf, 1986; Sharp and others, 1995) have demonstrated that chemical weathering rates are often approximately three times higher than the continental average. However, some of the high rates reported for glacial catchments can be attributed to high runoff (Kump and Alley, 1994). Conversely, White and Blum (1995) concluded that past glaciation does not greatly affect the present chemical weathering fluxes of $SiO_2$ and Na from granitoid rock types.

Glacial sediments have enormous surface area and might be mechanically strained due to glacial grinding, a feature shown by experimental studies to enhance dissolution rates (Dandurand, Gout, and Schott, 1982; Ferret and others, 1987). A high pH of basal melt water (8-10) could result in direct pH enhancement of the dissolution rates of minerals. However, a high pH stabilizes secondary weathering minerals and decreases the undersaturation of primary minerals. A low temperature (0.1°C) slows down chemical weathering rates and, in extreme cases, even stops it when glaciers are frozen to the bedrock.

Much of Iceland is covered with glacial sediments from the last glaciation. Thus it is difficult to assess the overall effect of glaciers on chemical weathering rates because there are no data available from areas with no glacial sediments. However, the effect of glacial cover can be studied. Glacial cover slows down the overall chemical denudation rates in southwest Iceland. It increases the probability of the precence of high pH weathering solutions by excluding direct and indirect (via vegetation) routes for the $CO_2$ from the atmosphere to the weathering site and by continuously exposing fresh rocks to the incoming solutions. A high pH (8-10) makes the primary Ca-silicates and the Mg-silicates stable or less unstable and also increases the probability of the deposition of zeolites and smectites. Thus, the relative mobility and fluxes of Ca and Mg slow

down during glacial cover and therefore retard the permanent consumption of atmospheric $CO_2$. This process supports the theory of a negative feedback mechanism for the long-term stabilization of the Earth's surface temperature (Walker, Hays, and Kasting, 1981).

The increase in Fe and Mn fluxes with glacier cover in southwest Iceland could be attributed to the enhanced solubility of metal oxides and hydroxides at high pH values. Thus glacier cover of land could result in enhanced flux of some metals to the ocean. This has implications for the short-term carbon cycle. Planktonic growth rates are determined not only by nutrients but also by the level of a number of metabolically important metals such as Fe, Mo, and Cu (de Baar and others, 1995).

*Overall chemical weathering rates in Iceland.*—The high chemical weathering rates in Iceland can be attributed to high runoff; soluble rock type (basalt); the age of the rocks, which in turn is linked to the abundance of unweathered basaltic glass and high permeability; rapid mechanical weathering; and possibly the presence of mechanically strained glacial sediments.

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