

IRON IN SURFACE AND SUBSURFACE WATERS,
GRIZZLY BAR, SOUTHEASTERN ALASKA

Iron in surface and subsurface waters, Grizzly Bar, Southeastern Alaska
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by

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ABSTRACT

IRON IN SURFACE AND SUBSURFACE WATERS, GRIZZLY BAR, SOUTHEASTERN ALASKA

Atomic absorption spectrophotometric measurements for total iron were made on 69 samples of water from 8 different environments in an outwash fan built by meltwater streams from the retreating Norris Glacier on granodiorite bedrock. Norris Glacier ice contained no iron (3 samples), a subglacial stream contained 5.5 ppm Fe (1 sample), and a meltwater lake fronting Norris Glacier contained 0.7 ppm Fe (3 samples). Iron content of ground water from outwash ranged between 0.0 and 17.0 ppm (6 samples); surface streams fed by emergent ground water on the fan periphery contained 0.0 to 0.2 ppm Fe (13 samples). Taku Inlet waters contained 6.4 ppm Fe (3 samples). Subsurface water from an intertidal mud flat contained between 0.0 and 27.0, \bar{X} 5.9, ppm Fe (31 samples). Surface and subsurface water from a bog and associated stream contained 1 ppm Fe (12 samples). Little exchangeable Fe was found. *In situ* measurements in water for Eh showed large positive values (+0.30 to +0.50 volts) and pH was slightly alkaline. The single most important source of iron was vermiculitized biotite. Iron was transported in water in the particulate state, except in outwash ground water where particulate Fe^{+3} was reduced to dissolved Fe^{+2} . Iron deposits of $Fe(OH)_3$ were found near the top of the outwash water table.

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PREFACE

This project was begun through the University of Alaska's Institute of Water Resources, (IWR), Dr. Charles E. Behlke, Director. It was our mutual understanding that this work would be the doctoral research for Mr. Roger M. Slatt in the Department of Geology. The completion report for this work was to be Mr. Slatt's Ph.D. dissertation, written in a format suitable for submission to nationally-circulated scientific journals. With Dr. Behlke's assistance, Mr. Slatt and I had previously completed and published a paper which included results from Mr. Slatt's master's degree research (Slatt and Hoskin, 1968), a water-related study funded by the United States Department of the Interior, Office of Water Resources Research, through the University of Alaska's Institute of Water Resources. We believed that a start had been made toward developing an on-going program of water-sediment studies, and so long as we were able to interest students in this work and to successfully complete and publish our findings (Slatt, 1971; Slatt, 1972), we believed we would have received assistance in the form of continued funding.

A change of Directors of IWR at the University of Alaska altered those plans. New goals were established, and Mr. Slatt's work was stopped short of completion because of lack of funding. Proposals submitted to Alaska's IWR, which would have enabled Mr. Slatt to complete his doctoral work, were judged to be not suitable for formal submission to Washington. Fortunately for Mr. Slatt, funds were made available from other sources; however, this required a major change in Mr. Slatt's research goals. As funding through IWR was no longer available, it was not possible to continue our studies on the iron project. Further, we respectfully suggest that a unique opportunity for students of the University of Alaska was also lost in that water-sediment studies, and cooperation with the Juneau Ice Field Research Project were no longer possible.

We continue in the belief that these goals are meritorious, and we respectfully suggest that the new Director of Alaska's IWR carefully consider supporting work which may lead toward achieving them.

This completion report for project A-019-ALAS contains all available data and is a complete statement of our findings.

CONTENTS

FIGURES vi
TABLES vi
INTRODUCTION 1
Background 1
Environmental Setting 1
METHODOLOGY 5
Field Work 5
Laboratory Analysis 5
DISTRIBUTION OF IRON 7
General 7
Norris Glacier, Subglacial Stream, and Meltwater Lake 7
Ground Water from Gravelly Outwash 9
Surface Water from the Intertidal Mud Flat and Taku Inlet 10
Subsurface Water from the Mud Flat 10
Bog Waters 11
SUMMARY 12
LITERATURE CITED 13

FIGURES

- Fig. 1. Map of Upper Taku Inlet and Environments of Grizzly Bar, southeastern Alaska 2
- Fig. 2. Aerial view of northeastern Grizzly Bar 4
- Fig. 3. Map of water sample stations and environments of northeastern Grizzly Bar . 6

TABLES

- Table 1. Physical and chemical data for waters from Norris Glacier: Grizzly Bar 8

INTRODUCTION

Background

Glacial sediment and outwash are common surface materials in Alaska, and they usually contain significant amounts of iron-bearing minerals. Surface and subsurface waters on and in these sediments have been observed to contain iron, and in places, some parts of the Fairbanks area for example, iron is abundant enough to restrict water usage. The authors believed that iron has been mobilized from some of the minerals in near-surface sediments, and it was felt that a study of mobilization processes would identify which minerals and which processes were major contributors of iron to water.

Norris Glacier outwash fan (58° 24' North Lat., 134° 04' West Long.) in upper Taku Inlet of southeastern Alaska (Fig. 1) was chosen as the site for this study. All the components (source, mode of transport, accumulation site) of an iron mobilization system were known to be present in this place from previous work, and disturbances of this system by man were essentially non-existent. A further potential benefit, we believed, was the possibility of adding the dimension of glacial sediment study to the glacial ice studies of Maynard Miller's (Michigan State University) Juneau Ice Field Research Project, which each summer fielded a team of about 30 students and scientists in the nearby upper reaches of Taku Glacier.

Environmental Setting

An eight-square-mile outwash fan named Grizzly Bar (Orth, 1967) adjoins the retreating Norris Glacier (Fig. 1) and has been built out into upper Taku Inlet by outwash streams over the immediately preceding 200 years (Lawrence, 1950). From the terminus of Norris Glacier eastward, we observed a succession of environments. Valley glacier environments are not static, and major changes in landforms and vegetation occur over periods of only a few years. The following description is intended to apply only to the period of our fieldwork - 1966 to 1969.

The first material contributed to the formation of Grizzly Bar was probably ice-contact sediment at the terminus of Norris Glacier. Analyses for three samples of contemporaneous deposits of this material from Grizzly Bar showed gravel to form about 35, sand 40, and mud 25 percent by weight (Slatt, 1970, Appendix A, p. 96). Adjoining Norris Glacier terminus was an oval-shaped meltwater lake, about 1365 m N-S x 304 m E-W. One outlet to this lake was an eastward-flowing stream. The apex, and topographically highest part of Grizzly Bar, is the eastern shore of the meltwater lake, and from this place, the outwash slopes eastward toward Taku Inlet. The major part of Grizzly Bar is sparsely covered with vegetation. Two samples of outwash from this part of Grizzly Bar have been described by Slatt (1967, Appendix A, p. 38) as gravel 60-75, sand 25-33, and mud 0.4-6.5 percent by weight.

Around the periphery of the non-tidal gravelly outwash, dense stands of Sitka Spruce and Western Hemlock are growing in wedge-shaped patches. This pattern suggested that perhaps the trees were on old inter-stream divides. Eastward, the gravelly outwash extends into the Taku River but is covered with a thin layer of mud accumulated by the settling lag effect (Kuenen, 1961); the mud probably had been derived from the Taku River and from Taku and Norris Glacier sediments. The tidal range in upper Taku Inlet is about 5 m (17 ft. U. S. Dept. of Commerce, 1971), and from the air, tide-related environments are easily seen. Bordering the belt of trees is a mud flat, which was naturally divided into two zones: (1) A drier zone inundated only by spring tides which in its southern parts supported a vigorous growth of marsh grass, *Carex sp.* (personal communication, R. Hadley 1969); to the north, the marsh grass was sparser; (2) A wetter and non-vegetated zone covered twice daily by the tides. Sediment from the intertidal part of Grizzly Bar has been described by Slatt and Hoskin (1968). An intermittently active meltwater stream channel separates the mud flat from a body of ripple-marked sand; this is best developed on the northern part of the Bar.

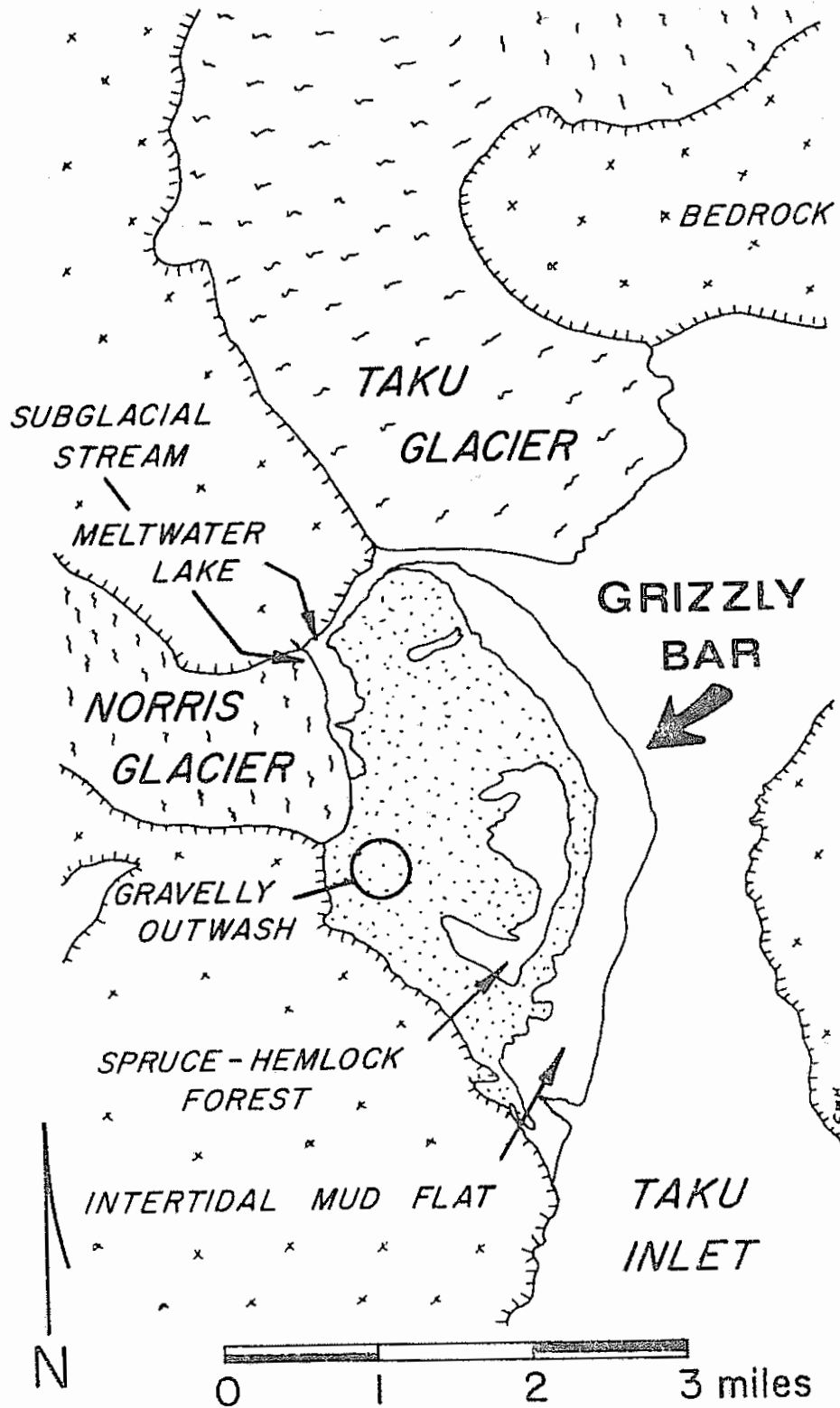


Fig. 1. Map of Upper Taku Inlet and environments of Grizzly Bar, southeastern Alaska. Stippling indicates gravelly outwash, x's represent plutonic igneous bedrock, and wiggles represent glacial ice wiggles elongated perpendicular to direction of flow.

Water in upper Taku Inlet has at least three sources: (a) river water from the Taku River, (b) meltwater from many glaciers, including Taku and Norris, and (c) saline water from the sea. The non-saline waters (a) and (b) (salinity $< 1\text{‰}$) form a thin surface layer less than a meter thick which mixes slightly with the denser underlying seawater (salinity $\approx 27\text{‰}$; Hood *et al.*, 1966). Fluctuating water level due to the tides caused a similar fluctuating water level and flow within the intertidal sediments. As the rippled sand body was the most permeable, the largest flows occurred there, and smaller flows occurred in the mud (Slatt and Hoskin, 1968; Fig. 9, p. 443).

Meltwater flow paths for the non-tidal environments of Grizzly Bar were more diverse. The lake was probably supplied both by meltwater produced at the glacier terminus and a subglacial stream which emerged at the north end of the lake. There were two main flow routes from the lake: (a) water very probably flowed in the subsurface through the gravelly outwash and emerged as springs and surface streams just seaward of the tree belt, and (b) water flowed from the lake and subglacial stream as a surface stream and entered Taku Inlet at the north end of Grizzly Bar. A smaller southward-flowing stream may, at times, have carried meltwater from the lake. Usually this smaller stream was not turbid, and therefore, was not directly supplied by meltwater from the lake.

In many places where water emerged from the gravelly outwash as springs, bogs and surface streams, a flocculent orange precipitate was observed (arrow, Fig. 2); this precipitate formed the focal point of this project.



Fig. 2. Aerial view of northeastern Grizzly Bar. From bottom to top: rippled sand body, intertidal mud flat with bog and streams of Fig. 3 (arrow), Spruce-Hemlock forest, gravelly outwash, terminus of Norris Glacier (left), terminus of Taku Glacier (right).

METHODOLOGY

Field Work

Water samples were collected (Fig. 3) and stored in new HCl-washed polyethylene bottles during May and June 1967. Subsurface water was obtained from auger and hand-dug wells; these were flushed by repeated pumping until non-turbid water was recovered. Samples from the subglacial stream, lake, Taku Inlet and Taku River were turbid; these samples were stored until clear, and the water was then decanted into clean bottles.

Data for pH and Eh were obtained *in situ* with a Beckman Model N battery-powered meter using a fiber-type calomel reference electrode and glass (pH) and bright-finish platinum (Eh) electrodes. Hydrogen ion concentration was read directly; electrical potentials measured in millivolts were converted to Eh by Back and Barnes (1965) relationship:

$$Eh(\text{volts}) = E_{\text{meas.}} + [0.2415 - (0.00076)(T^{\circ}\text{C} - 25)]$$

Sequential measurements to determine drift suggested that 3 to 4 minutes were required to obtain a constant reading and that probably represented temperature equilibration between electrodes and sample. Temperature was measured with a metal dial-type immersion thermometer. Sediment, soil, organic materials and iron deposits were stored wet and unpreserved in polyethylene bags.

Laboratory Analysis

Chlorinity was measured by replicate titration with AgNO_3 standardized against IAP0 seawater with a chlorinity of 19.373‰ (U. S. Hydrographic Office 1969). Total iron content (Fe_T) in water and melted ice was determined by atomic spectrophotometry after addition of an equal volume of 10 percent HCl, dilution, and equilibration for at least 24 hours.

Sediment grainsize analyses were done following the standard techniques of Folk (1968). Organic matter content of sediment was estimated by weight loss following heating to 650C for four hours in a Lindberg muffle furnace. Correction for carbonate content was applied as determined from HCl digestion of a separate aliquot. Cation exchange capacity (CEC) was measured at pH 7 by a modified version of Chapman's (1965) technique. Exchangeable iron (Fe_E) in the leachate was determined by AAS. Marsh grass, leaves, and roots, and Spruce-Hemlock forest litter were ground in a Wiley mill, and CEC and Fe_E determined by AAS following HClO_4 digestion (Olsen and Dean, 1965).

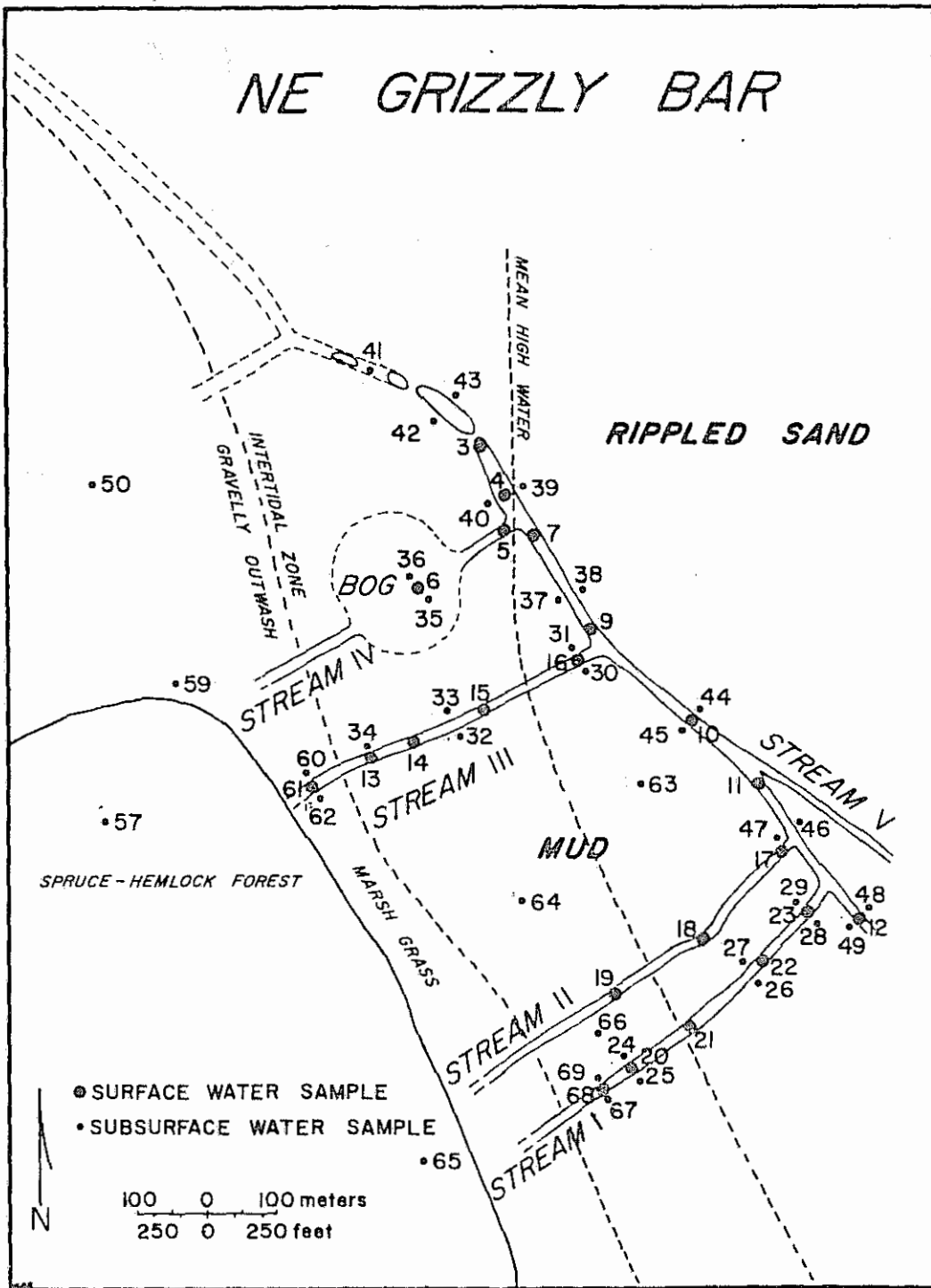


Fig. 3. Map of water sample stations and environments of northeastern Grizzly Bar.

DISTRIBUTION OF IRON

General

Major accumulations of the flocculent orange precipitate occurred in the bog and upper reaches of Stream V (Fig. 3). Emission spectrography (Jarrell-Ash 1.5 m Wadsworth Grating) and X-ray fluorescence (Norelco type 12045, tungsten tube, LiF crystal and scintillation detector) indicated that iron was the only major element present in the orange precipitate. Scanning X-ray diffraction and electron microscopy (Jem G-A) showed the precipitate to consist of non-crystalline material in particles smaller than 1 micron. These data supported our belief that the orange precipitate was $\text{Fe}(\text{OH})_3$.

The Eh measurements (Table 1) indicated the presence of dissolved oxygen. Eh measurements for surface waters are usually interpreted with the assumption that equilibration has occurred with atmospheric oxygen. Eh measurements for subsurface waters, however, are more difficult to interpret because of the possibility of sample contamination with oxygen during collection and analysis (Hem, 1960a). In ordinary subsurface water, the oxidation potential is highest near the top of the water table because of increased oxygen abundance (Hem, 1960b). Iron oxides which are stable under oxidizing conditions may accumulate at the top of the water table (Hem and Cropper, 1959). Most of the surface and subsurface waters reported on here have relatively high Fe_T contents (Table 1). These findings are anomalous when it is realized that the measured Eh and pH conditions of the water samples place them within Hem and Croppers' (1959) ferric hydroxide stability field. This suggests that the distribution of iron observed cannot be explained simply by one process for the entire regimen of Grizzly Bar. Iron in natural waters occurs in many phases - dissolved Fe^{+2} , particulate $\text{Fe}(\text{OH})_3$, and iron-organic complexes (Fe-R), to name but a few. Mobilization, transport, and accumulation of each iron phase is controlled in nature by the environment, each environment conceivably exerting its own, unique control. As there are several major environments comprising Grizzly Bar, the distribution might be best explained on an environment-by-environment basis.

Norris Glacier, Subglacial Stream, and Meltwater Lake

Three samples of melted Norris Glacier ice contained no iron, but turbid and unfiltered subglacial stream water contained 5.5 ppm Fe_T (Table 1). Samples from the subglacial stream collected during work on another project in 1969 were immediately filtered on collection, and subsequent analysis showed no iron present. Thus, it would first appear that iron in the subglacial stream was derived from solution of suspended sediment. Because of the high Eh and pH conditions of subglacial stream water, iron should be transported in the particulate state. Timed-sequence experiments (up to 120 days duration) were done with mixtures of iron-free Norris Glacier melted ice and ice-content sediment from Norris Glacier in attempts to determine if iron could be mobilized from the sediment. These experiments showed no iron released from sediment into water, and this result suggested that (a) the iron detected in the subglacial stream was not derived through solution of suspended sediment, and (b) the iron detected was in particulate form.

Bedrock in the Juneau Ice Field (the source of Norris Glacier) is a Mesozoic batholithic complex of acidic intrusive rocks - quartz diorite and associated plutonic rock types (Brew *et al.*, 1966) and granodioritic gneisses in the vicinity of the upper reaches of Norris Glacier (Forbes, 1959). These rocks contain three minerals which may have been sources of iron: magnetite (Fe_3O_4), hornblende, and biotite, the latter two being complex chain and sheet silicates, respectively. Inspection by microscope revealed no obvious corrosion features or other signs of chemical attack on magnetite or hornblende grains (Slatt and Hoskin, 1968; Fig. 17, p. 452). Biotite, however, was seen to be altered by the process of vermiculitization.

TABLE 1. PHYSICAL AND CHEMICAL DATA FOR WATERS FROM NORRIS GLACIER: GRIZZLY BAR

Location	Station No.	pH	Eh (volts)	Temp. °C	Chlorinity (‰)	Iron ppm ± 5%
Norris Glacier Ice	No data	—	—	—	—	—
Norris Glacial Subglacial Stream	56	9.1	+0.45	2.0	0.00	5.5
Norris Meltwater Lake	51	8.2	+0.48	12.0	0.00	0.7
	52	8.1	+0.47	3.5	0.00	0.8
	53	8.1	+0.48	4.0	0.00	0.7
Ground Water from Gravelly Outwash	50	7.2	+0.49	13.0	0.00	2.5
	54	7.8	+0.56	8.8	0.00	0.8
	57	6.4	+0.59	8.3	0.00	0.0
	58	6.0	+0.58	8.0	0.00	17.0
	59	5.9	+0.57	8.5	0.00	0.7
	65	—	—	—	0.00	0.7
Stream I Surface Water	20	7.7	+0.48	11.0	0.00	0.0
	21	7.5	+0.48	11.0	0.00	0.0
	22	7.4	+0.47	11.0	0.00	0.0
	23	7.1	+0.46	12.0	0.30	0.2
	68	—	—	—	0.00	0.0
Stream II Surface Water	17	7.0	+0.49	9.0	0.34	0.0
	18	7.1	+0.47	8.0	0.05	0.0
	19	7.2	+0.46	8.0	0.00	0.0
Stream III Surface Water	13	7.4	+0.52	8.0	0.00	0.1
	14	7.2	+0.49	10.0	0.00	0.0
	15	6.9	+0.44	11.0	0.00	0.1
	16	7.1	+0.44	14.0	0.00	0.0
	61	—	—	—	0.00	0.0
Stream V Surface Water	3	7.5	+0.46	19.0	0.24	0.2
	4	7.8	+0.44	19.0	0.33	0.4
	7	8.2	+0.43	25.0	0.38	1.2
	8	7.2	+0.40	20.0	0.41	0.2
	9	6.6	+0.37	15.0	0.82	1.2
	10	7.4	+0.45	21.0	0.71	1.2
	11	7.1	+0.45	19.0	0.72	1.7
	12	7.1	+0.47	14.0	0.53	1.4
Taku Inlet Surface Water	70	—	—	—	0.06	6.5
	71	—	—	—	0.00	6.3
Taku Inlet River Water	72	—	—	—	0.00	6.3
Mud Flat Subsurface Water	24	6.8	+0.38	7.5	0.21	20.0
	25	7.1	+0.33	6.0	0.09	16.0
	26	6.2	+0.48	9.0	1.00	0.0
	27	6.4	+0.27	8.8	0.44	7.2
	28	6.6	+0.34	12.0	4.00	6.9
	29	6.7	+0.31	9.8	2.60	17.0
	30	6.9	+0.41	12.0	0.65	4.6
	31	7.1	+0.40	11.0	0.04	8.3
	32	6.8	+0.26	10.0	0.60	7.2
	33	6.7	+0.23	9.0	0.67	11.0
	34	6.4	+0.38	7.0	0.00	1.6
	35	6.8	+0.30	9.5	0.26	3.0
	36	7.0	+0.25	8.5	0.13	8.6
	37	7.1	+0.42	14.0	0.30	11.0
	38	8.2	+0.37	14.0	0.68	0.7
	39	9.0	+0.35	15.0	0.30	1.4
	40	6.9	+0.30	14.0	0.38	3.6
	41	7.0	+0.24	13.0	0.28	27.0
	42	6.8	+0.24	12.0	0.32	11.0
	43	7.8	+0.41	21.0	0.26	0.2
	44	7.9	+0.40	18.0	0.51	0.0
	45	7.1	+0.22	14.0	0.93	8.7
	46	8.5	+0.35	14.0	0.49	9.3
	47	7.0	+0.38	20.0	2.00	0.7
	48	8.2	+0.37	—	0.83	4.0
	49	7.4	+0.17	15.0	6.80	0.3
	60	—	—	—	0.00	0.1
	62	—	—	—	0.00	0.0
	63	—	—	—	1.10	0.3
	64	—	—	—	0.00	0.3
	66	—	—	—	0.04	2.5
	67	—	—	—	0.00	1.1
	69	—	—	—	0.05	3.6
Bog Water	6	6.8	+0.38	17.0	0.00	1.5
Stream IV Surface Water	5	7.3	+0.48	22.0	0.05	1.1

This involves oxidation of Fe^{+2} to Fe^{+3} with migration of Fe^{+3} from the silicate lattice (Walker, 1949). Surfaces of biotite flakes were golden yellow, and numerous fractures in each grain were filled with granular bits of the orange iron oxide precipitate. In the turbulent environment of the subglacial stream, these bits of iron oxide would be dislodged from the biotite grains and transported by the stream. Iron physically removed from altered biotite grains is believed to be the most likely source of iron in this stream.

Total iron content of Norris meltwater lake was slightly greater than 0.7 ppm (Table 1), and from the Eh and pH conditions of lake surface water this iron was judged to be in the particulate state. As Norris Glacier ice contained no iron, the lake water must have received iron from some combination of subglacial stream water and iron oxide loosened from altered biotite grains in outwash along the lake shore.

Ground Water from Gravelly Outwash

The mean total iron content ($\bar{X} \text{Fe}_T$) of six samples of subsurface water from the gravelly outwash is 3.6 ppm, and the iron content ranged between 0.0 and 17.0 ppm (Table 1). The small number of samples and data overlap do not permit formulation of an unequivocal statement, but it appears that there is no real difference in iron content of subglacial stream water and subsurface water from gravelly outwash.

All samples of subsurface water from gravelly outwash were clear and not colored when collected. However, within an hour of collection, a flocculent orange precipitate formed, and this suggested that iron was present in the dissolved state. This iron may have been Fe^{+2} or Fe-R, but Fe^{+2} is considered the more likely phase for the following reasons. Iron-organic complexes tend to produce a yellow-brown color in water, and this was not seen in these samples. Hem (1960c) found that "appreciable" quantities of tannic acid must be present to form iron-organic complexes, and this should cause the water to have the characteristic yellow-brown color, which was not seen. Also, iron-organic complexes are much more stable than dissolved Fe^{+2} in the presence of dissolved oxygen. The rapid precipitation of $\text{Fe}(\text{OH})_3$ observed suggested to us that the dissolved iron phase was Fe^{+2} .

Considerable efforts were expended to measure the concentration of Fe^{+2} in the field by the colorimetric method of Lee and Stumm (1960). High concentrations (many ppm) of Fe^{+2} were indicated by this method, but serious objections to this analytical technique made interpretation of the results difficult (Shapiro, 1966; McMahon, 1967). The presence of dissolved Fe^{+2} is not questioned, but the semi-quantitative results of Fe^{+2} analysis are in doubt. The partition between Fe^{+2} and Fe^{+3} in natural waters is a general problem, and we strongly recommend that further research efforts be made to devise a suitable method for determination of ferrous and ferric iron in the field.

Large positive Eh potentials and dissolved Fe^{+2} are not compatible under equilibrium conditions, but in nature, iron is not usually in chemical equilibrium with water (Hem and Cropper, 1959), and non-equilibrium conditions seem to have been the case for Grizzly Bar.

If, as we believe, iron is supplied to the outwash ground water in Fe^{+3} particles, the iron must be chemically reduced as it is transported through the outwash by the water. The oxidation potential of ground water usually decreases with depth due to absence of oxygen (Hem, 1960b) and this appears to match the situation for Grizzly Bar. Iron oxide accumulations at the top of the water table suggested that as a parcel of subsurface water with its contained Fe^{+2} flowed towards the ground surface, oxidation occurred, and the iron was precipitated.

A pit dug to the top of the water table through the Spruce-Hemlock forest litter and outwash (in the patch of trees on the far left and about four tenths of the way down from the top of the photograph, Fig. 2) revealed downward-extended stringers of iron stain. Outwash sediment not in the Spruce-Hemlock forest contained no exchangeable iron, as measurements for two samples showed 0.00 and 0.00 me/100 gms exchangeable iron. The total iron content of Spruce-Hemlock litter, $\text{Fe}_T = 0.77$ ppm for one sample, was judged to be high for plant materials (personal communication, K. VanCleve, 1970). Spruce-Hemlock

litter contained 0.09 me/100 gms exchangeable iron (one sample) and this suggested that biological processes may have been involved. Iron in living plant tissue may be mobilized during decomposition (Oborn, 1960). Organic "acids" are among the products of plant decomposition, and these are capable of mobilizing iron as Fe-R (DeLong and Schnitzer, 1955a, 1955b; Bloomfield, 1952; Weinstein *et al.*, 1954). These data support the idea that iron has been mobilized from the outwash through life processes of the trees, returned to the forest floor in the form of litter and decayed wood, transported downward in the form of iron-organic complexes (Fe-R), and accumulated near the top of the water table due to oxidation and subsequent precipitation as an oxide.

Surface Water from the Intertidal Mud Flat and Taku Inlet

The small amounts of total iron, 0.0 to 0.2 ppm, (Table 1), found in Streams I to III of the intertidal zone and the x-axis intercept value for these waters [$Fe_T = -0.18 + (2.7)(\text{chlorinity})$] suggested that iron had been lost from outwash subsurface water at, or during, the time when it emerged as surface flows. Bright red iron stains in stream bed sediments supported the idea that at least some of the precipitation occurred just as the ground water emerged.

A linear relationship was discovered between Fe_T and chlorinity (correlation coefficient $r = 0.793$) for these waters, and this suggested that some of the iron found in the stream beds may have come from Taku Inlet surface waters. Total iron content of Taku Inlet surface waters was found to be between 6.3 and 6.5 ppm (3 samples, Table 1). The iron deposit in the upper reaches of Stream V was probably due, at least in part, to transport and subsequent deposition of particulate iron during flood tides. This deposition may have been augmented by the flocculating effect of sea water (Oborn and Hem, 1961).

Subsurface Water from the Mud Flat

The presence of iron in subsurface water from the mud flat ($\bar{X} Fe_T = 5.9$ ppm for 31 samples) and the lack of correlation ($r = 0.038$) between Fe_T and chlorinity of subsurface water suggested that the iron in water from this environment was not supplied from Taku Inlet surface waters. Large positive values for Eh potential and alkaline pH indicated an oxidizing environment in subsurface water from the intertidal mud flat. However, we believe a reducing environment existed within these sediments. Evidence for the reducing environment was (a) abundant decaying plant material, (b) lack of red iron oxide stains, (c) presence of H_2S odor, and (d) presence of black mud, particularly surrounding decaying plant fragments (mud elsewhere on Grizzly Bar is gray). The black mud has been generally attributed to reaction of dissolved iron with H_2S produced during anaerobic decomposition of plant material by sulfate-reducing bacteria (Berner, 1967). These observations suggested iron in mud flat subsurface water was mobilized *in situ*.

Iron sources in fine-grained and thus potentially reactive mud flat sediment are (1) the minerals biotite and iron-rich chlorite (thuringite-identified by scanning X-ray diffraction; Slatt and Hoskin, 1968), and (2) fragments of *Carex sp.*, the marsh grass. The total iron content of *Carex sp.* leaves (0.11 ppm) and roots (0.87 ppm) suggested that during decay, iron would be mobilized as Fe^{+2} or Fe-R. The lack of exchangeable iron in mud flat sediment and *Carex sp.* roots and very small amount in *Carex sp.* leaves (0.03 me/100 gms) suggested that ion-exchange was not a significant source of iron in this environment.

Dispersion of iron in mud flat subsurface water following mobilization might have occurred in three ways: (a) diffusion (Berner, 1969), (b) flushing by tide-produced changes in the mud flat water table, and (c) expulsion by de-watering of fine-grained sediments under gravity compaction. Mobilized iron from sediment of the mud flat was probably contributed to Taku Inlet water; depositional sites within the mud flat sediment were not seen. The rippled sand body was porous, permeable, and lacked vegetation; aerobic conditions probably prevailed, and no evidence of mobilization of iron was detected.

Bog Waters

The bog contained a large accumulation of the bright orange precipitate. Unfortunately, the iron content of surface water flowing into the bog was not measured. The upper reaches of Streams I, II and III contained little or no iron (Table 1), and therefore it has been tentatively assumed that no iron was supplied to the bog from the upper reaches of Stream IV. Bog surface water ($Fe_T = 1.5$ ppm, one sample) all contained significant amounts of iron (Table 1). Iron in bog water and accumulated $Fe(OH)_3$ precipitate argued for *in situ* mobilization of iron. Sources of iron would be the same as those for the mud flat.

An additional mechanism for iron deposition was seen in the form of a thin bacterial film on the bog surface water. Filamentous bacteria, similar in morphology to iron bacteria (Pringsheim, 1949), were seen in the bog iron deposit. Iron bacteria, which grow well in the high positive Eh and slightly acidic pH conditions of bog water (Baas Becking *et al.*, 1960), are capable of accumulating large amounts of $Fe(OH)_3$ on their gelatinous sheaths, and these may form iron deposits following death of the bacteria (Harder, 1919). although there is some disagreement in the literature as to the exact role iron bacteria play in iron chemistry, it is generally believed that they utilize energy released during oxidation of Fe^{+2} or oxidation of organic matter (Alexander, 1961). In the bog of Grizzly Bar, iron bacteria may either act as a catalyst (Hem, 1960b) in oxidation, thereby releasing iron which is subsequently precipitated, and/or accumulate $Fe(OH)_3$ on their sheaths, with subsequent formation of an iron deposit. Rankama and Sahama (1950) attributed bog iron deposits to breakdown of Fe-R through bacterial activity.

SUMMARY

Physical, chemical, and biological processes have been operative in different environments of Grizzly Bar. It is suggested that the distribution of iron in this place can be best explained by examination of these processes and environments individually.

Physical dislodgement of particulate iron from vermiculitized biotite and subsequent transport accounted for iron in Norris subglacial stream and meltwater lake. Chemical processes accounted for iron in outwash ground water. In outwash ground water, particulate iron, $\text{Fe}(\text{OH})_3$ from meltwater and iron solubilized through biological processes from minerals in the outwash was reduced and transported as Fe^{+2} . In those places where transport as Fe^{+2} in ground water resulted in contact with the upper part of the water table, oxidation occurred, with precipitation of iron as $\text{Fe}(\text{OH})_3$. Biochemical processes within intertidal mud mobilized iron from the sediment. In the bog, biochemical processes mobilized iron, and chemical processes resulted in iron precipitation and accumulation.

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