Glacial influence on the geochemistry of riverine iron fluxes to the Gulf of Alaska and effects of deglaciation

Andrew W. Schroth,[1] John Crusius,[1,2] Fanny Chever,[3] Benjamin C. Bostick,[4] and Olivier J. Rouxel[3,5,6]

[1] Riverine iron (Fe) derived from glacial weathering is a critical micronutrient source to ecosystems of the Gulf of Alaska (GoA). Here we demonstrate that the source and chemical nature of riverine Fe input to the GoA could change dramatically due to the widespread watershed deglaciation that is underway. We examine Fe size partitioning, speciation, and isotopic composition in tributaries of the Copper River which exemplify a long-term GoA watershed evolution from one strongly influenced by glacial weathering to a boreal-forested watershed. Iron fluxes from glacierized tributaries bear high suspended sediment and colloidal Fe loads of mixed valence silicate species, with low concentrations of dissolved Fe and dissolved organic carbon (DOC). Iron isotopic composition is indicative of mechanical weathering as the Fe source. Conversely, Fe fluxes from boreal-forested systems have higher dissolved Fe concentrations corresponding to higher DOC concentrations. Iron colloids and suspended sediment consist of Fe (hydr)oxides and organic complexes. These watersheds have an iron isotopic composition indicative of an internal chemical processing source. We predict that as the GoA watershed evolves due to deglaciation, so will the source, flux, and chemical nature of riverine Fe loads, which could have significant ramifications for Alaskan marine and freshwater ecosystems. **Citation:** Schroth, A. W., J. Crusius, F. Chever, B. C. Bostick, and O. J. Rouxel (2011), Glacial influence on the geochemistry of riverine iron fluxes to the Gulf of Alaska and effects of deglaciation, *Geophys. Res. Lett.*, *38*, L16605, doi:10.1029/2011GL048367.

1. Introduction

[2] In 30–50% of the ocean's euphotic zone, including much of the offshore subarctic North Pacific, iron (Fe) is thought to limit phytoplankton productivity [*Moore et al.*, 2001]. However, it has been proposed that in coastal regions where offshore Fe-limited, nitrate-rich waters mix with relatively Fe-rich coastal waters, areas of high phytoplankton productivity and rich fisheries result [*Hickey et al.*, 2010; *Ware and Thomson*, 2005]. Indeed, an observed northward increase in phytoplankton biomass along the North American Pacific Coast has been partially attributed to higher input of Fe-bearing river runoff to northern coastal waters, indicating that many of the coastal ecosystems of the North Pacific rely heavily on riverine Fe as a nutrient source [*Chase et al.*, 2007; *Hickey et al.*, 2010].

[3] Additionally, with northward progression from California to Alaska along the western margin of North America, glacial weathering increasingly influences watershed hydrology, geochemistry and particulate flux; all are critical components in determining both the amount and chemical form of iron delivered to coastal waters and ecosystems from riverine sources [*Moore et al.*, 2009; *Raiswell et al.*, 2008a; *Schroth et al.*, 2009; *Statham et al.*, 2008]. Recent work has suggested that glacial weathering is the primary source of Fe and other nutrients (P, DOM) to the highly productive coastal ecosystems of the Gulf of Alaska (GoA) [*Hood and Scott*, 2008; *Lippiatt et al.*, 2009; *Wu et al.*, 2009], however very little is known about the chemical nature of Fe in glacially-dominated river systems and its role in coastal marine ecosystem productivity. Furthermore, an understanding of Fe behavior in these river systems is likely critical to predicting the coastal ecosystem's response to deglaciation, considering the rate at which glaciers are receding in this region [*Arendt et al.*, 2002; *Berthier et al.*, 2010]. The tremendous amount of sediment-laden freshwater that is currently supplied to the GoA from glacial runoff ($410 \ km^3 \ yr^{-1}$) is forecast to increase as regional ice loss and subarctic warming continues [*Milly et al.*, 2005; *Neal et al.*, 2010]. Only a few recent studies have characterized Fe biogeochemistry in glacierized systems, focusing on large ice sheets in Greenland and Antarctica and icebergs in the Southern Ocean. In two streams draining the Greenland Ice Sheet, dissolved and colloidal Fe concentrations were relatively similar and low, averaging 22.4 and 30.8 nM respectively, with significant temporal variability in concentrations of both size fractions. Recently, Raiswell and coworkers have examined the chemical nature of particulate Fe entrained in ice sheets and icebergs, the dominant source of terrestrial Fe to the waters of the Southern Ocean [*Raiswell et al.*, 2006, 2008a, 2008b, 2009]. These studies highlight the importance of secondary Fe (III) oxidation products such as goethite, ferrihydrite, and schwertmannite as critical components of ice-entrained particulate Fe loads.

[4] While these studies have advanced our understanding of Fe chemistry in iceberg and ice sheet systems, these environments are not analogous to the extensive network of

[1]Woods Hole Coastal and Marine Science Center, U.S. Geological Survey, Woods Hole, Massachusetts, USA.

[2]Coastal and Marine Geology Program, U.S. Geological Survey, School of Oceanography, University of Washington, Seattle, Washington, USA.

[3]European Institute for Marine Studies, University of Brest, Technopôle Brest-Iroise, Plouzané, France.

[4]Lamont-Doherty Earth Observatory, Palisades, New York, USA.

[5]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA.

[6]Centre de Brest, IFREMER, Plouzané, France.
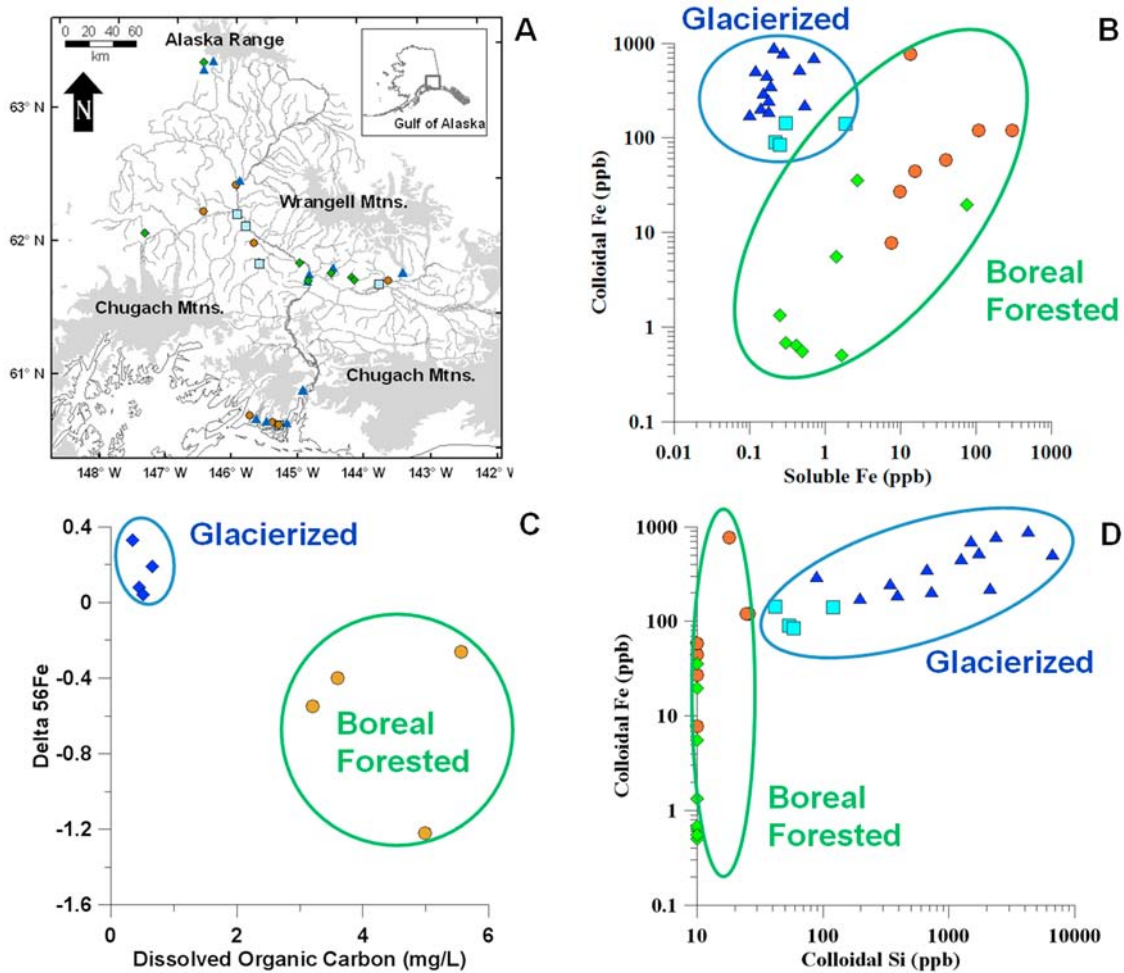
Figure 1. (a) The Copper River watershed with the location of river sample stations. Areas within the watershed that are glacierized are shaded in grey, and the main stem of the Copper River is delineated with a bold shaded line. For all figures, tributary type is delineated by symbols and color with glacial (dark blue triangles), proglacial lake fed (light blue square), boreal blackwater (brown circle) and boreal montane (green diamonds). Additional description of each sample location is given in Table S1. (b) Colloidal (0.45–0.02 μm) and soluble (<0.02 μm) iron concentrations. (c) δ^{56}Fe values and dissolved organic carbon concentrations for select glacierized and boreal forested rivers. (d) Colloidal iron and silicon concentrations. For Figures 1b and 1d, all axes are logarithmic in scale due to the dramatic differences in concentrations and size partitioning observed between the studied watershed types. Concentrations of dissolved silica in blanks were sufficiently high and noisy to produce negative values for colloidal silica in some boreal samples, so a value of 10 ppb is given for these samples for visual clarity. This value is close to the average difference in dissolved silica concentration between the full process blank and unfiltered ultrapure MilliQ water from clean lab facilities at the USGS in Woods Hole.

montane glacier systems draining into the GoA. Furthermore, links between watershed processes and Fe flux and speciation have not been established in these rapidly changing regions. Here we present Fe size partitioning, speciation and isotopic compositional data for tributaries within the Copper River watershed (Figure 1a). The tributaries sampled within the larger Copper River watershed are representative end members of landscape evolution from glacial weathering-dominated catchments to boreal-forested catchments, the distribution of which, and their relative contribution to riverine Fe fluxes to the GoA, will change due to continued warming of subarctic climate and glacial recession in the region [*Hood and Scott*, 2008; *Milner et al.*, 2007; *Stephenson et al.*, 2006]. Based on these data, we examine the relationship between chemistry and

source of Fe in riverine loads and the evolving Alaskan landscape from which they are derived.

2. Methods

[5] See auxiliary material for a full description of the methods.[1]

3. Results and Discussion

[6] Four broad classes of tributaries representative of end members of landscape evolution during continued regional

glacial recession and warming climate were identified and sampled within the Copper River Basin (August and October 2008) (Figure 1a). These tributary classes include: 1) Glacial tributaries that are milky brown in appearance, indicative of extremely high suspended sediment loads where direct glacial melt is the primary source of water. 2) Proglacial lake-fed tributaries where a significant lake has developed at the terminus of the glacier which feeds the tributary. These tributaries typically have a blue milky color with relatively high fine grained suspended sediment loads. 3) Boreal-forested montane streams that are not glacierized and have relatively clear waters and low suspended sediment loads. 4) Boreal-forested 'blackwater' tributaries draining large lowland areas in the Copper River basin and delta, visually characterized by their tea-colored appearance associated with high concentrations of organic compounds. As the Alaskan landscape evolves in response to a warming climate and continued ice loss, in the near term glacial and proglacial lake systems will continue to dominate the dissolved and particulate flux of these watersheds, perhaps with an increasing abundance of proglacial lakes during rapid recession [*Sugden et al.*, 2009]. However, on longer timescales as glaciers continue to recede, the hydrologic system could evolve into one typical of northern boreal-forested watersheds with a mosaic of periglacial streams and blackwater tributaries, their distribution dependant on local watershed characteristics [*Milner et al.*, 2007; *Moore et al.*, 2009; *Pokrovsky et al.*, 2006; *Stephenson et al.*, 2006]. It is critical to determine how riverine Fe biogeochemistry may evolve as the relative abundance and contribution of these tributary types change in the GoA watershed, particularly considering the importance of Fe cycling to the health and productivity of marine and freshwater ecosystems.

[7] The operational size fraction partitioning scheme used here was developed by *Shiller* [2003] for analysis of large-scale remote watersheds, and our rationale for using this scheme, as well as its limitations, are discussed in the auxiliary material and more thoroughly elsewhere [*Shiller*, 2003]. Upon examination of Fe size partitioning data (Figure 1b), it is clear that there are significant and systematic differences in not only the concentration of Fe in the river systems, but in the size fractionation of Fe based on tributary type. Iron in glacial and proglacial lake fed tributaries is present in high colloidal (0.45–0.02 μm) Fe concentrations, but extremely low soluble (<0.02 μm) Fe concentrations, often well below 1 part per billion (μg/kg) (Figure 1b).This indicates that glacial weathering produces an Fe flux dominated by the colloidal fraction, with circumnuetral pH (Table S1) and low DOC concentrations (Figure 1c) that keep soluble Fe at very low levels. While differences in bulk Fe concentration within watershed types can also be related to differences in geology within watersheds, the different tributary classes and even single tributaries span the multiple and varied geologic formations of the region [*Plafker et al.*, 1989], so a systematic difference in bedrock geology does not explain the distribution of data in Figure 1b. Furthermore, recent work has suggested that landscape cover and hydrology primarily determine Fe size partitioning in pristine boreal systems rather than bedrock composition [*Bjorkvald et al.*, 2008; *Vasyukova et al.*, 2010]. Our soluble Fe concentrations are comparable to, or slightly lower than, time series observations from the Greenland ice sheet, while our glacial tributary colloidal Fe

concentrations are comparable to or higher than those observed in the Greenland system [*Statham et al.*, 2008].

[8] In contrast to glacial tributaries, boreal-forested mountain stream systems within the GoA watershed have relatively low colloidal Fe loads, with soluble concentrations that are generally comparable to or slightly higher than those of glacial systems (Figure 1b). Lowland blackwater systems, however, have very high soluble and colloidal Fe concentrations, presumably associated with Fe complexation with ground/soil water-derived DOC, and perhaps oxidation of groundwater-derived Fe(II) in the stream or adjacent soils to form colloidal Fe (III) precipitates. Indeed, DOC concentrations in boreal-forested blackwater streams are higher by an order of magnitude than those of glacial systems (Figure 1c), and ochreous precipitates were often visually observed in their streambeds. Iron concentrations and size partitioning in these streams are broadly consistent and within the range found by other researchers in similar pristine boreal systems in Siberia, where similar sources of colloidal and dissolved Fe have been proposed [*Pokrovsky et al.*, 2006]. It is important to note here that much of the soluble Fe fraction is likely complexed to humic substances and present as nano-organic colloids [*Pokrovsky et al.*, 2006], however, this only further displays the fundamental and dramatic differences in Fe chemical partitioning between the studied tributary systems. A detailed study of soluble Fe complexation with DOC comparing glacierized and boreal forested systems is clearly warranted, but beyond the scope of this work.

[9] The stable isotope composition of Fe can provide valuable insights into the sources of Fe and its biogeochemical cycling in the marine and terrestrial environment [*Rouxel et al.*, 2008]. In this study, the isotopic composition of Fe (soluble and colloidal, <0.45 μm) further demonstrates a fundamental difference in Fe source between the studied types of tributaries. In glacial and proglacial lake-fed tributary systems, the Fe isotopic signature is similar to crustal values defined as 0.09‰ (+/−0.1‰) (Figure 1c) [*Dauphas and Rouxel*, 2006]. This suggests that glacially-derived Fe is not significantly fractionated by glacial weathering. As Fe isotopic variability in rivers is likely related to the weathering regime (physical and/or chemical), those results are in agreement with a mechanical weathering source of Fe where chemical fractionation does not occur [*Escoube et al.*, 2009]. In contrast, the boreal-forested systems display much lighter Fe isotopic values, which correspond to higher concentrations of DOC (Figure 1c). It has been shown that mineral dissolution in the presence of Fe chelating organic ligands releases light Fe into solution, and plant uptake may also favour light Fe isotopes that may be released to rivers during decomposition of soil organic matter [*Brantley et al.*, 2004]. In addition, Fe redox cycling in soil or groundwaters can provide a source of low δ^{56}Fe [*Rouxel et al.*, 2008]. The light values measured in boreal-forested tributaries would tend to confirm the presence of ground/soil water- derived Fe input to tributaries as well as complexation of Fe with DOC derived from organic matter decomposition. Overall, the isotopic composition of Fe in these streams further confirms a fundamental difference in Fe source between the studied types of tributaries, with systems dominated by glacial weathering processes having a mechanical weathering source of Fe where chemical fractionation does not occur, whereas Fe mobilization is driven by internal chemical processing in boreal forested

Table 1. Suspended Sediment Concentration and Speciation Data From Select Copper River Tributaries[a]

Measurement	Glacial	Proglacial Lake Fed	Boreal Montane	Blackwater
Suspended Sediment $(g*L^{-1})$	0.87	0.21	0.05	0.02
HFO+Fe(III)-H(%)	0–20	10–40	40–60	80–100
MAG (%)	0–15	0–10	0–10	0
MVS (%)	60–90	60–80	40–60	0–20
PY(%)	0–5	0	0–5	0–5
Fe(II)/(FeIII)	1.9–1.2	1.6–0.7	0.8–0.2	0.4–0

[a]Suspended sediment speciation data was determined by linear combination of known Fe standards. Iron phase spectra used for fits consist of HFO(iron (hydr)oxides- ferrihydrite spectra was used for XAS fits, but goethite and hematite may also be present due to similarities XANES spectra), Fe(III)-H (Fe(III) humic materials standard), MAG(magnetite), PY (pyrite), MVS (mixed valence silicates-biotite and hornblende were used for fits). It should be noted that here we use spectral fitting of XANES data to delineate species/mineral 'classes' rather than distinct mineral phases, which is discussed thoroughly in *Prietzal et al.* [2007]. As an example, while the fraction of MVS was determined using biotite and amphibole as the standards for fitting, this fraction could consist of other Fe(II/III) silicate phases (i.e. chlorite, smectite) due to similarity in Fe oxidation state and coordination chemistry within this mineral class, which is confirmed by XRD data (Sup. Figure 1). Example XANES spectra are shown in Auxiliary Figure 2.

watersheds which produces a relatively light Fe isotopic signature. Additionally, these data suggest that it is possible that changes in watershed land cover could be recorded by Fe isotopic records influenced by riverine Fe.

[10] Since riverine Fe loads, irrespective of tributary type, are dominated by colloidal and particulate phase Fe (Figure 1b), a detailed study of the speciation of Fe in these phases is warranted to better assess the potential bioavailability and reactivity of Fe in riverine solid phase Fe. Additionally, in many forested coastal watersheds, Fe tends to undergo significant estuarine removal due to colloidal flocculation, a process that is strongly affected by Fe speciation, colloidal composition, and DOC concentration [*Sholkovitz*, 1976]. However such removal has not been demonstrated in glacial river plumes where freshwater/saline transition zones occur over a few meters, DOC concentrations are extremely low (Figure 1c), and, as we demonstrate (Figures 1b and 1d), colloidal Fe chemistry differs dramatically from forested rivers. Typically, in boreal watersheds, Fe colloids are thought to be predominantly composed of Fe (hydr)oxides and organic complexes with negligible colloidal silica concentrations, which is supported by our boreal-forested tributary data (Figure 1d) [*Allard et al.*, 2011]. However, in the glacial and proglacial lake-fed tributaries sampled in Alaska, high colloidal Fe concentrations correspond with high colloidal silica concentrations; whereas no such trend is observed in tributaries where glacial weathering is not occurring (Figure 1d). This association in glacial tributaries suggests that glacial systems may have unique Fe-bearing silicates colloids produced by glacial weathering that are not present in typical boreal watersheds. This fundamental difference in the colloidal chemistry in glacial systems compared to forested watersheds is likely due to the unique weathering processes occurring in glaciated watersheds associated with mechanical weathering of bedrock by ice, which must generate these Fe-bearing silicate colloids.

[11] Synchrotron-based X-ray absorption near-edge spectra (XANES) analysis of coarser suspended sediment (>0.45 μm) confirms distinct glacial flour Fe speciation that was inferred for colloidal phases based on solution data. Indeed, glacial and proglacial-fed suspended sediment Fe is associated primarily with mixed valence silicate phases, and a large portion of that is in the ferrous form (Table 1). X-ray diffraction data further establishes that these silicates are present in recently deposited glacial flour with potential Fe-bearing silicates amphibole, biotite, chlorite and smectite all present

in the <1 μm fraction (Figure S1). These independent direct measurements demonstrate that Fe associated with silicate minerals dominates the solid phase flux of Fe from glacial watersheds(glacial flour), which is reflective of the primary Fe speciation in the bedrock (mixed valence silicates), even to within the colloidal size fraction (Table 1 and Figures 1d and S1). While our Fe speciation and mineralogical data differ to some extent from the Fe mineralogy identified by *Raiswell et al.* [2009] of particles entrained in ice, this is to be expected, considering the differences in environment of sampled sediments. Our samples consist of suspended, recently mechanically weathered glacial flour, while *Raiswell et al.* [2009] analyzed sediment entrained in ice for an unknown time that had significantly interacted with water and/or atmosphere, as suggested by the extensive secondary Fe (III) oxidation products observed. Furthermore, our data are consistent with the observation of *Raiswell et al.* [2009] that Fe in suspended glacial stream sediments (glacial flour) corresponded to 'unidentified Fe-bearing nanoparticulates rich in Ti and Si', which is in fact characteristic of elemental associations in mixed valence Fe silicate minerals such as biotite, chlorite, and hornblende. By coupling these solution and mineralogical/ speciation measurements to describe Fe partitioning in these glacial streams, we can unequivocally demonstrate that Fe-bearing silicates are an integral component of the glacial riverine Fe loads, and represent the primary colloidal and suspended sediment species of the micronutrient Fe delivered to Alaskan coastal waters by glacial meltwater.

[12] The speciation of Fe in suspended sediment of boreal montane and blackwater streams is fundamentally different from that in glacial systems. Boreal-forested streams have a higher fraction of Fe (hydr)oxides and percent ferric iron (Table 1 and Figure S1) than do glacial tributaries, but also contain some Fe associated with primary silicates, perhaps sourced in resuspended streambed sediments or other agents of mechanical weathering within the watershed. Blackwater suspended sediments consist of primarily Fe(hydr)oxides and Fe(III) organics, which would be predicted to form by the oxidation of high concentrations of ferrous iron during redox processing within these tributary systems and iron complexation with humic acids associated with organic matter decomposition in soils and sediments respectively (Table 1). It should be noted here that there has been some difficulty separating Fe(hydr)oxides from Fe(III) organic complexes by XANES [*Prietzel et al.*, 2007]. As such, these phases are grouped together in Table 1. However, in such

systems both forms of Fe are typically observed and often associated when organics are adsorbed to the surface of suspended Fe (hydr)oxides [*Allard et al.*, 2011]. Furthermore, these secondary phases are consistent with the Fe isotopic data, suggesting internal chemical processing as the dominant source of Fe, and fundamentally different from Fe species dominating glacierized catchment Fe fluxes.

[13] The results described here have significant ramifications for the GoA in the context of environmental change considering the importance of glacially-derived Fe to these coastal ecosystems. Our research suggests that as the Alaskan landscape evolves during glacial recession and mass loss, so will the source, speciation, and partitioning of riverine iron delivered to coastal waters. As glacial weathering continues and potentially increases as glaciers continue to lose ice mass and recede within the watershed, local riverine iron loads will continue to be characterized by high suspended sediment and colloidal Fe loads dominated by mixed valence primary silicate mineral species. As such, determining the bioavailability of Fe in these particulate and colloidal phase Fe species is critical to predicting the ecosystem response to watershed deglaciation. However, on longer timescales, assuming the GoA watershed eventually evolves under continued subarctic warming to a boreal forest-dominated catchment, there will be a fundamental shift in the chemistry and partitioning of riverine Fe. Increasingly, Fe colloids and particles delivered to the GoA will be oxidation products, primarily Fe (hydr)oxides, formed by redox processes in soil or groundwater systems. Additionally, as the contribution to the riverine flux of Fe from boreal-forested watersheds increases, a higher percentage of riverine Fe will be associated with smaller size fractions and complexed to humic substances. Considering that the suspended sediment concentration in glacierized tributaries is at least an order of magnitude higher than in forested catchments (Table 1), and the colloidal and particulate Fe species are chemically distinct, it is worth speculating on impacts to the riverine flux of Fe to the coastal GoA as the watershed becomes increasingly forested. Our study suggests that this long-term shift from primarily glacierized to boreal-forested catchments could result in a decrease in riverine total Fe and mixed valence silicate Fe species delivered to subarctic coastal waters due to this fundamental change in the source and speciation of riverine Fe loads. Furthermore, since glacierized riverine particulate Fe is ultimately the primary source of offshore bioavailable Fe derived from resuspended continental shelf sediments [*Lam and Bishop*, 2008], eddies [*Lippiatt et al.*, 2009], and glacial flour dust storms [*Crusius et al.*, 2011], such a change in riverine Fe sources could also affect the bioavailable Fe supply to Fe-limited waters of the GoA. These changes would likely have significant but poorly understood consequences for those marine ecosystems.

References

Allard, T., et al. (2011), Tracing source and evolution of suspended particles in the Rio Negro Basin (Brazil) using chemical species of iron, *Chem. Geol.*, *280*(1–2), 79–88, doi:10.1016/j.chemgeo.2010.10.018.

Arendt, A. A., et al. (2002), Rapid wastage of Alaska glaciers and their contribution to rising sea level, *Science*, *297*(5580), 382–386, doi:10.1126/science.1072497.

Berthier, E., et al. (2010), Contribution of Alaskan glaciers to sea-level rise derived from satellite imagery, *Nat. Geosci.*, *3*(2), 92–95, doi:10.1038/ngeo737.

Bjorkvald, L., et al. (2008), Hydrogeochemistry of Fe and Mn in small boreal streams: The role of seasonality, landscape type and scale, *Geochim. Cosmochim. Acta*, *72*(12), 2789–2804, doi:10.1016/j.gca.2008.03.024.

Brantley, S. L., et al. (2004), Fe isotopic fractionation during mineral dissolution with and without bacteria, *Geochim. Cosmochim. Acta*, *68*(15), 3189–3204, doi:10.1016/j.gca.2004.01.023.

Chase, Z., P. G. Strutton, and B. Hales (2007), Iron links river runoff and shelf width to phytoplankton biomass along the U.S. West Coast, *Geophys. Res. Lett.*, *34*, L04607, doi:10.1029/2006GL028069.

Crusius, J., et al. (2011), Glacial flour dust storms in the Gulf of Alaska: Hydrologic and meteorological controls and their importance as a source of bioavailable iron, *Geophys. Res. Lett.*, *38*, L06602, doi:10.1029/2010GL046573.

Dauphas, N., and O. Rouxel (2006), Mass spectrometry and natural variations of iron isotopes, *Mass Spectrom. Rev.*, *25*(5), 831–832, doi:10.1002/mas.20101.

Escoube, R., O. J. Rouxel, E. Sholkovitz, and O. F. X. Donard (2009), Iron isotope systematics in estuaries: The case of the North River, Massachusetts, *Geochim. Cosmochim. Acta*, *73*(14), 4045–4059, doi:10.1016/j.gca.2009.04.026.

Hickey, B. M., et al. (2010), River Influences on Shelf Ecosystems: Introduction and synthesis, *J. Geophys. Res.*, *115*, C00B17, doi:10.1029/2009JC005452.

Hood, E., and D. Scott (2008), Riverine organic matter and nutrients in southeast Alaska affected by glacial coverage, *Nat. Geosci.*, *1*(9), 583–587, doi:10.1038/ngeo280.

Lam, P. J., and J. K. B. Bishop (2008), The continental margin is a key source of iron to the HNLC North Pacific Ocean, *Geophys. Res. Lett.*, *35*, L07608, doi:10.1029/2008GL033294.

Lippiatt, S. M., et al. (2009), Reactive iron in the northern Gulf of Alaska, *Geochim. Cosmochim. Acta*, *73*(13), A771.

Milly, P. C. D., et al. (2005), Global pattern of trends in streamflow and water availability in a changing climate, *Nature*, *438*(7066), 347–350, doi:10.1038/nature04312.

Milner, A. M., et al. (2007), Interactions and linkages among ecosystems during landscape evolution, *BioScience*, *57*(3), 237–247, doi:10.1641/B570307.

Moore, J. K., et al. (2001), Iron cycling and nutrient-limitation patterns in surface waters of the world ocean, *Deep Sea Res., Part II*, *49*(1–3), 463–507, doi:10.1016/S0967-0645(01)00109-6.

Moore, R. D., et al. (2009), Glacier change in western North America: Influences on hydrology, geomorphic hazards and water quality, *Hydrol. Processes*, *23*(1), 42–61, doi:10.1002/hyp.7162.

Neal, E. G., E. Hood, and K. Smikrud (2010), Contribution of glacier runoff to freshwater discharge into the Gulf of Alaska, *Geophys. Res. Lett.*, *37*, L06404, doi:10.1029/2010GL042385.

Plafker, G., W. J. Nokleberg, and J. S. Lull (1989), Bedrock geology and tectonic evolution of the Wrangellia, Peninsular, and Chugach terranes along the Trans-Alaska Crustal Transect in the Chugach Mountains and southern Copper River Basin, Alaska, *J. Geophys. Res.*, *94*(B4), 4255–4295, doi:10.1029/JB094iB04p04255.

Pokrovsky, O. S., et al. (2006), Trace element fractionation and transport in boreal rivers and soil porewaters of permafrost-dominated basaltic terrain in central Siberia, *Geochim. Cosmochim. Acta*, *70*(13), 3239–3260, doi:10.1016/j.gca.2006.04.008.

Prietzel, J., et al. (2007), Iron speciation in soils and soil aggregates by synchrotron-based X-ray microspectroscopy (XANES, mu-XANES), *Eur. J. Soil Sci.*, *58*(5), 1027–1041, doi:10.1111/j.1365-2389.2006.00882.x.

Raiswell, R., et al. (2006), Contributions from glacially derived sediment to the global iron (oxyhydr)oxide cycle: Implications for iron delivery to the oceans, *Geochim. Cosmochim. Acta*, *70*(11), 2765–2780, doi:10.1016/j.gca.2005.12.027.

Raiswell, R., et al. (2008a), Nanoparticulate bioavailable iron minerals in icebergs and glaciers, *Mineral. Mag.*, *72*(1), 345–348, doi:10.1180/minmag.2008.072.1.345.

Raiswell, R., et al. (2008b), Bioavailable iron in the Southern Ocean: The significance of the iceberg conveyor belt, *Geochem. Trans.*, *9*, 7, doi:10.1186/1467-4866-9-7.

Raiswell, R., et al. (2009), Schwertmannite in wet, acid, and oxic micro-environments beneath polar and polythermal glaciers, *Geology*, *37*(5), 431–434, doi:10.1130/G25350A.1.

Rouxel, O., et al. (2008), Iron isotope fractionation in subterranean estuaries, *Geochim. Cosmochim. Acta*, *72*(14), 3413–3430, doi:10.1016/j.gca.2008.05.001.

Schroth, A. W., et al. (2009), Iron solubility driven by speciation in dust sources to the ocean, *Nat. Geosci.*, *2*(5), 337–340, doi:10.1038/ngeo501.

Shiller, A. M. (2003), Syringe filtration methods for examining dissolved and colloidal trace element distributions in remote field locations, *Environ. Sci. Technol.*, *37*(17), 3953–3957, doi:10.1021/es0341182.

Sholkovitz, E. R. (1976), Flocculation of dissolved organic and inorganic matter during mixing of river water and seawater, *Geochim. Cosmochim. Acta*, *40*(7), 831–845, doi:10.1016/0016-7037(76)90035-1.

Statham, P. J., M. Skidmore, and M. Tranter (2008), Inputs of glacially derived dissolved and colloidal iron to the coastal ocean and implications for primary productivity, *Global Biogeochem. Cycles*, *22*, GB3013, doi:10.1029/2007GB003106.

Stephenson, T. R., et al. (2006), Spatio-temporal constraints on moose habitat and carrying capacity in coastal Alaska: Vegetation succession and climate, *Rangeland Ecol. Manage.*, *59*(4), 359–372, doi:10.2111/04-063.1.

Sugden, D. E., et al. (2009), Influence of Patagonian glaciers on Antarctic dust deposition during the last glacial period, *Nat. Geosci.*, *2*(4), 281–285, doi:10.1038/ngeo474.

Vasyukova, E. V., et al. (2010), Trace elements in organic- and iron-rich surficial fluids of the boreal zone: Assessing colloidal forms via dialysis and ultrafiltration, *Geochim. Cosmochim. Acta*, *74*(2), 449–468, doi:10.1016/j.gca.2009.10.026.

Ware, D. M., and R. E. Thomson (2005), Bottom-up ecosystem trophic dynamics determine fish production in the northeast Pacific, *Science*, *308*(5726), 1280–1284, doi:10.1126/science.1109049.

Wu, J., A. Aguilar-Islas, R. Rember, T. Weingartner, S. Danielson, and T. Whitledge (2009), Size-fractionated iron distribution on the northern Gulf of Alaska, *Geophys. Res. Lett.*, *36*, L11606, doi:10.1029/2009GL038304.

B. C. Bostick, Lamont Doherty-Earth Observatory, 61 Rte. 9W, Palisades, NY 10964, USA.

F. Chever, European Institute for Marine Studies, University of Brest, Technopôle Brest-Iroise, Place Nicolas Copernic, F-29280 Plouzané CEDEX, France.

J. Crusius and A. W. Schroth, Woods Hole Coastal and Marine Science Center, U.S. Geological Survey, 384 Woods Hole Rd., Woods Hole, MA 02543, USA. (aschroth@usgs.gov)

O. J. Rouxel, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, MS 25, Woods Hole, MA 02543, USA.