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Andrew W. Schroth,¹ John Crusius,¹,2 Fanny Chever,³ Benjamin C. Bostick,⁴ and Olivier J. Rouxel⁵,6

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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., John 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

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].

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 km³ 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, ferrhydrite, and schwertmannite as critical components of ice-entrained particulate Fe loads.

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...
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

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

3. Results and Discussion

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

1Auxiliary materials are available in the HTML. doi:10.1029/2011GL048367.
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 glaciarized 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 dependent on local watershed characteristics [Miller 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 Glacial watershed, particularly considering the importance of Fe cycling to the health and productivity of marine and freshwater ecosystems.

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 circumneutral 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 [Bjorkvall 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].

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/solid 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 glacialized and boreal forested systems is clearly warranted, but beyond the scope of this work.

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 [Rouel 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 Rouel, 2006]. This suggests that geologically-derived Fe is not significantly fractionated by glacial weathering. As Fe isotope 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 δ56Fe [Rouel et al., 2008]. The light values measured in boreal-forested tributaries would tend to confirm the presence of ground/solid water-derived Fe input to tributaries as well as complexation of Fe with DOC derived from organic matter. 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...
rather than distinct mineral phases, which is discussed further. 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.

Tabular data:

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Glacial</th>
<th>Proglacial Lake Fed</th>
<th>Boreal Montane</th>
<th>Blackwater</th>
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<td>HFO-Fe(III)-H(%)</td>
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<td>0</td>
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<td>60-80</td>
<td>40-60</td>
<td>0-20</td>
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<tr>
<td>PY(%)</td>
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<td>1.6-0.7</td>
<td>0.8-0.2</td>
<td>0.4-0</td>
</tr>
</tbody>
</table>

*Note: Suspected sediment speciation data was determined by linear combination of known Fe standards. Iron phase spectra used for fits consist of HFO iron (hydr)oxides- ferrhydrite spectra was used for XAS fits, and goethite and hematite may also be present due to similarities XANES spectra, Fe(II)-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 Prietz 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.

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

- Suspended sediment concentrations and speciation data from select Copper River tributaries were measured. The data includes iron content and speciation across different tributary types, such as proglacial, boreal, and blackwater. The data shows variations in iron concentration and speciation, which are critical for understanding the fate and transport of iron in these systems. This information is essential for assessing the potential bioavailability of iron and its role in aquatic ecosystems.
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 glacialized 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 complexes to humic substances. Considering that the suspended sediment concentration in glacialized 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 glacialized 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 glacialized 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.

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References


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.


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