Auxiliary Material

Methods

In August of 2008 and October of 2009, water samples were collected from the main stem and tributaries within the Copper River watershed, the largest point source of freshwater to the GoA (Figure 1, watershed described in detail by *Anders et al.* [2003]). Samples for trace metal analyses were collected following the ultra clean method of *Shiller* [2003] where Fe partitioning in river water is determined as soluble (<0.02µm) and colloidal (<0.45-0.02µm) size fractions using trace metal clean syringe filtration of small volume samples(~15 mL). Colloidal Fe and Si data presented in this manuscript are calculated based on the difference between the concentration of each analyte in a filtrate that has been filtered through a 0.45 µm filter and one that has been filtered through stacked 0.45 and 0.02 µm filters [*Shiller, 2003*]. Although more detailed filtration schemes exist (i.e. ultra filtration [*Pokrovsky et al.*, 2006]) and although this method, like others, is constrained by its operational definition of elemental pools , *Shiller's* [2003] method is ideal for our study because it is designed for 'clean' sampling in remote regions, and is also consistent with the common size fractionation schemes used in the marine literature studying Fe as a nutrient [*Bergquist et al.*, 2007; *Wu et al.*, 2009]. Field blanks were collected daily using the same filtration and acidification procedure with ultra pure MilliQ water transported in zip lock bags from our class 10,000 clean lab at the USGS in Woods Hole. Field blanks were always less than 30% of our lowest measured soluble Fe concentrations, but more importantly, less than 1% of the differences in concentrations discussed here based on 'river type', evident by the use of logarithmic scale for both axes in Figure 1B,D. Samples were acidified to pH ~2 with ultrapure Optima HNO_3. Concentrations were measured on a Thermo Element II ICP-MS at the Woods Hole Plasma Facility using Sc and In as internal standards.

NRCC reference material SLRS-4 was used to confirm method accuracy (always within 10%) in the range of concentrations measured. Dissolved organic carbon (DOC) was measured by the USGS National Water Quality laboratory on a limited subset of samples by uv-promoted persulfate reduction and infared spectrometry [*Brenton and Arnet, 1993*].

The iron isotope measurement procedure is as follows. A volume of ~5mL of riverine water was evaporated to dryness in Teflon vials with 1 mL of concentrated distilled HNO_3 to release the iron from organic complexes. The acid solution was taken to dryness at 80 °C on a hot plate. A subsequent evaporation was done with 5 mL of distilled 7N HNO_3 with 0.5 mL of H_2O_2 (ultrapure grade). The solid residues were dissolved with 1 mL of distilled 6N HCl and one drop of H_2O_2 to ensure the complete oxidation of Fe. This solution was loaded onto a chromatography column filled with 0.6 mL (wet volume) of anion-exchange resin (AG1-X8, Bio-rad) previously cleaned with 10 mL of 4N HNO_3 and 10 mL of 18 Mohm.cm H_2O. Prior to sample loading, the resin was conditioned with 2.8 mL of distilled 6N HCl and 2.8 mL of distilled 2% HCl followed by 1.4 mL of distilled 6N HCl. After loading the sample, 4.2 mL of distilled 6N HCl was passed through the resin to elute the matrix. Iron was then eluted with 4.2 mL of distilled 0.24N HCl and collected in 7 mL Teflon vials. Samples were evaporated to dryness on a hot plate at 80 °C and dissolved with 3 mL of distilled 0.24N HNO_3 to prepare for isotope analysis. Fe-isotope compositions were determined with a Thermo-Neptune multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) at IFREMER (operated at the Pole Spectrometrie, Brest, France) [*Dauphas and Rouxel*, 2006]. All analyses are reported in delta notation relative to the IRMM-014 standard, expressed as $\delta^{56}Fe$, which represents the deviation in per mil relative to the reference material:

$$\partial^{56}Fe = \left(\frac{(^{56}Fe/^{54}Fe)_{sample}}{(^{56}Fe/^{54}Fe)_{IRMM-014}} - 1 \right) x1000$$

We also measured δ^{57}Fe values but, since the relationships between $\delta\,^{56}$Fe and $\delta\,^{57}$Fe of the samples plot on a single mass fractionation line, only $\delta\,^{56}$Fe values are discussed in this paper.

Suspended sediment samples were collected from each sampling station (Table S1 and Figure S1) by saturating an acid-cleaned, 0.45 µm pore size, 47 mm diameter, polyethersulfone membrane filter (GE Osmonics) in the field using a peristaltic pump. Sediment-bearing filters were dried in a laminar flow hood and refrigerated until analysis. Solid-phase Fe speciation (oxidation state and bonding environment) was measured by synchrotron–based X-ray absorption spectroscopy (XAS) utilizing pre-edge (oxidation state) and near edge (speciation), features of the spectra for analysis, which is thoroughly outlined elsewhere [*O'Day et al.*, 2004; *Prietzel et al.*, 2007; *Wilke et al.*, 2001]. Data were fit by linear combination of standard reference materials using SIXPAK. Data were collected on beamline 11-2 at Stanford Synchrotron Radiation Lightsource. X-ray diffraction was used to identify the minerals present in the <1 µm fraction (briefly agitated and then separated by centrifugation) from a bulk Copper River sediment sample collected from the Copper River Delta sampling station (closest to the Gulf of Alaska) using facilities in D. Eberl's laboratory at the USGS in Boulder. While it would be ideal to collect and analyze the colloidal fraction by XANES and XRD, this is beyond our current field or laboratory capabilities and an active area of research that we hope will provide valuable information regarding the composition and structure of glacial silicate colloids in the future.

Figure S1. XRD data from <1 micron fraction of Copper River riverbed sediment that identify chlorite(C), smectite(S), amphibole(H) and biotite (B) as likely Fe-bearing mixed valence silicate mineral phases present in this size fraction. The sample from this site was characterized by the following concentrations: colloidal Fe = 800 ppb; soluble Fe = 0.28 ppb; colloidal Si = 1500 ppb; DOC = 0.45 ppm; and δ^{56}Fe = 0.08.

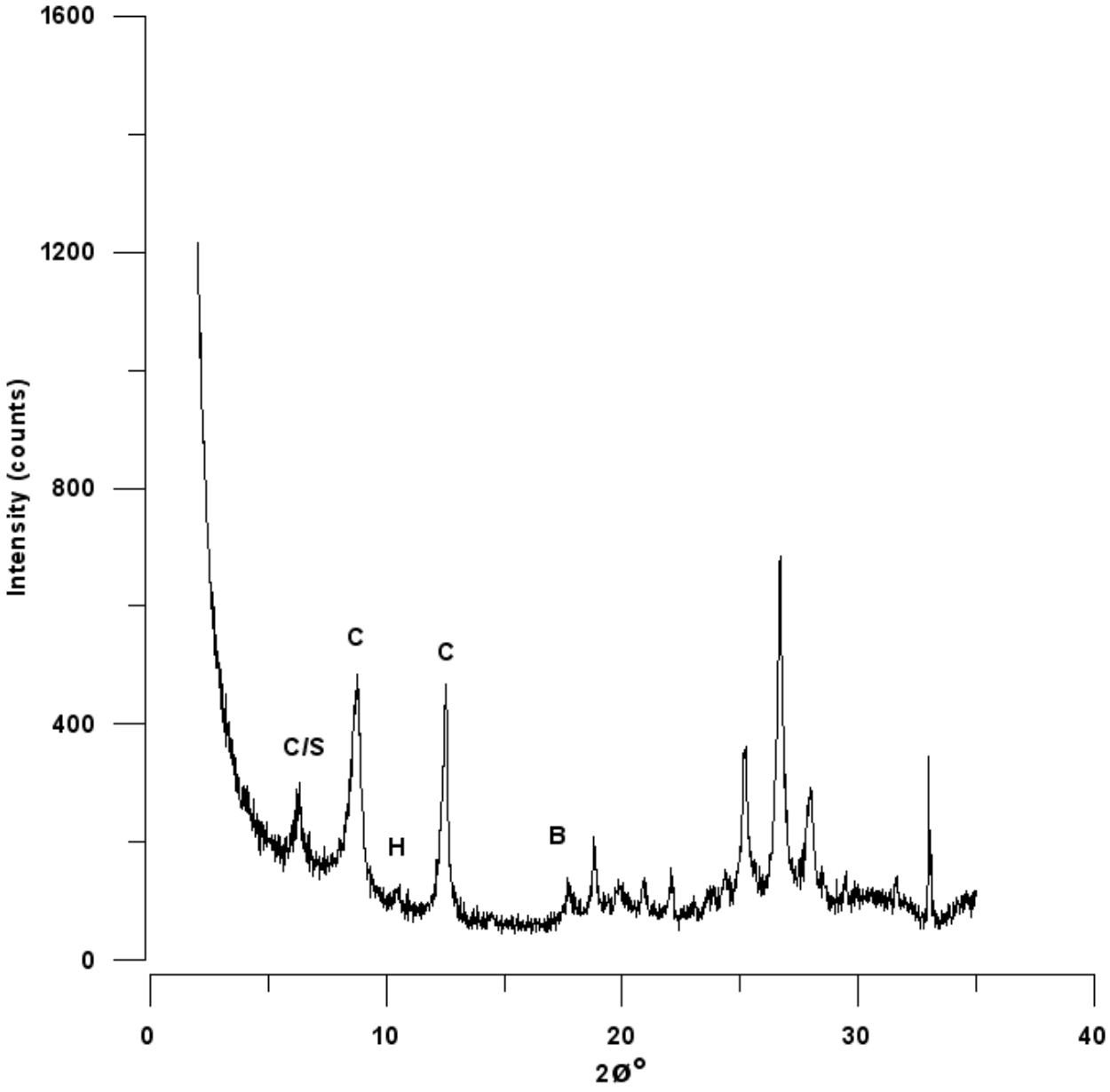

Figure S2. Example XANES spectra of glacial and boreal forested river suspended sediment illustrating the stark differences in Fe oxidation state and speciation between suspended sediments of these river 'types'. Data was collected from beamline 11-2 at the Stanford Synchrotron Radiation Lightsource.

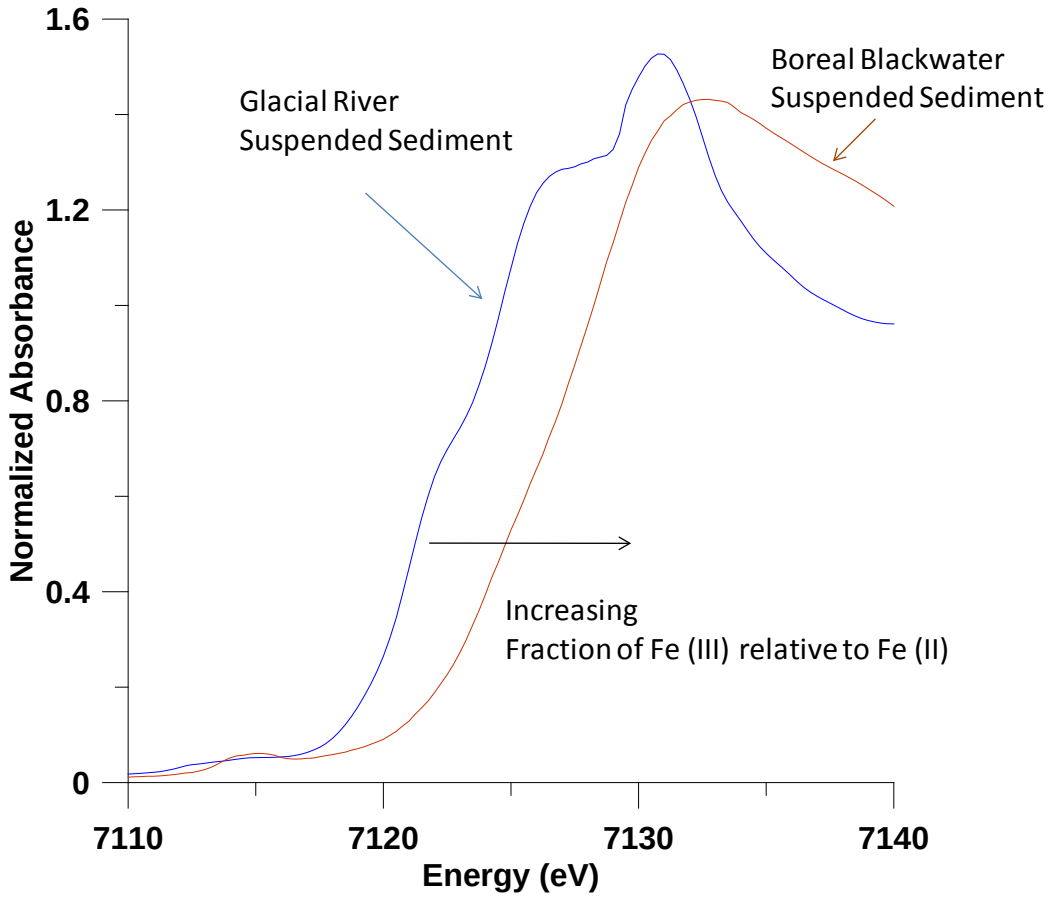

Table S1. Locations, tributary classification and field measured pH data for all tributary and main stem Copper River sampling sites used for this study.

Site Name	LAT	LON	Tributary Type	pH
Willow Creek	61.817	145.216	Boreal Lowlands	7.3
Squirrel Creek	61.667	145.175	Boreal Lowlands	7.6
Gulkana River	62.270	145.385	Boreal Lowlands	7.7
Tolsona Creek	62.101	145.969	Boreal Lowlands	7.6
Eyak River	60.529	145.64	Boreal Lowlands	7.3
Airport Creek	60.461	145.293	Boreal Lowlands	7.3
Swampy Creek	60.435	145.214	Boreal Lowlands	7.4
McCarthy R	61.431	142.926	Glacially Fed	8.0
Copper River (Above Chitina River)	61.529	144.408	Glacially Fed	7.9
Kotsina	61.581	144.408	Glacially Fed	7.7
Copper River Below Chitina	61.482	144.452	Glacially Fed	7.8
Kuskulana R	61.556	144.022	Glacially Fed	8.0
College Creek	63.227	145.485	Glacially Fed	7.9
McCallum Cr	63.223	145.653	Glacially Fed	7.6
Kennicott R	61.434	142.943	Glacially Fed	8.6
Copper River(Delta)	60.445	145.080	Glacially Fed	7.9
Ibeck Cr	60.508	145.541	Glacially Fed	7.5
CR above Childs glacier	60.673	144.755	Glacially Fed	8.1
Gakona River	62.302	145.302	Glacially Fed	8.1
Sheridan River	60.474	145.385	Glacially Fed	8.0
Little Nelchina Creek	61.990	146.944	Montane Boreal Forest	7.8
Liberty Creek	61.623	144.547	Montane Boreal Forest	7.6
Obrian Creek	61.482	144.455	Montane Boreal Forest	7.8
Gunn Creek	63.170	145.653	Montane Boreal Forest	7.6
Strelna Creek	61.510	144.068	Montane Boreal Forest	8.1
Chokosna River	61.455	143.764	Montane Boreal Forest	7.9
Gilahina River	61.438	143.719	Montane Boreal Forest	8.0
Tractor Creek	61.388	143.197	Montane Boreal Forest	6.9
Tazlina R.	62.054	145.426	Proglacial Lake Fed	7.4
Klutina R	61.954	145.322	Proglacial Lake Fed	7.4
Tonsina River	61.663	145.183	Proglacial Lake Fed	7.4

Auxiliary Material References

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