C. R. Geoscience 347 (2015) 377–385

Contents lists available at ScienceDirect

Comptes Rendus Geoscience

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Hydrology, Environment (Surface Geochemistry)

Iron isotope systematics in Arctic rivers

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ARTICLE INFO

Article history:
Received 8 February 2015
Accepted after revision 23 April 2015
Available online 2 July 2015

Keywords:
Iron isotope
Colloids
River
Weathering
Arctic
Iron speciation

ABSTRACT

The input of iron to the Arctic Ocean plays a critical role in the productivity of aquatic ecosystems and is potentially impacted by climate change. We examine Fe isotope systematics of dissolved and colloidal Fe from several Arctic and sub-Arctic rivers in northern Eurasia and Alaska. We demonstrate that the Fe isotopic (δ^{56}Fe) composition of large rivers, such as the Ob' and Lena, has a restricted range of δ^{56}Fe values ca.–0.11 ± 0.13‰, with minimal seasonal variability, in stark contrast to smaller organic-rich rivers with an overall δ^{56}Fe range from–1.7 to + 1.6‰. The preferential enrichment with heavy Fe isotopes observed in low molecular weight colloidal fraction and during the high-flow period is consistent with the role of organic complexation of Fe. The light Fe isotope signatures of smaller rivers and meltwater reflect active redox cycling. Data synthesis reveals that small organic-rich rivers and meltwater in Arctic environments may contribute disproportionately to the input of labile Fe in the Arctic Ocean, while bearing contrasting Fe isotope compositions compared to larger rivers.

1. Introduction

The boreal zone of the Russian Arctic and glaciered systems of Greenland and Alaska are systems that are currently experiencing rapid environmental change associated with climate change. The observed warming in the Arctic is much greater than the global average (IPCC, 2007) and on-going permafrost thaw is considered to induce large perturbations on the global water discharge and organic carbon inventory in Arctic rivers (Dittmar and Kattner, 2003; Holmes et al., 2012) as well as the flux and speciation of trace elements input into the Arctic Ocean (Pokrovsky and Schott, 2002; Pokrovsky et al., 2010, 2012). The Arctic Ocean receives about 10% of the global river discharge, yet it has the highest input of continental freshwater per basin surface area compared to all other oceans in the world. In addition, the three largest Arctic rivers, the Yenisey, Lena, and Ob', are each comparable in watershed area and annual discharge to the Mississippi River (Holmes et al., 2012).

Riverine iron (Fe) plays a critical role in regulating the concentration and bioavailability for a variety of chemical

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http://dx.doi.org/10.1016/j.crte.2015.04.005
1631-0713/

elements in aquatic ecosystems, including nutrients and pollutants. In general, the behavior of Fe and its partitioning between dissolved, colloidal, and suspended sediment loads is controlled by local hydrogeochemical and biogeochemical environments that are themselves likely to be affected by climate change (Allard et al., 2004; Schroth et al., 2009). Likewise, glacial weathering has been recently recognized as a primary source of Fe and other nutrients (phosphate, dissolved organic matter) to the highly productive coastal ecosystems of the Gulf of Alaska (Crusius et al., 2011; Schroth et al., 2011; Hood and Scott, 2008; Schroth et al., 2014) and enhanced iron input has been observed during high run-off periods of snowmelt in spring and glacial melt in the summer. Understanding the mechanisms and external forcing of Fe delivery into the Arctic Ocean therefore requires:

- time-series-based analyses of Arctic and sub-Arctic river biogeochemistry to assess climatic and seasonnally-driven variations;
- assessment of the speciation and mobility of Fe in high-latitude watershed;
- determination of the potential impact of glacier or permafrost thaw on the speciation, timing and provenance of Fe input to the high-lattitude oceans.

A growing number of studies have reported Fe isotope compositions of bulk rivers, as well as particulate, dissolved and colloids Fe pools in rivers (Bergquist and Boyle, 2006; Chen et al., 2014; Escoube et al., 2009; Fantle and DePaolo, 2004; Ilina et al., 2013; Ingri et al., 2006; Pinheiro et al., 2013, 2014; Poitrasson et al., 2014; Schroth et al., 2011). The results showed significant variability in Fe isotopes, which has been attributed to a range of processes and parameters, including hydrology, climate, and anthropogenic influences, as well as bedrock geology, topography, and soil–plant interactions. To date, only two studies have reported the isotope composition of dissolved Fe in Arctic/sub-Arctic environments (i.e. referred to as $\delta^{56}Fe_{DFe}$, with DFe for dissolved Fe < 0.45 or < 0.22 μm) that yielded one of the largest range observed in river systems, between–1.2 and 1.8 ‰ (Ilina et al., 2013; Schroth et al., 2011). The lightest $\delta^{56}Fe_{DFe}$ values were reported for organic-rich rivers and stream-draining areas, with the largest vegetal cover in Alaska (Schroth et al., 2011), while the heaviest values were measured in colloidal and dissolved fractions of boreal and temperate organic-rich rivers in Karelia (Ilina et al., 2013).

Here, we investigate Fe isotope systematics in northern European and Siberian rivers (Fig. 1), including:

- a time-series of $\delta^{56}Fe_{DFe}$ of two of the largest rivers draining Arctic watersheds (the Ob' and Lena) focusing on the peak flow that provides a first-order assessment of the annual Fe budgets;
- $\delta^{56}Fe$ values of colloidal and suspended pools (ranging from 1 kDa to 1.2 μm) of smaller northern European rivers, including the Severnaya Dvina River to assess the influence of Fe-rich colloids on the Fe isotopic composition of freshwater sources in the Arctic.

We further compare the results with our previously reported Fe isotope composition of Alaskan rivers (Schroth et al., 2011) to determine how Fe isotope signatures may vary among high-latitude watersheds. Without such characterization of the present state of the system, future changes in the response of these river systems to global change cannot be properly evaluated.

2. Materials

Field sampling of the Ob' and Lena have been performed by the Arctic Great Rivers Observatory during the 2007 base-flow-to-high-flow transition, as reported by Holmes et al. (2012). The sampling sites were located the nearest to the river mouths at Salekhard for Ob' and Zhigansk for Lena. With a discharge of 427 km^3/year and 588 km^3/year, respectively, the Ob' and Lena represent 18 and 25% of riverine freshwater inputs to the Arctic Ocean (Holmes et al., 2012).

Rivers draining into the White Sea (between latitudes 67°N and 63°N and longitudes 30°E and 36°E) were sampled in the boreal and sub-Arctic region of European Russia. This region typically experiences a very large range of temperature varying from −50 °C to 30 °C between winter and summer. The mean annual river discharge in the White Sea is 231 km^3/yr, out of which 47% correspond to the Severnaya Dvina watershed (Pokrovsky et al., 2010). The sampled sites are on an unpopulated area and represent a diverse collection of geochemical environments with bedrock lithologies ranging from granites, basalts, ultramafic rocks, and carbonate-rich sediments (*Table S1, Supplementary material*) and hydrological settings (soil depression, river, bog and meltwater). Based on the geographic location, we divided the studied area into three zones:

- Yukova watershed, including the Yukova, Ladreka and Ruiga Rivers and stagnant waters;
- Peschanaya River and pit water;
- the Severnaya Dvina, including its tributaries Pinega River and Sotkas River as well as local bog water.

Samples from the Yukova (zone 1) were collected from small streams or rivers and stagnant water (e.g., ice, pit water; Vasyukova et al., 2010). The Peschanaya (zone 2) is a pristine river draining to the Kuloy estuary of the White Sea. Water samples were collected during August 2006 and were affected by the input of peat bogs and swamps. The Severnaya Dvina (zone 3) was sampled in 2007 during three contrasted hydrological regimes: at the end of February, representing the base-flow winter conditions; in the beginning of May, when most of the thawing occurred; and the middle of June, at the beginning of summer base-flow conditions (Pokrovsky et al., 2010). In general, the spring flood (snow melt) lasts from 30 to 50 days and contributes about 60% of the annual water flux.

Additional river, stream and meltwater samples from Alaska were analysed as part of the sample set previously reported by Schroth et al. (2011) (*Table S2, Supplementary material*). Four broad classes of tributaries representative of main landscape of the Copper River watershed were sampled in August and October 2008, and include:

glacial tributaries that are milky brown in appearance, indicative of extremely high suspended sediment loads corresponding to the contribution of glacial meltwater;