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Geochimica et Cosmochimica Acta 239 (2018) 49–60

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Iron isotope pathways in the boreal landscape: Role of the riparian zone

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Received 20 November 2017; accepted in revised form 23 July 2018; Available online 4 August 2018

Abstract

Stable Fe isotope compositions have been measured in water samples of the subarctic Kalix River, a first-order stream, and soil water samples from a riparian soil profile adjacent to the first-order stream (Northern Sweden). In the first-order stream, dominated by forest, both the particulate (>0.22 μm) and dissolved (<0.22 μm) phase showed negative $\delta^{56}Fe$ values (relative to IRMM-014) during base flow and meltwater discharge in May (−0.97 to −0.09‰). The Fe isotope composition in the water from the riparian soil profile varied between −0.20 and +0.91‰ with sharp gradients near the groundwater table. A linear correlation between the $\delta^{56}Fe$ values and the TOC/Fe_{bulk} ratio was measured during snowmelt in the unfiltered river waters ($\delta^{56}Fe$ from −0.02 to +0.54‰), suggesting mixing of two Fe components. Two groups of Fe aggregates, with different Fe isotope compositions, are formed in the boreal landscape. We propose that carbon-rich aggregates, Fe(II)(III)-OC, have negative $\delta^{56}Fe$ values and Fe-oxyhydroxides have positive $\delta^{56}Fe$ values. A mixture of these two components can explain temporal variations of the Fe isotope composition in the Kalix River. This study suggests that stable Fe isotopes can be used as a tool to track and characterize suspended Fe-organic carbon aggregates during transport from the soil, via first-order streams and rivers, to coastal sediment. Furthermore, the differences in Fe isotope values in the Kalix River and the first-order stream during base flow conditions suggest that the primary Fe sources for river water change throughout the year. This model is combining the Fe isotope composition of first-order streams and rivers to weathering and transport processes in the riparian soil.

Keywords: Fe aggregates; Fe isotope; soilwater; Krycklan Catchment; first-order stream; snowmelt; spring flood

1. INTRODUCTION

Iron species in stream and river waters persist mainly as particles and colloids in the micrometer to sub-micrometer size range. Iron-organic carbon (Fe-OC) aggregates are an important carrier phase for metal transport in the boreal landscape (Hamon et al., 2005; Neubauer et al., 2013). Iron-rich aggregates show strong association with OC, and co-precipitation between Fe and OC plays a crucial role in controlling the structure, reactivity, and mobility of natural Fe colloids and particles. Co-precipitation of Fe and dissolved organic carbon (DOC) is common in organic-Fe-rich systems with significant variations in redox state and/or pH (e.g., Pokrovsky and Schott, 2002). Two main pools of Fe, consisting of Fe(II)(III)-OC complexes and Fe-oxyhydroxides were identified by Sundman et al. (2014). Iron(II) rich phases are prevalent throughout oxic aquatic regimes (von der Heyden et al., 2014). Allard et al. (2004) identified two pools of Fe using ultrafiltration

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https://doi.org/10.1016/j.gca.2018.07.030
0016-7037/© 2018 The Author(s). Published by Elsevier Ltd.

and paramagnetic resonance spectroscopy. The origin and pathways of these two Fe species are unclear. We propose that the two types of Fe aggregates present in stream and river waters can be traced using Fe isotopes. The most significant changes in the Fe isotope composition occurs between the oxidized and reduced phases of Fe, where Fe(III) species tend to have higher $^{56}Fe/^{54}Fe$ isotope values (Polyakov and Mineev, 2000; Anbar et al., 2005). The Fe isotope composition varies in organic-rich rivers with high Fe concentrations. Bergquist and Boyle (2006) showed that the Negro River, Brazil, has positive $\delta^{56}Fe$ values in the dissolved fraction and negative $\delta^{56}Fe$ values in the particulate fraction. Similarly, several studies have shown two groups of Fe isotope compositions in rivers (Escoube et al., 2009, 2015; Ilina et al., 2013; Mulholland et al., 2015). The processes behind the formation of these two groups and temporal variations are unclear. Patel-Sorrentino et al. (2007) concluded that soils actively control the physicochemical characteristics in stream water. Solid soils display a range of variations in the $\delta^{56}Fe$ values from −0.61‰ to +1.04‰ (e.g. Emmanuel et al., 2005; Wiederhold et al., 2007a,b; Poitrasson et al., 2008; Huang et al., 2018), indicating that pedogenic processes generate Fe isotope fractionation. Dos Santos Pinheiro et al. (2014) suggested that variations in the Fe isotope composition in the Negro River suspended matter indicate that a negative $\delta^{56}Fe$ composition (fractionated during pedogenesis) is transported from soils to the river, especially during storm events. The changing redox state at the stream water-soil interface influences the Fe isotope composition. It is essential to study Fe isotopes in defined small catchments (first-order streams) to understand the Fe isotope composition in rivers and estuaries. We have analyzed Fe isotopes in three key compartments in the boreal landscape: a major river (Kalix River), riparian soil water, and a first-order stream, dominated by forest.

2. STUDY AREA

Several studies investigated the geochemistry of the Kalix River (e.g., Ingri and Widerlund, 1994; Ingri et al., 2000, 2005, 2006; Andersson et al., 2006; Dahlqvist et al., 2007; Engström et al., 2010). The river is pristine and has no dams. Samples were taken close to the river mouth, at Kamlunge (Fig. 1). Kalix River has its source in the Caledonian Mountains, dominated by mica schist, quartzite, and amphibolite, and flows into the Bothnian Bay. Granite dominates in the rest of the catchment (Gaál and Gorbatschev, 1987). The drainage area consists of forest (55–65%), peatland (17–20%), lakes (4%) and farmland cover (<1%) (after SMHI, 2018). Till covers the granitic bedrock below the mountains. In the forested lowland the till shows well-developed podzol profiles (Fromm, 1965). Podzol profiles typically consist of, from top to bottom, (1) the O-horizon, which is a black or dark brown organic-rich layer, (2) the E-horizon, which is a gray sandy and silty layer, as minerals, organic matter, and clays are leached out of the layer, (3) the B-horizon, enriched by illuviation and coloured by organic matter (Bh) and iron oxides (Bs) (Wiederhold et al., 2007a), (4) the C-horizon, containing relatively unweathered rock fragments and lacks

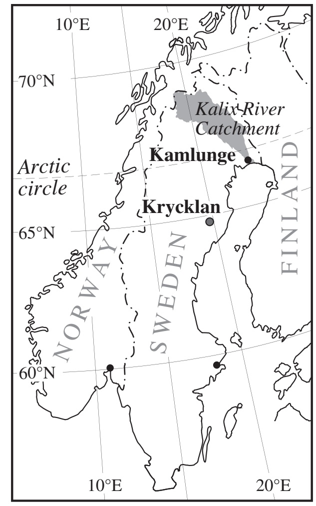

Fig. 1. The Kalix River catchment is displayed in light gray, showing the sampling station of Kamlunge close to the river mouth. The Krycklan Catchment is shown as a single dot, including the sampling station Västrabäcken.

organic materials. The process of developing a podzol profile is called podzolization (e.g. Anderson et al., 1982; Lundström et al., 2000; Buurman and Jongmans, 2005; Sauer et al., 2007, 2008; Cornu et al., 2009; Fekiacova et al., 2017). The yearly precipitation ranges from 1000–1500 mm in the mountains to 400–700 mm at the coast. About 45% of the annual precipitation is snow.

The Krycklan Catchment, located south of the Kalix River (Fig. 1), encompasses a natural mosaic of boreal landscapes consisting of forests, mires, streams, and lakes. The site provides the most advanced long-term field research facility in operation in a boreal biome (Laudon et al., 2013). The forest-dominated sampling station Västrabäcken (98.7% forest; 1.3% wetland; 0.12 km^2) is instrumented with continuous discharge measurement and stream water sampling. The main types of tree in the catchment of the first-order stream are Scots pine (64%) and Norway spruce (36%). The mean annual precipitation is 600 mm and about 50% falls as snow (Laudon et al., 2007). The first-order streams in the Krycklan catchment eventually drain into the Ume River. As in the Kalix River catchment, the soils are dominated by podzol profiles developed from locally derived till, except for the riparian zone, which has more organic soils (Lidman et al., 2017).

The composition of the catchments of Kalix and Ume River, respectively, is almost identical, both catchments consist mainly of forest, grassland and mires, with minor percentages of mountainous areas and lakes (SMHI, 2018). The main soils are moraine, peat, and thin soils. The similarity in geology, landscape type, and climate allows us to compare a first-order stream from the Krycklan catchment with the Kalix River.

3. METHODS

This study includes samples from three different sampling campaigns. The Kalix River was sampled at Kamlunge between April and October 2006 (23 samples). The