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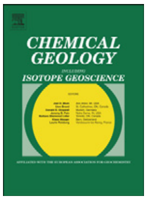

Silicon isotope variations in Central Siberian rivers during basalt weathering in permafrost-dominated larch forests

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ABSTRACT

This work is devoted to the characterization of natural mechanisms of silicon isotope fractionation within Siberian watersheds and predicting the climate warming effect on Si fluxes from the land to the Arctic Ocean. To unravel the different sources of silica generated by basalt weathering in Central Siberia under permafrost and larch deciduous forest conditions, we measured the Si isotopic composition of large and small rivers, surface flow, interstitial soil solutions, plant litter and soils. The average annual discharge-weighted δ^{30}Si values of the second largest tributary of the Yenissei River, Nyzhnaya Tunguska and its main northern tributary (Kochechum) are equal to 1.08 ± 0.10‰ and 1.67 ± 0.15‰, respectively, while their average annual Si concentrations are very similar (3.46 and 3.50 mg/L, respectively). During summer baseflow, the dissolved Si isotope composition of both large rivers and a small stream ranges between 1.5 and 2.5‰. This is much heavier compared to the source basaltic rocks but similar to the fresh litter of *Larix gmelinii*, the dominating tree species in this region. It could be consistent with litter degradation in the uppermost soil horizons being the dominant source of solutes annually exported by Central Siberian rivers. During spring flood, accounting for 60–80% of annual Si flux, the δ^{30}Si of the large rivers' dissolved load decreases by 1–1.5‰, thus approaching the value of the bedrock and the silicate suspended matter of the rivers (RSM). This may reflect the dissolution of the silicate suspended load at high water/mineral ratio. The winter δ^{30}Si values of the large river dissolved load range between 1.0 and 2.5‰. During this period, contributing to $\leq$ 10% of the annual Si chemical flux, the interaction between bedrock (porous tuffs) and deep ground waters occurs at a very high solid/solution ratio, leading to the precipitation of isotopically light secondary minerals and enrichment of ^{30}Si in the fluids that feed the river through the unfrozen flowpaths. Results of this study imply that more than a half of the silica transported by Siberian rivers may transit through the biogenic pool and that, like in other stable basaltic regions, bedrock–water interactions account for a lesser fraction of the silica flux. As a result of projected future climate warming and weathering increases in boreal regions, the δ^{30}Si isotopic composition of large Siberian rivers is likely to shift towards less positive values.

1. Introduction

Understanding the silicon cycle within the boreal and subarctic watersheds is of primary importance for assessing the consequences of climate warming on Si fluxes from the land to the Arctic Ocean. This ocean receives by far the largest proportion of dissolved Si riverine flux normalized to the ocean's volume (a factor of 3 and 5 times higher than that of the Atlantic Ocean and the Global Ocean, respectively, Dürr et al., 2011). This is likely to control the primary productivity and CO_2 exchange with the atmosphere in high latitudes (Holmes et al., 2012). Temperature increase in the future may modify subarctic Si riverine fluxes due to the increases of *i*) the depth of the active layer (unfrozen soil layer); *ii*) plant biomass and land primary productivity linked to the northward migration of the treeline and *iii*) atmospheric precipitation, permafrost thaw and river discharge. With Si being among the main limiting nutrients for plankton primary productivity in high latitude seas, this increase in Si riverine fluxes may turn out to be of primary importance for the coupled carbon cycle (cf. Bernard et al., 2010). However, the mechanisms controlling Si release from the frozen soils and rocks of Siberian larch forests, by far the dominant vegetation type of Northern Eurasia, remain poorly understood, especially with regard to the seasonal variations of Si fluxes.

Over the past decade, significant progress in the characterization of different sources of Si and the mechanisms controlling its mobilization and transfer has been achieved via systematic analyses of Si stable isotopes in the surface environment (Ding et al., 2004; Alleman et al., 2005; Ziegler et al., 2005; Georg et al., 2006a; Engström et al., 2008; Cardinal et al., 2010; Opfergelt et al., 2012). The majority of these studies have shown that the waters that drain continents are enriched in heavy

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Si isotopes relative to the source rocks. Secondary mineral formation in soils at low water/rock ratios removes ^{28}Si from the solution (Ziegler et al., 2005; Opfergelt et al., 2008, 2010, 2012; Delstanche et al., 2009) and thus tends to enrich pore waters in ^{29}Si and ^{30}Si. Concurrently, high discharge events are likely to enrich river water in the light isotope due to the dissolution of surface clays, especially at high water/rock ratios (Georg et al., 2006a). Besides, plants and plant phytoliths are known to be enriched in light isotopes relative to the source Si pool (Ding et al., 2005; Opfergelt et al., 2006, 2008, 2010). As such, plant uptake of Si is capable of enriching the interstitial soil solutions and surface waters in the heavy isotope, especially at the end of the vegetation growing season. On the other hand, degradation of plant litter and tree wood should release isotopically-light Si during the high water discharges. These various processes, wholly or in part, have been shown to operate in several climatic and lithological areas, including tropical (Ziegler et al., 2005; Bern et al., 2010; Hughes et al., 2011), temperate (Georg et al., 2006a; Cornelis et al., 2010), and boreal non-permafrost environments (Georg et al., 2007; Engström et al., 2010; Pogge von Strandmann et al., 2012). However, a still unresolved question is to what degree these mechanisms can be extended to the permafrost-dominated environments that cover the essential part of Northern Eurasia and control the carbon and nutrients fluxes to the Arctic Ocean.

Here, we have investigated chemical weathering over a large monolithological (basaltic) area in Central Siberia. The importance of silicate rock weathering to carbon transport to the Arctic Ocean from Siberian watersheds is fairly well known (Tank et al., 2012b). Chemical weathering in Siberia is highly distinctive because of the permafrost conditions and the extremely large seasonality in terms of water discharge and biological productivity (Vedrova et al., 2006; Bagard et al., 2011). The largest element fluxes from the watersheds occur during the high discharge spring flood period. Although the ultimate source for most of the river solutes is derived from base rock weathering rather than atmospheric deposition (Pokrovsky et al., 2005; Zakharova et al., 2005, 2007), there is a large annual turnover of the biomass that strongly affects the water chemistry, and, potentially, Si fluxes. The specificity of Si transport in Central Siberian rivers, making them drastically different from the rest of the world (i.e., Dürr et al., 2011), is the dominance of dissolved over suspended Si flux (Pokrovsky et al., 2005). Indirect evaluation of the relative contribution of plant litters to annual dissolved Si fluxes ranges from 34 to 100% in Central Siberia (Pokrovsky et al., 2005, 2006) and reaches 40% in Northern Karelia and Kola Peninsula (Zakharova et al., 2007). Such a high contribution of terrestrial plants to Si fluxes, also consistent with the results of other field studies (Lucas et al., 1993; Derry et al., 2005; Gérard et al., 2008), is supported by recent experimental evidence of extremely high plant biomass reactivity in terms of Si release at ambient conditions (Ehrlich et al., 2010; Fraysse et al., 2010).

Towards distinguishing between the different sources of dissolved Si in large Siberian rivers and smaller streams, this study aims to answer the following specific questions:

- How large are seasonal variations of δ^{30}Si in rivers and streams?
- What is the average annual discharge-weighted Si isotope ratio in the river water that can serve as a proxy for all Siberian rivers?
- Is it possible to link these variations to the contribution of main end-member Si-bearing pools (bed rocks, soils, river suspended matter, organic litter, fresh vegetation)?
- Can the isotopic composition of source fluids (soil porewaters, groundwaters) be used as a proxy for dissolved Si isotopes in rivers?
- What are the most likely physico-chemical mechanisms controlling Si isotope partitioning between the fluid phase and the solid source pools during different seasons?

Through a detailed follow-up of Si isotopic compositions in the main compartments of Siberian watersheds based on year-round time series, we demonstrate the importance of biotic versus inorganic reservoirs in controlling Si fluxes from the land to the ocean and we predict the evolution of the Si isotopic composition of Siberian large rivers under a climate warming scenario. This information can be extremely useful to trace water mass transfer, biological productivity and paleoenvironments in the Arctic with Si isotopes, following the approaches developed for other oceanic settings (Reynolds et al., 2006a; Ehlert et al., 2012).

2. Description of the study area and sampling collection procedure

The watershed of the studied rivers is underlain by flood basalts, forming part of the 248 Ma old Siberian Traps that are up to 2 km thick. This basaltic terrain provides a very homogeneous lithology, detailed elsewhere, in terms of mineralogical and chemical compositions (Pokrovsky et al., 2005; Bagard et al., 2011 and references therein). Riverine erosion of this terrain over millions of years has left a large, relatively flat plateau, cut by steep-sided valleys of the major tributaries of the river Nizhnyaya Tunguska (Fig. 1). This area has not been affected by glacial erosion, but is covered by thick permafrost, which is estimated to vary between 200 and 400 m in thickness (Brown et al., 1998). The soil exhibits a thin seasonally active layer (unfrozen from June to August) ranging from barely 0.2–0.7 m thick on north-facing slopes to 1.0–1.5 m thick on south-facing slopes. The climate is strongly continental with variation of the mean monthly air temperature from −35.9 °C (January) to +16.6 °C (July). Mean annual air temperature is −8.9 °C and mean annual precipitation is 370 mm (1928–2012, WMO 24507: Tura meteostation). The snow period lasts from October to May and winter precipitation accounts for about 35% of the annual value.

The soils and vegetation are also quite homogeneous around the plateau, with open larch forests (*Larix gmelinii*) at the lower elevations with gelisols (north-facing slopes, valleys and plateau flats above 300 m a.s.l.) and inceptisols (south-facing slopes), and tundra dominating above ~900 m elevation with a regosol. An uppermost ~0.15 m thick organic soil horizon is typically well developed, with the rooting zone appearing mostly in the upper 0.2 m of the soil active layer (Prokushkin et al., 2007, 2010). Plant growth is limited to the summer months from June to September. The vegetation of the area is dominated by larch (*L. gmelinii*), dwarf shrubs (*Ledum palustre* L., *Vaccinium vitis-idaea* L., and *Vaccinium uliginosum* L.) and mosses (*Pleurozium schreberi*, *Hylocomium splendens* and *Aulacomnium palustre*), along with patches of lichens.

The river flow mainly occurs during the frost-free period (May–October). From November to April the minor rivers are completely frozen (no flow), and the larger rivers are covered with a 1 to 2 m thick ice cover, resulting in low discharges during this period (less than 10% of the annual water flux occurs during the 6 winter months). The river winter discharge is presumably fed by deeper soil and groundwater reservoirs via the unfrozen paths, called taliks, underneath the river bed. Three different periods can be distinguished in the annual hydrology: (*i*) a month or two of extremely high discharge during the snowmelt phase, followed by (*ii*) a low discharge during the winter period, and (*iii*) highly variable discharges in the summer to fall months driven by precipitation events.

The two large rivers sampled in this study belong to the Yenisey drainage basin (Fig. 1A). The Kochehumo River ($S = 96{,}400$ km^2, annual discharge $= 28.9$ km^3, 100% permafrost and 69% forest coverage) flows from the northwest to southeast and has continuous permafrost (100 to 300 m depth) on its watershed. The Nizhnyaya Tunguska River ($S = 174{,}334$ km^2, annual discharge $= 51$ km^3, 62% permafrost and 95% forest coverage) flows from south to north over discontinuous and continuous permafrost that can extend downwards for up to 10 m. Both rivers drain tholeiitic basalts underlain by tuffs. Further details on the watershed vegetation and permafrost coverage are presented in Prokushkin et al. (2011) and Bagard et al. (2011). It has to be noted that while the Kochechum river basins is fully situated within Early Triassic flood basalts, one third of the N. Tunguska watershed at Tura