Constraints on the source of reactive phases in sediment from a major Arctic river using neodymium isotopes

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Abstract

Riverine suspended particulate matter (SPM) is essential for the delivery of micronutrients such as iron (Fe) to the oceans. SPM is known to consist of multiple phases with differing reactivity, but their role in the delivery of elements to the oceans is poorly constrained. Here we provide new constraints on the source and composition of reactive phases in SPM from the Mackenzie River, the largest sediment source to the Arctic Ocean. Sequential leaching of SPM shows that river sediments contain labile Fe phases. We estimate the labile Fe flux is substantial (0.21(±0.06,-0.05) Tg/yr) by quantifying Fe concentrations in weak leaches of the SPM. The labile Fe phase hosts a considerable amount of rare earth elements (REE), including neodymium (Nd). We demonstrate that the labile Fe phase and dissolved load have radiogenic Nd isotope ratios that are identical within uncertainty, but up to 8 epsilon units distinct from the silicate phase. We interpret this as evidence for dynamic cycling between Fe-oxide phases in SPM and the river water, demonstrating the high reactivity of the labile Fe phase. Nd isotope and elemental molar ratios suggest that a significant amount of labile Fe- and Nd-bearing phases are derived from Fe-oxides within the sedimentary source rock rather than silicate mineral dissolution. Thus, sedimentary rock erosion and weathering provides an important source of labile Fe, manganese (Mn) and by extension potentially other trace metals. Our results imply that both past and future environmental change in the Arctic, such as permafrost thaw, may trigger changes to the supply of reactive trace metals. These results demonstrate that a re-evaluation of sediment reactivity within rivers is required where uplifted sedimentary rocks are present.
Key words: iron oxides; bioavailable; neodymium isotopes; Arctic

1. Introduction

Rivers are conduits for the transfer of particulate and dissolved material derived from weathering to the oceans (Gaillardet et al., 1999). Weathering plays a critical role in the cycling of elements at the Earth’s surface and is a key regulator of the Earth’s climate over geological timescales (Walker et al., 1981). Rivers also transport essential nutrients to the oceans sustaining marine primary productivity (e.g., Deutsch and Weber, 2012). Changes to the flux of nutrients that limit productivity in the oceans have been linked to large scale perturbations in the carbon cycle and past climate change (Martin, 1990; Vincent and Berger, 1985). The flux of suspended particulate matter (SPM) sustains the supply of certain elements to the oceans and plays an important role in bio-geochemical cycling (Jeandel and Oelkers, 2015; Jones et al., 2012).

Micronutrients (e.g., Fe), the rare earth elements (REE, particularly Nd) and many other trace elements have low solubility in natural waters. In the dissolved load (<0.2 μm) these elements are predominately associated with nanoparticulate and colloidal phases (Gaillardet et al., 2014, and references therein). Their concentrations in river dissolved loads are low (ppb to ppt, Gaillardet et al., 2014); concentrations in SPM are several orders of magnitude higher (Jeandel and Oelkers, 2015). Salt-induced flocculation of many such nonmobile elements in estuaries further removes most of
these low concentration elements prior to reaching the oceans (Elderfield et al., 1990).

Basalts and volcanic particulates are important sources of key bio-limiting nutrients (e.g. Fe) as they are easily weatherable and enriched in those elements (Jones et al., 2012). However, the importance of sedimentary rocks has not been similarly evaluated. Marine sediments contain phases, including Fe-Mn oxyhydroxides with elevated REE concentrations, which are formed from precipitation and exchange with seawater and pore fluids (e.g., Chester and Hughes, 1967). Marine sedimentary rocks tectonically emplaced on the continents retain some of these characteristics (Hindshaw et al., 2018; Jang et al., 2020). This results in a reservoir of inherited phases which can be more reactive than silicate minerals and may supply a greater amount of bioavailable Fe to riverine sediments (Hindshaw et al., 2018). For instance, amorphous Fe (oxy)hydroxides (e.g. ferrihyrite) contained within riverine sediments are easily reducible and potentially bioavailable (Bhatia et al., 2013, Hawkings et al., 2018).

Since Fe-oxides are enriched in REEs, their origin can be traced using radiogenic Nd isotopes (\(^{143}\text{Nd}/^{144}\text{Nd}\), expressed as \(\varepsilon\text{Nd}\)), a source tracer in riverine and marine sediments (Goldstein and Jacobsen, 1988; Goldstein and Hemming, 2003). Since there is limited fractionation of the Sm/Nd ratio in particulate phases during weathering and the decay constant is long compared to the timescales of recent weathering (Babechuk et al., 2014), \(\varepsilon\text{Nd}\) is only controlled by changes in source. Nd in the dissolved load typically has \(\varepsilon\text{Nd}\) greater (more radiogenic) than in the SPM in
rivers with abundant sedimentary rocks in their catchments (Goldstein and Jacobsen, 1987; Hindshaw et al., 2018). This offset is attributed to dissolved Nd sourced from the preferential weathering of marine precipitates and other reactive components contained within the parent rock (Goldstein and Jacobsen, 1987). Nonetheless, a clear link between these reactive phases and dissolved riverine chemistry has not been shown.

With knowledge of the source composition, $\varepsilon$Nd is a valuable tool for tracing the origin of reactive phases from sedimentary rock weathering and their transport in river systems. We apply this tracer to a large Arctic river system. The Mackenzie River, as the first and third largest source of suspended sediment and water, respectively, to the Arctic Ocean (Macdonald et al., 1998, Holmes et al., 2002), provides a good representation of basin-scale fluxes. It is dominated by shale weathering with a low abundance of volcanic or mafic rocks and limited influence from the weathering of crystalline rocks (Millot et al., 2003, Fig. 1B). This makes the Mackenzie an ideal location to investigate the mobilisation of reactive, micronutrient-bearing phases during shale weathering on a large scale.

In this study we characterize the $\varepsilon$Nd of the dissolved load (<0.2 μm and ultrafilters) and suspended sediment (sequential extractions and residue) in the Mackenzie and key tributaries over two years (2017, 2018) sampled within a few days of the peak discharge after ice-break up. We show that the $\varepsilon$Nd is within uncertainty between the dissolved load and easily leachable phases in the SPM. We use REE patterns to constrain the mineralogy of the leachable phases. We quantify
the concentrations of major and some trace elements in leachable phases and estimate the flux of labile Fe from the Mackenzie to the Arctic Ocean.

2. Materials and Methods

Full analytical and procedural methods are given in Supplementary Text 1 and summarised briefly here. All analysis was carried out at the University of Cambridge, Department of Earth Sciences.

2.1 Study area and sample collection

The Mackenzie River system is large (Fig. 1, area $1.78 \times 10^6 \text{km}^2$). The weathering of sedimentary rocks dominates the dissolved and SPM loads of the river (Calmels et al., 2007; Horan et al., 2019; Huh et al., 2004; Millot et al., 2003) despite the large surface area of crystalline rocks (29.2% of the basin geology, Fig. 1b). Less than 1% of the basin is underlain by volcanic rocks (Fig. 1b). The river is characterised by a sharp peak in discharge each year after the seasonal melting (freshet) of river ice in May-July (Fig. 2). Samples were collected at this period of maximum flux.

The Mackenzie mainstem and two large tributaries which enter at the delta, the Peel River and the Arctic Red River, were sampled at 3 main sites (Fig. 1) in early June in 2017 and 2018. Suspended sediment samples were taken at different depths in the channel using a 5L Van-Dorn type depth sampler (following Hilton et al., 2015). Discharge was quantified using an acoustic-Doppler current profiler (ADCP, Rio
Grande II (1200 kHz), Teledyne Instruments, Fig. 2, Supplementary Table S4).

Additionally, in 2018 a small Peel River tributary and meltwater from the surface Arctic Ocean (seawater diluted by sea and river ice melt) were sampled. Dredged bed load, bank sand and rock fragments were also collected.

River samples were filtered at 0.2 μm, collecting both water and sediment. Filtered waters collected for major cation and REE concentrations were acidified using distilled HNO₃ to pH 2 in acid cleaned bottles. In 2018, ultrafiltration was carried out on <0.2 μm filtrates from the Mackenzie (Middle Channel) and the Peel River, using dialysis membranes with molecular cut off weights of 10 kDa and 1 kDa (Supplementary Text 1.2). Approximately 10 L of <0.2 μm water was collected for the analysis of Nd isotopes using a Fe co-precipitation method (Hindshaw et al., 2018).

To characterize the longer-term integrated composition of the Mackenzie River SPM leachate compositions from 5 offshore sediment cores from the Mackenzie delta and one from deeper in the Beaufort Sea were analysed (Natural Resources Canada, Geology Survey of Canada’s Marine Geoscience Collection, Supplementary Table S5). Two silicate residue samples were analysed from two of the shallowest core sites. The sedimentation rate at shallow sites in the Canadian Beaufort sea is high (on the order of 2-3 m/ka, O'Regan et al., 2018), indicating that the range and depth sampled within the cores (~10 cm) represents sediment that is likely several decades old, and homogenises inter-annual and seasonal variability.
2.2 Sequential extractions

Approximately 50-100 mg of dry sediment was leached sequentially to extract: 1) exchangeable phases (1M NH₄Cl), 2) reactive Fe-Mn (oxy)hydroxides (a weak acid-reductive leach of 5 mM hydroxylamine hydrochloride (HH)-3 mM Na-EDTA-1.5% acetic acid buffered to a pH of ~4 with NaOH), 3) calcite and additional carbonates (1.7M acetic acid, 4) dolomite, and any remaining authigenic components (e.g., crystalline Fe-Mn oxides, 1M HCl). The focus of this study is the weak acid-reductive leach, hereafter referred to as the HH leach, targeting amorphous reactive Fe-Mn oxides. This is a more dilute HH leach than previous methods (e.g. Bhatia et al., 2013; Chester and Hughes, 1967) carried out on non-decarbonated sediments, following Blaser et al., 2016. This method minimizes dissolution of silicate phases and avoids the loss of other reactive Fe phases during removal of carbonates. Due to the buffering of this reaction in the presence of varying amounts of carbonate, it represents a minimum estimate of the reactive Fe-Mn oxyhydroxides rather than a fully quantitative leach. This leach will mobilise reactive carbonate phases and potentially some REEs associated with phosphates. Residue sediment was digested following lithium borate fusion (Supplementary Text S1.3).

2.3 Major and trace concentration analysis

Major and selected trace element (e.g. Fe, Mn) concentrations on acidified waters were determined by ICP-OES (Agilent 5100, with a precision and accuracy of better
than 10% based on repeated analysis of certified water standards (Supplementary Text 1.4.1).

Leachate phases and dissolved sediment residues were similarly analysed for major and some trace element concentrations by ICP-OES, with matrix-matched calibration lines. External reproducibility (typically better than 10%) was monitored using certified standards (Supplementary Text 1.4.1).

Mass balance was verified by comparison of the sum of concentrations in the leachates and residue with bulk sediment and a leached USGS shale standard with certified values (Supplementary Table 8). The sum reproduced expected values usually within 10%, and always within 20%.

2.4 REE Analysis

REE concentrations on filtered waters were measured by isotope dilution (Supplementary Text 1.5). Nd (alongside REE) concentrations in sediments and sediment leachates were determined using ICP-OES (Agilent 5100, Nd concentrations > ~4 ppb only) and using a Thermo Element-XR ICP-MS with a matrix-matched calibration line. Reproducibility was monitored using certified standards and values were within ±10%. Two residue samples and all sequential extraction steps from one SPM sample were determined by isotope dilution, as described for filtered water samples (Supplementary Text 1.5).
2.5 Nd and Sr isotopes

Nd was separated from the leachate and residue solutions using established chromatographic procedures; the light REE’s were separated using TRUspec resin, and Nd from Sm using LNspec resin. Radiogenic Sr isotope ratios (\(^{87}\text{Sr}/^{86}\text{Sr}\)) were determined on a subset of water, sediment leachate and sediment samples. Sr was isolated using SrSpec resin (following Hindshaw et al, 2018). Nd was separated from water samples using two stages of cation exchange (Biorad AG50W-X8) and LnSpec resin (Supplementary Text 1.1).

Nd and Sr isotopes were measured on a Thermo Neptune Plus MC-ICP-MS. \(^{146}\text{Nd}/^{144}\text{Nd}\) was normalised to 0.7219 using an exponential correction. Samples were corrected to the accepted value of reference standard JNd-i-1;

\(^{143}\text{Nd}/^{144}\text{Nd}=0.512115\) (Tanaka et al., 2000) which was repeatedly analysed at the sample concentration throughout each measurement session. Two times the standard deviation (2σ) on JNd-i-1 for each measurement session is quoted as the analytical uncertainty. \(\epsilon\text{Nd}\) was calculated in parts per 10,000 relative to the chondritic uniform reservoir (CHUR), \(^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}=0.512638\) (Jacobsen and Wasserburg, 1980). For Nd isotopes, long-term reproducibility was monitored using rock standards (Supplementary Text 1.4.2). Unless otherwise stated, where Nd isotope replicates (measurement or full procedural) were carried out, the value reported is the average of the replicates and the associated 2σ, if higher than the measurement session uncertainty. For Sr isotopes, \(^{85}\text{Rb}\) was monitored to correct for Rb interferences on \(^{87}\text{Sr}\) and Kr interferences were corrected for by measurement of
the baseline in a blank solution (on-peak zeros). Values were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ using an exponential correction. For Sr isotopes, samples were analysed in duplicate, and the uncertainty quoted is the associated 2σ. Repeated measurements of the standard NBS 987 yielded $^{87}\text{Sr}/^{86}\text{Sr} = 0.710275 \pm 0.000046$ ppm (2σ, n=20).

3. Results

3.1 Dissolved Nd

Nd was partitioned between nano-particulate and colloidal phases and the ‘truly’ dissolved (<1 nm; ≈ 1 kDa) phase (Table 1). Approximately 70% of Nd in the <0.2 µm filtrate is hosted in colloids or nano-particulates (Table 1). In the Mackenzie River (Middle Channel) $\varepsilon$Nd values between the <0.2 µm and <1 kDa fractions agreed within 0.43 epsilon units (Table 1). This demonstrates that nano-particulate and colloidal phases and the ‘truly’ dissolved load have the same source and so the <0.2 µm $\varepsilon$Nd value is representative of the ‘truly’ dissolved composition, consistent with previous observations in large rivers (Merschel et al., 2017).

3.2 Paired sediment and dissolved $\varepsilon$Nd

As the <0.2 µm fraction is indicative of the ‘truly’ dissolved $\varepsilon$Nd, it is possible to use these measurements to compare with leachable phases and assess their reactivity. We therefore refer to the <0.2 µm as the dissolved load. The dissolved load is always more radiogenic than the sediment residue, with the offset ranging from 1.4
to 8.2 epsilon units (Fig. 3, average = 3.2). This is consistent with, and in some cases far exceeds, the offset observed by Goldstein and Jacobsen, 1987, for large rivers with significant marine sedimentary source rocks in their catchments. In contrast, $\varepsilon_{\text{Nd}}$ in the dissolved load is in close agreement with HH leachates targeting reactive Fe-Mn oxides with a linear regression within error of the 1:1 line (Fig. 3). The dissolved vs. residue $\varepsilon_{\text{Nd}}$ linear regression is systematically offset from the 1:1 line, with a weaker correlation (Fig. 3).

Residue $\varepsilon_{\text{Nd}}$ compositions are in close agreement with previous measurements of sediment already reported for the Mackenzie River (Vonk et al., 2015). Dissolved $\varepsilon_{\text{Nd}}$ reported herein for the Mackenzie River at Tsiigehtchic (-13.4 ±0.2 (2$\sigma$, n=1, 2018) and -12.3±0.3 (2$\sigma$, n=2, 2017)) is consistent with the only previous dissolved measurement (2003, -12.9±0.3 (Zimmermann et al., 2009)).

SPM in the Middle Channel of the Mackenzie River is hydrodynamically sorted, due to faster settling velocities of coarser sedimentary particles (e.g. Bouchez et al., 2011). This is illustrated by Al/Si, a proxy for grain size (Fig. 4), indicating the dominance of finer sediments towards the surface and coarser at the bottom. Despite this hydrodynamic sorting, there is no appreciable variation of $\varepsilon_{\text{Nd}}$ with depth in either the sediment residue or HH leachate (Fig. 4). Dissolved $\varepsilon_{\text{Nd}}$ from the surface and base of the water column demonstrate that the water is well mixed.

There are systematic differences in dissolved $\varepsilon_{\text{Nd}}$ between 2017 and 2018. The furthest downstream site (Mackenzie, Middle Channel) dissolved composition
changes from $\varepsilon_{\text{Nd}}=-10.71\pm0.41$ (2$\sigma$, n=3, 2017) to $-12.97\pm0.15$ (2$\sigma$, n=1, 2018), likely driven by changes in the Peel River which shows similar differences, changing from $\varepsilon_{\text{Nd}}=-9.83\pm0.16$ (2$\sigma$, n=1, 2017) to $-11.47\pm0.15$ (2$\sigma$, n=1, 2018). This could represent inter-annual $\varepsilon_{\text{Nd}}$ variability, as is argued to be the case for changes in organic carbon and dissolved nutrient sources on the same sample set (Schwab et al., 2020), but additional data would be needed to determine if this is the case.

The average HH leach $\varepsilon_{\text{Nd}}$ from sediment cores was $-11.3\pm1.9$ (2$\sigma$, n=6), consistent with the same fraction in riverine sediments (Fig. 3) with the leachate always more radiogenic compared to the silicate residue (two cores, <10m deep, average offset = 2.7±1.2, 2$\sigma$, n=2). Shallow (<100 m) seawater in the Beaufort Sea is more radiogenic than these leachate compositions ($\varepsilon_{\text{Nd}} = \sim-6$ to -9, Porcelli et al., 2009). Therefore, the offset between residue and leachate is preserved and exported in sediment to the shelf. $\varepsilon_{\text{Nd}}$ in the HH leach at the deepest and least proximal core site ($\varepsilon_{\text{Nd}} = -9.55$, 1054 m water depth) overlaps with $\varepsilon_{\text{Nd}}$ measured in deep (> 1000 m) seawater in the Beaufort Sea, which is less radiogenic ($\varepsilon_{\text{Nd}}$ between -9 and -11, Porcelli et al., 2009).

### 3.3 Sediment partitioning and characterisation

The partitioning of selected elements amongst all leachates relative to the bulk sediment is shown in Fig. 5. In the NH₄Cl leach, targeting exchangeable phases, Fe and Nd were below detection. This is consistent with a previous study which reported low concentrations of REEs in a river sediment exchangeable fraction (Adebayo et
Elemental concentrations in the NH₄Cl leach which were not below detection are reported in Tipper et al., 2021. The HH leach contains on average 3%, 8% and 30% of the total sediment Fe, Nd and Mn respectively (Fig. 5). Ca, Mg and Sr are also high in the HH leach (Fig. 5) consistent with significant carbonate lithologies present within the Mackenzie Basin (Millot et al., 2003). On average 60% of the Fe and Nd are hosted within the silicate residue.

REE on the HH leach show a middle REE (MREE) enrichment (Fig. 6a). A MREE enrichment of this magnitude is typical of an Fe-Mn oxyhydroxide signature (Fig. 6a) and is consistent with that previously reported for similar sediment extractions (e.g. Leybourne and Johannesson, 2008).

REE in the SPM leachate phases were partitioned relative to the bulk (sum of leachates and residue; Middle Channel, 2017, Fig 6b). 15% of REEs relative to the total sediment are mobilised during the HH leaching step. A smaller fraction (<1%) of REEs are released during the subsequent acetic acid leach step (Fig. 6b), despite the large amount of Ca and Mg (22% of total sediment Ca, 11% of total sediment Mg). Less Fe and Mn are mobilised in the acetic acid leach (1% of total Fe, 5% of total Mn), relative to the HH leach (4% of total Fe, 42% of total Mn). This demonstrates that the REE are not associated with carbonate phases.

87Sr/86Sr on the dissolved load and sediment residues (Fig. 6c) are in agreement with previously published data for this river (e.g. Millot et al., 2003). 87Sr/86Sr values indicate carbonate and silicate sources in the HH leach and residue respectively. Sr
isotopes do not indicate extensive leaching into the silicate detrital fraction. Although there is scatter in the leachable $\varepsilon$Nd compositions (Fig. 6c), on stronger leaching $\varepsilon$Nd is not substantially more radiogenic than the HH leach.

4. Discussion

$\varepsilon$Nd values from paired dissolved load and SPM, alongside the characterisation of elemental concentrations in sequential extractions, are used to trace both the source and the reactivity of different phases within the SPM. Firstly, we seek to assess the reactivity of the phases in the HH leach and then characterise sources. We then estimate the flux of labile Fe from the Mackenzie to the Arctic Ocean and address the implications of this study in terms of the oceanic Nd budget.

4.1 Reactivity of the labile phases in SPM

The reactivity of phases hosted in the HH leachate are traced with $\varepsilon$Nd and elemental partitioning. Significant fractions of Fe, Mn, Ca, Mg, and REEs relative to the bulk sediment are present in what is an extremely weak and buffered leach (5 mM HH, 1.5% acetic acid, Fig. 5, Fig. 6). Although subsequent leaches use stronger reactants and are not buffered, they release smaller amounts of Nd compared to the HH leach (Fig. 6b). This suggests that some of these reactive phases are susceptible to acid-reductive dissolution with small changes in pH or redox conditions (which may occur in the delta or offshore). Nd and REEs are depleted in carbonate rocks and are unlikely to be directly incorporated into biogenic calcite (e.g.
Less Nd is released in the 1.7 M acetic acid leach, compared to the HH leach, confirming that during the HH leaching step the Nd released is not associated with carbonates.

Although an MREE enrichment in the HH leach is typical of an Fe-Mn oxyhydroxide phase, this could also be consistent with some phosphate phases (such as biogenic apatite, Fig. 6a., Leybourne and Johannesson, 2008, and references therein).

Secondary precipitation of phosphates could also result in an MREE enrichment (Leybourne and Johannesson, 2008), but the lack of an LREE enrichment (low HREE/LREE, Fig. 6a) in HH leaches makes this unlikely (Köhler et al., 2005).

The dissolved εNd composition is always similar to the HH leachate composition (Fig. 3). This similarity is prevalent in different sampling localities and tributaries, which differ in sediment and water characteristics. This points to a fundamental process that is shared between these catchments and suggests that this observation is not unique to the time of year sampled (freshet). In rivers, the SPM is supplied by bank erosion and hillslope processes (Hilton et al., 2015), which are likely to be decoupled in space and time from the hydrological pathways that deliver river water (Vonk et al., 2019). Therefore, the consistency in εNd between dissolved and HH leach εNd is most likely explained by rapid and recent cycling within riverine implying equilibrium between the dissolved load and Fe-oxide phases in the HH leach.

Dissolved and HH leachate εNd are always similar at each site in the Mackenzie River, both upstream and downstream of major confluences with the Peel and Arctic
Red Rivers (Tsiigehtchic to Middle Channel, Fig. 1a). Previous discharge and sediment flux estimates demonstrate that water and suspended sediment do not mix in the same proportions downstream of the Peel confluence, with the Peel supplying 17% of the sediment load (Carson et al., 1998), but only 7% of the total water discharge (Schwab et al., 2020 and references therein). This implies the potential for rapid cycling between the dissolved load and HH leach phases during transit between the upstream and downstream sites, despite only limited changes in pH and Nd concentration (supplementary Table S4 and S10).

Although the mechanism for equilibration of Nd between HH leach phases and the dissolved load is unclear, since the weakly adsorbed exchangeable phases are removed in the leaching step prior to the HH leach, this rapid cycling is likely driven by dissolution of Nd from phases such as Fe-Mn oxyhydroxides. The concentration of Nd in the HH leach (ppb to ppm, Supplementary Table S9 and S11) is several orders of magnitude higher than the dissolved concentration (Supplementary Table S10), suggesting that phases within the HH leach may drive the dissolved composition.

Our findings demonstrate dynamic cycling between the dissolved load and phases soluble in the HH leach, such as Fe-Mn oxyhydroxides. The similarity of the dissolved load and HH leach phases and decoupling from the silicate residue suggests that the HH leach phases are labile and likely bioavailable. These results imply not only rapid cycling of Nd but potentially other immobile elements contained within the HH leach.
4.2 Marine authigenic phases as a source of radiogenic Nd in river waters

The mass balance of sources of radiogenic Nd that contribute to higher $\varepsilon$Nd in the dissolved and HH fractions relative to silicates provides information on the relative supply of Nd from different phases. Here we discuss possible sources of radiogenic Nd that could explain both the HH leaches and dissolved load. Average global seawater $\varepsilon$Nd (~-8.8, Lacan et al., 2012) and modern core top authigenic fractions (Haley et al., 2017) are more radiogenic than the upper continental crust (-11.4±2.5, Goldstein et al., 1984). Therefore, when marine sediments are emplaced on the continents, they can provide a distinct source of radiogenic Nd to the weathering reactor. Measurements of $\varepsilon$Nd on Fe-Mn oxides and other inherited authigenic phases of marine origin hosted in sedimentary rocks show that they are on average more radiogenic than associated silicates (Jang et al., 2020, Hindshaw et al., 2018). They can be reactive and so result in a more radiogenic dissolved and leachate composition when compared to the bulk source rock in rivers (Bayon et al., 2020; Goldstein and Jacobsen, 1987; Hindshaw et al., 2018; Jang et al., 2020).

Preferential weathering of inherited marine authigenic phases is the most likely reason for decoupled $\varepsilon$Nd between dissolved and silicate residue sediment in the Mackenzie. Radiogenic Nd in Fe-Mn oxyhydroxides of Mackenzie River SPM is likely derived from the weathering of these phases through physical transportation, and equilibration with waters. These radiogenic phases become mixed with Fe-oxides resulting from the weathering of silicate minerals, with $\varepsilon$Nd inherited from the source
432 silicate. Nonetheless, it is possible that alternate sources contribute labile and
433 radiogenic Nd, and these are addressed below.
434
435 4.3 Alternative sources of radiogenic Nd to river waters
436 Accessory minerals enriched in REEs and garnet can have more radiogenic $\varepsilon$Nd
437 than their bulk source rocks (e.g. Rickli et al., 2017). However, radiogenic release of
438 Nd during incongruent weathering of crystalline rocks is minimal (Dausmann et al.,
439 2019). Another possible source of radiogenic Nd is the preferential weathering of
440 volcanic rocks, but they are rare in the Mackenzie basin (Fig 1b, Millot et al., 2003).
441
442 Several studies indicate the dominance of shale and carbonate weathering on the
443 Mackenzie dissolved load, with no evidence of large volcanic or crystalline rock
444 contributions (Horan et al., 2019; Huh et al., 2004; Millot et al., 2003). $\varepsilon$Nd
445 decoupling between dissolved and silicate residue is at a maximum in a small Peel
446 River tributary that, to the best of our knowledge, does not have crystalline or
447 volcanic rocks in its catchment and drains almost exclusively shales. Moreover,
448 preferential weathering of a specific rock type would not explain the coupling of the
449 dissolved load with the HH leach, and their decoupling from the silicate residue, in all
450 sampling sites, with differing source lithologies.
451 Phosphates in sedimentary rocks are enriched in REEs and may be partially
452 mobilised in the HH leach. Phosphates in the main source rock type (shales) are
453 likely to have formed during marine diagenesis, so can be considered as inherited
454 authigenic phases, with a comparable $\varepsilon$Nd to concurrent Fe-Mn oxides. Fe-oxides
455 are ubiquitous in all sediments and sedimentary rocks. Given the range in source
rock age (Proterozoic to Cenozoic, Wheeler, 1996) and depositional environment, Fe-Mn oxides are the most probable universal constituent consistent with the high fraction of Fe and Mn in the HH leach, whereas phosphates may not always be present in sufficient abundance. Equilibration between the dissolved load and phosphates hosted in the HH leach would not likely result in the observed REE patterns, as secondary phosphates are typically LREE enriched (Fig. 6a, Köhler et al., 2005). Therefore, it is unlikely that phosphate minerals play a significant role, and the more positive Nd is derived from the preferential weathering of inherited Fe-Mn oxides.

While Fe-Mn oxides are insoluble in oxygenated and neutral range pH which typify large rivers including the Mackenzie (Tank et al., 2016) mobilization of amorphous and nano-particulate Fe can occur, and in acidic environments dissolution of Fe-oxides may occur. Extensive pyrite oxidation provides the majority of dissolved sulfate in the Mackenzie (Calmels et al., 2007). A product of the oxidative weathering of pyrite is Fe-oxide, and if instantaneous buffering of this reaction by dissolution of carbonate minerals does not occur, it will result in an acidic pH alongside high sulfate concentrations (Horan et al., 2019). This is seen in one tributary of the Peel River where high sulfate concentrations (4660 μM) and relatively low pH of ~6 are coupled to elevated Nd (950 ppt), high Fe (1 μM) and Mn (7.8 μM) concentrations in the dissolved load (<0.2 μm, Supplementary Tables S9 and S12) with the highest observed offset between the residue and HH leach εNd (8 epsilon units, Supplementary Table S10).
Nd is not likely to be incorporated directly into pyrite but will be present in 'contaminant' phases in pyrite or in other phases within a sedimentary rock succession, namely Fe-Mn oxyhydroxides or phosphates (Raiswell and Plant, 1980). High Nd and Mn dissolved concentrations indicate the dissolution of reactive Fe-Mn oxides within the source rock (shale), with differing $\varepsilon$Nd to silicate sources, coupled to the oxidative weathering of pyrite.

The HH leach of a shale fragment from this catchment has comparable $\varepsilon$Nd to the bedload HH leachate and dissolved load (Fig. 3, Supplementary Table S10). Although the mineralogical source of Nd and Fe is different (Fe from pyrite and Nd from other phases) these observations imply that the mobilization of Fe and Nd are coupled during the oxidative weathering of pyrite. This suggests that oxidative weathering of pyrite may provide an important source of reactive Nd and Fe bearing phases, with radiogenic $\varepsilon$Nd. Once the REEs are in solution, they can be incorporated into secondary Fe-oxides upon increasing pH, when Fe-oxides bearing REEs will precipitate out of solution. Close coupling between riverine Nd and Fe has been noted in previous studies (e.g. Elderfield et al., 1990; Ingri et al., 2000).

### 4.4 Constraints on the contribution of different sources of labile Fe and Nd

Using a simple mass balance model it is possible to estimate the fraction of Nd and Fe sourced from inherited authigenic phases contained within the sedimentary source rocks.
Dissolved εNd is set by exchange with labile HH leach phases in the SPM. The labile εNd is considered to be a mixture of Fe-oxides derived from modern-day weathering of silicate minerals (εNd_{sil}) and Nd derived from inherited authigenic phases (εNd_{auth}, equation 1, Figure 7).

\[ εNd_{labile} = f_{Nd, auth}εNd_{auth} + f_{Nd, sil}εNd_{sil} \quad (1) \]

where \( εNd_{labile} \) is the average of the leachate and dissolved composition, and \( f \) is the fraction of Nd in either the inherited authigenic or silicate phases where \( f_{Nd, auth} + f_{Nd, sil} = 1 \).

Equation 1 was solved for \( f_{Nd, auth} \), with \( εNd_{sil} \) given by the residue silicate composition measured for sample set. \( εNd_{labile} \) is the average of the HH leachate composition and (if measured) the dissolved composition for each sample set. \( εNd_{auth} \) is unknown and given the range of ages and types of sedimentary rocks in the Mackenzie basin, will be variable. \( εNd_{auth} \) was considered over the range \( εNd_{auth} = 0 \) to \( εNd_{auth} = εNd_{labile} \) sampled from a synthetic uniform distribution to account for the uncertainty of this end-member. \( εNd_{labile} \) and \( εNd_{sil} \) were measured at each sampling location and considered as normal distributions. We used Monte-Carlo methods to estimate the error when solving for \( f_{Nd, auth} \) (calculating \( f_{Nd, auth} \) for 100,000 values of each variable). \( f_{Nd, auth} \) was calculated for 4 individual sample sets (2017 and 2018 Middle Channel, Arctic Ocean and in shelf sediment cores, Fig. 8, Supplementary Table S13). Taking the interquartile range from the sum of all four sample sets it estimated that, at the mouth of the Mackenzie River a minimum of 23-50% of labile Nd is derived from inherited authigenic phases (Fig. 8).
Given this significant estimate for $f_{\text{Nd, auth}}$, it is likely that a similarly high fraction of other immobile elements such as Fe are also sourced from inherited authigenic phases. The fraction of labile Fe sourced from inherited authigenic phases (including from pyrite and inherited Fe-oxides) was estimated using mass balance:

$$\left( \frac{\text{Nd}}{\text{Fe}} \right)_{\text{labile}} = f_{\text{Fe,sil}} \left( \frac{\text{Nd}}{\text{Fe}} \right)_{\text{sil}} + f_{\text{Fe,auth}} \left( \frac{\text{Nd}}{\text{Fe}} \right)_{\text{auth}}$$

where $f_{\text{Fe,auth}} + f_{\text{Fe,sil}} = 1$, and $\left( \frac{\text{Nd}}{\text{Fe}} \right)$ is the molar ratio of Nd to Fe in each phase.

This equation was solved for $f_{\text{Fe,auth}}$, the fraction of labile Fe sourced from inherited authigenic phases. $\left( \frac{\text{Nd}}{\text{Fe}} \right)_{\text{auth}}$ is unknown, and the largest source of error and was based on the range from HH leaches of a shale fragment and coarse bank sediment

$$\left( \frac{\text{Nd}}{\text{Fe}} \right)_{\text{sil}} \times 1000 = 0.63 \text{ to } 2.4$$

was taken as the average of the measured silicate residue values which are within error of average upper continental crustal estimates

$$\left( \frac{\text{Nd}}{\text{Fe}} \right)_{\text{sil}} \times 1000 = 0.33 \pm 0.1$$

is the measured HH leachate composition at each sampling site. Using Monte Carlo methods to estimate errors, $f_{\text{Fe,auth}}$ is estimated to be between 11-29% (interquartile range, from sum of Middle Channel samples sets, 2017 and 2018, Supplementary Table S14).

Despite the uncertainty it is clear that the SPM in the Mackenzie must host a significant fraction of labile Nd and Fe which is derived from inherited authigenic phases in sedimentary rocks. Accordingly, the weathering of sedimentary rocks, especially marine shales, must supply a significant amount of reactive immobile elements (Nd, Fe) in the Mackenzie basin.

4.5 The flux of labile, potentially bioavailable, Fe
We have demonstrated that the SPM in the Mackenzie River has a labile Fe phase. To estimate its supply to the Arctic Ocean, we use the suspended sediment flux, which is well documented for the Mackenzie in the years 1974-1994. There is significant inter-annual variability ranging from 81 Tg/yr to 224 Tg/yr (Carson et al., 1998) with a consistent seasonal peak in the summer months following freshet, the time period over which our samples were collected (Fig. 2).

The labile, potentially bioavailable, Fe concentration was considered to be equal to the HH leach Fe concentration measured on SPM from the Mackenzie (Middle Channel, 2017 and 2018), which approximated to a normal distribution (1466±350 μg/g (±1σ, n=16)). The uncertainty was estimated using Monte-Carlo methods (n=100000), similar to that used by Hilton et al., 2015. The sediment flux was considered as a uniform distribution, taking into account all potential values at equal probability (81 Tg/yr to 224 Tg/yr, Carson et al., 1998), a maximum approximation of error. The median (±interquartile range) flux of labile Fe associated with SPM in the Mackenzie River was calculated to be 0.21(+0.06,-0.05) Tg/yr. We do not include dissolved (<0.2 μm) Fe concentrations in this estimate as they are negligible in comparison to Fe hosted in the reactive sediment phase (estimated dissolved Fe flux represents <0.03% of the labile sediment Fe flux, Supplementary Text 4).

The calculated flux of potentially bioavailable Fe in the SPM of the Mackenzie is substantial; comparable to that from the Greenland Ice Sheet (~0.3 Tg/yr, Bhatia et al., 2013). Greenland Ice Sheet fluxes are estimated using the sum of strong SPM
leaching and dissolved Fe followed by the application of an estuarine loss factor (90%, Bhatia et al., 2013).

Much of the SPM from the Mackenzie is rapidly buried offshore or trapped in the delta, and the loss due to estuarine processes is unknown. Even if ~90% of the bioavailable Fe in the SPM is removed or trapped, the resulting flux to the oceans is still significant (~0.02 Tg/yr). Moreover, benthic release of this particulate associated Fe, alongside Nd, on the Mackenzie shelf may play an important role in delivering a higher proportion of this labile phase to the Arctic Ocean.

For every two moles of sulfate released from the oxidative weathering of pyrite in the Mackenzie basin, 1 mole of Fe will be incorporated into an Fe-oxide. Using the pyrite-derived sulfate flux of Calmels et al., 2007 it is estimated that the oxidative weathering of pyrite will result in the production of ~3.6 Tg/yr of Fe, as Fe-oxides. This is around an order of magnitude greater than the labile Fe flux associated with SPM that we estimate herein (0.2 Tg/yr). This implies a large accumulation of Fe-oxides derived from the oxidative weathering of pyrite within the critical zone in the Mackenzie basin, which are not exported to labile phases in the SPM.

4.6 Nd isotopic end-member compositions and inputs to the Arctic ocean

The Mackenzie River is a large point source of sediment and water to the Arctic Ocean; therefore, it is an important finding that labile Nd has an isotopic composition that is distinct from the bulk SPM. This finding is potentially applicable to all riverine
catchments with marine sedimentary source rocks. It is equally noteworthy that there is variability in dissolved $\varepsilon$Ndc between sampling years. Although our data is similar to the only previous dissolved data point on the Mackenzie (Zimmermann et al., 2009), it extends the range with implications for studies involving $\varepsilon$Nd in the Arctic Ocean (e.g. Deschamps et al., 2019). Despite variability the HH leachates from shallow marine core sites reflect the average dissolved composition of the Mackenzie over decadal timescales. Therefore, such leachates from shelf sediment may provide a more useful integrated $\varepsilon$Nd end-member. This isotopically distinct, labile, phase is maintained offshore, meaning that any labelling of seawater via ‘boundary exchange’ processes on the shelf will have a significantly more radiogenic composition than the bulk sediment. This suggests that bulk shelf sediment and continental margin $\varepsilon$Nd may be systematically offset from the likely oceanic source (Jeandel et al., 2007) as it is the reactive (leachable) compositions which will characterise any shelf inputs.

5 Conclusions

This study highlights the potential for sedimentary rock weathering in the Arctic to provide a critical source of labile Fe. As approximately half of the rocks weathered on land draining into the Arctic Ocean are shales (Amiotte Suchet et al., 2003), similar observations to this study would be expected in other Arctic rivers. The on-going state of permafrost thaw in the Mackenzie basin has resulted in increased slumping in the Peel catchment which has exposed fresh pyrite minerals and resulted in increased sulfuric acid weathering (Zolkos et al., 2018). Increased exposure of pyrite may also lead to increased mobility and dissolution of REEs (and Fe) within this
catchment. However, it is also important to note that delivery of bioavailable Fe from the Mackenzie basin to the Arctic Ocean will have changed in the past, including during periods of glaciation and glacial retreat in this region. Melt water and ice-rafting could have allowed for more direct delivery of un-weathered labile Fe phases to the Arctic Ocean.

Recycled sedimentary components within source rocks may provide labile micronutrients and other trace elements, a process which is likely applicable globally, and not just in the Arctic. Fe, and the supply of other micronutrients that limit primary productivity, are thought to be capable of having long-term and far-reaching effects on global climate, by way of their potential for increasing productivity and organic carbon burial in the oceans. Therefore, when considering increases in nutrient availability in the past, the source lithology and its reactivity must be taken into consideration. We highlight the impact of source lithology on the budget of labile trace elements (Nd) and micronutrients (Fe) in rivers, which has implications for both present and past fluxes to the oceans and paves the way for restructuring how riverine SPM is viewed in terms of its reactivity when sedimentary rocks are present in the source catchment.

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References

Adebayo, S.B., Cui, M., Hong, T., White, C.D., Martin, E.E., Johannesson, K.H., 
2018. Rare Earth Elements Geochemistry and Nd Isotopes in the Mississippi 
River and Gulf of Mexico Mixing Zone. Front. Mar. Sci. 5. 
https://doi.org/10.3389/fmars.2018.00166 

continental rock lithology: Implications for the atmospheric/soil CO₂ uptake by 
continental weathering and alkalinity river transport to the oceans. Glob. 
https://doi.org/10.1029/2002GB001891


...
river; the role of colloidal particles. Chem. Geol. 166, 23–45. https://doi.org/10.1016/S0009-2541(99)00178-3


Figure Captions

Figure 1. Area of study A. Sample locations and elevation (GDEM, resolution 30 Arc second). B. Bedrock geology of the Mackenzie Basin (shaded black line), categorized by rock type (Wheeler et al., 1996). White circles indicate the location of sampling sites identified in A.

Figure 2. Water discharge from the Mackenzie River (2017 and 2018). Daily discharge (lines) from Environment Canada gauging station at Tsiigehtchic, retrieved from the ArcticGro database (https://www.arcticrivers.org/data, Supplementary text S2). ADCP Discharge at the Middle Channel and Tsiigehtchic (this study, light blue, 2017, dark blue 2018).

Figure 3. $\varepsilon$Nd on coupled HH leachates (circles), dissolved (<0.2 $\mu$m only shown) and silicate residue sediment (triangles) at all sampling localities (2017 and 2018). Probability density of sediment residue (green) and leachate (pink) shown, difference in modes (dashed grey line) is indicated (black arrow). Open symbols are bank sediment and coloured symbols, SPM, coloured diamonds are sediment core data. Coloured squares are a shale fragment HH leachate and residue (pink and green respectively), which was not used in the linear regression. Error bars are 2σ analytical uncertainty (where visible or smaller than the symbol size). 1:1 line (dashed line) is shown.
Figure 4. Two sediment depth profiles from the Mackenzie River (Middle Channel, 2017). Water depth is normalised to the deepest sample. Error bars are $2\sigma$ analytical uncertainty. Dissolved compositions are from waters obtained at the surface and at depth.

Figure 5. Probability density of the fraction of a suite of elements in leachates relative to the total (sum of leachates and residue). Data is from all sampling sites across both years. The fraction of the HH leachate, acetic acid leachate, and the sum of all leaching steps are shown. Symbols are data points that form the probability distribution.

Figure 6. Characterisation of sequential extractions A. MREE/MREE* HREE/LREE cross-plot, following Martin et al., 2010, alongside a non-exhaustive literature compilation (plotted for reference, Supplementary Text S2). HREE= $\Sigma$(Tm, Yb, Lu) LREE= $\Sigma$(La, Pr, Nd), MREE= $\Sigma$(Gd, Tb, Dy), MREE*=(HREE+LREE)/2. All concentrations are normalised to PAAS (after Pourmand et al., 2012). Foraminiferal coatings and marine leachates are extractions thought to represent Fe-Mn oxyhydroxides. B. A REE partitioning in a Mackenzie (Middle Channel, 2017) SPM sequential extraction. Left hand side axis is the REE concentration, right hand side axis fraction of total (sum of leachates and residue) REE concentration (bars) in each phase. C. $^{87}$Sr/$^{86}$Sr against $\varepsilon$Nd on Mackenzie (Middle Channel, 2017) SPM sequential extractions and water ($^{87}$Sr/$^{86}$Sr data point from Tipper et al., 2021). $2\sigma$ analytical uncertainty is shown, unless smaller than the symbol size.
Figure 7. Schematic indicating the mechanisms presented herein that may lead to more radiogenic $\varepsilon$Nd in the HH leachates of SPM and the dissolved load of the Mackenzie river, when compared to the SPM silicate residue.

Figure 8. Probability density of calculated $f_{\text{Nd, auth}}$ (equation 1) for 4 sampling sites generated using Monte Carlo methods. Median value (white line) and interquartile range (dashed lines) are shown. Input compositions for this calculation are listed in Table S13.
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

acetic acid
hydrochloric acid
HH leach

fish teeth/debris
foraminiferal coatings
marine sediment leachates
marine detrital sediment
sedimentary rock leachates
shale residue

This study

Bell-shaped
MREE Bulge
Flat

HREE/LREE

Sample/PAAS

Fraction of total

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

residue
acetic acid
hydrochloric acid
HH leach

Sm/Nd = 0.15
Sm/Nd = 0.31
Sm/Nd = 0.26

Silicate

Leachable

δSr/86Sr

εNd

0.725

0.720

0.715

0.710

-14

-12

-10

0.710

0.715

0.720

0.725

0.15

0.31

0.26

δSr/86Sr

εNd

residue
hydrochloric acid
acetic acid
HH leach
dissolved (<0.2 μm)
Table 1. $\varepsilon$Nd and Nd concentrations on different filtrates from the Mackenzie River and a major tributary (2018).

<table>
<thead>
<tr>
<th>River</th>
<th>Filter Size/MWCO</th>
<th>$\varepsilon$Nd</th>
<th>Error (2$\sigma$)$^1$</th>
<th>[Nd]</th>
<th>Error (2$\sigma$)$^2$</th>
<th>% of &lt;0.2μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mackenzie River</td>
<td>&lt;0.2μm</td>
<td>-12.97</td>
<td>0.15</td>
<td>20.7</td>
<td>0.7 (n=2)</td>
<td></td>
</tr>
<tr>
<td>(Middle Channel)</td>
<td>10kda</td>
<td>-12.41</td>
<td>0.51</td>
<td>10.4</td>
<td>1.4 (n=2)</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>1kda</td>
<td>-13.40</td>
<td>0.34</td>
<td>5.9</td>
<td>0.4 (n=2)</td>
<td>29%</td>
</tr>
<tr>
<td>Peel River</td>
<td>&lt;0.2μm</td>
<td>-11.47</td>
<td>0.15</td>
<td>12.1</td>
<td>n/a (n=1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10kda</td>
<td>-11.61</td>
<td>0.34</td>
<td>7.1</td>
<td>0.1 (n=2)</td>
<td>59%</td>
</tr>
<tr>
<td></td>
<td>1kda</td>
<td>n.d</td>
<td>n.d</td>
<td>4.1</td>
<td>0.8 (n=2)</td>
<td>34%</td>
</tr>
</tbody>
</table>

$^1$Analytical uncertainty, $^2$Average and 2$\sigma$ of two replicate measurements during different analytical sessions, $^3$Average and 2$\sigma$ of two full procedural replicates (including filtration)
Supplementary information for

Constraints on the source of reactive phases in sediment from a major Arctic river using neodymium isotopes

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This file contains:

Supplementary text 1-4
Supplementary data tables S1 to S3
Supplementary figure S1
Supplementary references
Supplementary data file contains supplementary data tables S4 to S15
1. Complete analytical and procedural details

Samples used in this study are listed in Supplementary Table S4. Suspended sediment (>0.2 μm) retained from filters and the corresponding <0.2 μm filtered waters have the same sample name. Alkalinity was determined by Gran Titration (Stumm and Morgan, 1996) in field, and is given in Supplementary Table S4, alongside the pH, temperature and discharge obtained with an Acoustic Doppler Current Profiler (ADCP, Rio Grande II (1200 kHz), Teledyne Instruments) deployed from a moving boat. Sediment core material was supplied by the Geological Survey of Canada (Supplementary Table S5).

1.1 Fe-precipitation for dissolved Nd isotope analysis

Following Hindshaw et al., 2018, approximately 10 L of filtered <0.2μm waters were acidified to pH 2 using 9M HCL, 100-200 mg of pre-cleaned (following the methods of Arendt et al., 2015) Fe as FeCl₃ in 3M HCl was added and allowed to equilibrate, the pH was then raised to 8-9 using concentrated ammonia or NaOH, and Fe allowed to precipitate, alongside the REEs. Ammonia is typically used in order to raise the pH in Fe co-precipitation methods (e.g. Greaves et al., 1989; Hindshaw et al., 2018). Fe co-precipitation methods were developed in order preconcentrate REEs and other trace elements from seawater (e.g. Greaves et al., 1989, and references therein) where ammonia would be preferable to NaOH as to not add additional Na to the sample. However, NaOH was found as a suitable alternative reagent for use in the field for the preconcentration of Nd from
freshwaters, as it can be more easily transported and added to the sample solution as solid pellets. The Fe co-precipitate was retrieved either through filtration at 0.45 μm in a separate custom-built closed system filtration unit (which was pre-cleaned with filtered <0.2 μm waters of the same sample), with the filter paper retained (in 2018), or allowed to settle over ~48 hours with the remaining water poured off, and ~1L slurry retained and stored in an acid cleaned HDPE bottle (in 2017). Nd sample sizes used in this method varied with the concentration of the waters from which they were obtained (concentrations are given in Table S10 in the supplementary data tables), although typically were around 100 ng. The range was from approximately 60 ng to nearly 8000 ng (CAN18-39, from the small Peel River tributary with a concentration of 950 ppt Nd).

The Fe co-precipitate was re-dissolved in 10M HCl and dried down before being treated overnight in concentrated aqua-regia to destroy organics. Fe was removed using a large (bed volume 20 ml) cation exchange column (Bio-rad AG50W-X8, 200-400μm mesh-size), where the sample was redissolved and loaded in 15ml 1M HCl/0.05M HF, with a further 15ml 1M HCl/0.05M HF added to elute hafnium. Fe was flushed out in 75ml of 3M HCl, and the REEs and other remaining matrix elements (e.g. Ba, Sr) were eluted in 100ml 6M HNO_3 and retained. The REEs were then separated from any remaining (~1% of the total) Fe and matrix elements (e.g. Ba) using a smaller (resin bed 250 µl) cation exchange column (Bio-rad AG50W-X8, 200-400 μm mesh-size) following the
method of Greaves et al., 1989, before Nd was separated from Sm using LnSpec resin.

In order to test reproducibility several full procedural replicates were carried out and all reproduced values within error (Table S1). Filtered water taken from different depths in the same river at the same location on the same day that underwent separate in field Fe co-precipitation was deemed a full procedural replicate for dissolved analysis, as the waters are well mixed within the river channel. The Mackenzie River (middle channel) was resampled after one week after the initial sampling during the 2017 field campaign, and a 500 ml <0.2 μm water sample retained in an acid cleaned HDPE bottle representing a Nd sample size of 6.5 ng. In order to test check if there were any differences between laboratory and in field Fe co-precipitation, this sample underwent Fe-co-precipitation in a class 1000 clean laboratory at the University of Cambridge before the same column and analytical procedures as the other in field co-precipitates and produced an εNd within analytical uncertainty of in field Fe co-precipitated samples taken a week prior (Table S1). Several full procedural blanks and column chemistry blanks were analysed using a $^{150}$Nd spike on a Neptune Plus MC-ICP-MS at the University of Cambridge, and ranged from 4-7 pg, always representing < 1% of the sample size, and < 0.5% of a typical sample.

In addition to replicates, tests were carried out on 10L of MQ water spiked with 150ng, 100ng and 50ng of the reference standard JNd1-1, and co-precipitated with iron under normal laboratory conditions with the same equipment, method
and reagents as used during field trips. One 150 ng JNdi-1 spiked MQ water was co-precipitated with NH₃, in addition to 3 (150 ng, 100 ng, 50 ng) JNdi-1 spiked MQ waters which were co-precipitated with NaOH. All reproduced the accepted value of JNdi-1 within analytical uncertainty (Fig. S1).

Figure. S1. εNd values for 4 different tests: 150ng JNdi-1, co-precipitated with ammonia (NH₃), and 150 ng, 100 ng, and 50 ng, co-precipitated with sodium hydroxide (NaOH). The accepted value of JNdi-1 is shown for reference as the grey bars (Tanaka et al., 2000). Error bars represent 2σ analytical uncertainty.
Table S1. Dissolved (<0.2 μm) εNd procedural replicates

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Depth (m)</th>
<th>εNd (±2σ)¹</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mackenzie (middle channel) 03/06/2017 and 10/06/17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAN17-04</td>
<td>0</td>
<td>-10.67(±0.11)</td>
<td>In field Fe co-precipitation</td>
</tr>
<tr>
<td>CAN17-05-08</td>
<td>7-10</td>
<td>-10.52(±0.19)</td>
<td>In field Fe co-precipitation</td>
</tr>
<tr>
<td>CAN17-53</td>
<td>0</td>
<td>-10.93(±0.51)</td>
<td>500ml &lt;0.2μm filtered water, lab Fe co-precipitation</td>
</tr>
<tr>
<td>Mackenzie River (Tsiigehtchic) 05/06/17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAN17-16</td>
<td>0</td>
<td>-12.40(±0.15)</td>
<td>In field Fe co-precipitation</td>
</tr>
<tr>
<td>CAN17-17-20</td>
<td>8.5</td>
<td>-12.19(±0.15)</td>
<td>In field Fe co-precipitation</td>
</tr>
<tr>
<td>Arctic Red River (Tsiigehtchic) 05/06/17</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CAN17-26-29</td>
<td>3.5-4</td>
<td>-8.50(±0.20)</td>
<td>In field Fe co-precipitation</td>
</tr>
<tr>
<td>CAN17-30</td>
<td>0</td>
<td>-8.59(±0.18)</td>
<td>In field Fe co-precipitation</td>
</tr>
</tbody>
</table>

¹analytical uncertainty

1.2 Ultrafiltration

Tubular dialysis membranes, with a molecular weight cut-off of 1 kDa and 10 kDa from Spectra/Por 7® were pre-cleaned in 2% HNO₃ and rinsed with MQ. 4L of prefilted water was collected in acid cleaned HDPE bottles, to which the dialysis tubing filled with MQ was added and left to equilibrate for 72 hours. Around 200-400 ml of water was retained from the dialysis tubing for each ultrafiltrate. Both quantities of water (filtered sample and MQ) were pre-weighed in order to dilution correct the ultra-filtrate. Full procedural replicates for both pore sizes (1 kDa and 10 kDa) and sampling sites were carried out.
Unacidified samples both inside and outside the dialysis tubing were collected and analysed for Cl\textsuperscript{-} concentrations on a Thermo Scientific Dionex ICS-5000+ High Performance Ion Chromatographer (HPIC) using a 4 x 250mm Ionpac AS18 column with 24-31mM potassium hydroxide eluent, at the University of Cambridge to check equilibrium was reached. Cl\textsuperscript{-} concentrations outside and inside the dialysis reproduced with 4%.

The ultra-filtrated sample was acidified to a pH of 2 using 9M HCl. Acidified <0.2 μm and ultra-filtrated waters were analysed for a suite of cations (Ba, Ca, K, Mg, Na, Si, Sr) alongside sulfur, on an Agilent 5100 ICP-OES, at the University of Cambridge (summarised in Table S2). Full procedural replicates show no significant difference in concentration when compared with the corresponding <0.2 μm filtered water, verifying that equilibrium was reached for these elements (Table S2). Full procedural replicates for both pore sizes (1 kDa and 10 kDa) were analysed for Nd concentrations (shown in Table 1), but due to the small sample sizes involved for isotopic analysis the replicated filtrates of the same molecular cut off weight were combined after other major and elemental concentrations were determined.
In order to minimize blank due to the low concentration of these samples, ultra-
filtrated waters were collected in acid cleaned HDPE bottles in the field, and then
subsequently co-precipitated with ~3 mg Fe as FeCl$_3$ for Nd isotope analysis in a
class 10000 clean lab at the University of Cambridge, rather than in the field. Due
to the smaller concentration of Fe used, the first stage of cation exchange
chemistry used for other Fe co-precipitate samples was not necessary. Fe and
other matrix elements were removed using the second stage small (250 μl bed
volume) cation-exchange column, and Nd separated from Sm using LnSpec
resin. A procedural blank, measured using a $^{150}$Nd spike on a Neptune Plus MC-

### Table S2. Major elemental analysis on ultra-filtrated water full procedural replicates

<table>
<thead>
<tr>
<th>Filter size/MWCO</th>
<th>Ba μM</th>
<th>Ca μM</th>
<th>K μM</th>
<th>Mg μM</th>
<th>Na μM</th>
<th>Si μM</th>
<th>Sr μM</th>
<th>S μM</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.2 μm</td>
<td>0.396</td>
<td>884</td>
<td>28.4</td>
<td>389</td>
<td>277</td>
<td>63.7</td>
<td>2.02</td>
<td>445</td>
</tr>
<tr>
<td>10 kda</td>
<td>0.392</td>
<td>885</td>
<td>28.8</td>
<td>386</td>
<td>279</td>
<td>64.3</td>
<td>2.01</td>
<td>448</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>99%</td>
<td>99%</td>
<td>101%</td>
<td>99%</td>
<td>102%</td>
<td>100%</td>
<td>99%</td>
<td>101%</td>
</tr>
<tr>
<td>1 kda</td>
<td>0.380</td>
<td>858</td>
<td>27.8</td>
<td>378</td>
<td>274</td>
<td>63.0</td>
<td>1.97</td>
<td>441</td>
</tr>
<tr>
<td>Recovery (%)</td>
<td>97%</td>
<td>98%</td>
<td>99%</td>
<td>98%</td>
<td>100%</td>
<td>99%</td>
<td>98%</td>
<td>100%</td>
</tr>
</tbody>
</table>

| Recovery (%)     | 99%   | 99%   | 101% | 99%   | 102%  | 100%  | 99%   | 101% |
| 10 kda           | 0.402 | 1297  | 19.1 | 788   | 191   | 59.4  | 1.66  | 1054 |
| Recovery (%)     | 103%  | 104%  | 109% | 101%  | 105%  | 103%  | 101%  | 102% |
| 1 kda            | 0.384 | 1232  | 17.0 | 760   | 177   | 56.8  | 1.58  | 997  |
| Recovery (%)     | 98%   | 98%   | 97%  | 97%   | 97%   | 98%   | 98%   | 97%  |

10 kda

| Recovery (%)     | 99%   | 99%   | 101% | 99%   | 102%  | 100%  | 99%   | 101% |
| 1 kda            | 0.405 | 1309  | 18.4 | 789   | 192   | 59.1  | 1.65  | 1064 |
| Recovery (%)     | 103%  | 104%  | 109% | 101%  | 105%  | 103%  | 101%  | 102% |
| 1 kda            | 0.386 | 1220  | 16.7 | 758   | 177   | 57.6  | 1.58  | 996  |
| Recovery (%)     | 98%   | 98%   | 97%  | 97%   | 97%   | 98%   | 98%   | 97%  |
ICP-MS was 7 pg, representing <1% of the smallest sample analysed (~ 1 ng). In total 3 ultrafiltrate samples were processed for Nd isotope analysis, the lowest sample size processed was 1.4 ng of Nd (CAN18-02, 1 kDa) and the others were 2.4 ng and 2.6 ng.

1.3 Sequential extractions

Suspended sediment was extracted from filters, freeze-dried and lightly ground with a mortar and pestle and aliquoted at Durham University, Department of Geography prior to sequential extraction. Bedload samples were dried in an oven at 40°C overnight and ground with a mortar and pestle at the University of Cambridge.

Sequential extractions were carried out on dried sediment samples in a class 1000 clean laboratory at room temperature. The amount of reagent used was scaled to the sample size (rounded to the nearest 50 mg), and the volume of reagent specified in Table S3 is representative of a sample size of ~100 mg.
### Table S3. Sequential extraction procedure

<table>
<thead>
<tr>
<th>Stage</th>
<th>Reagent</th>
<th>Volume of reagent</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1M NH₄Cl</td>
<td>4ml</td>
<td>Shake vigorously, react for 20mins in ultrasonicator, centrifuge 15mins @ 5000rpm</td>
</tr>
<tr>
<td>2</td>
<td>5mM hydroxylamine hydrochloride-3mM Na-EDTA-1.5% acetic acid buffered to a pH of ~4 with NaOH</td>
<td>2.5ml</td>
<td>Shake vigorously, 50-60mins on shaker, water wash sediment with MQ 3 times, centrifuging each time (15min) @ 5000rpm</td>
</tr>
<tr>
<td>3</td>
<td>1.7M Acetic Acid</td>
<td>4ml</td>
<td>Shake vigorously, react for 20mins in ultrasonicator, 3 hours on shaker, centrifuge 15mins @ 5000rpm</td>
</tr>
<tr>
<td>4</td>
<td>1M HCl</td>
<td>4ml</td>
<td>Shake vigorously, leave overnight on shaker, water wash sediment 3 times in MQ @ 5000rpm</td>
</tr>
</tbody>
</table>

After leaching dried sediment residues were ignited at 950°C. Residue sediment was then fused with lithium tetraborate/metaborate flux (1:4 ratio) before dissolution in 2.5% HNO₃. For both sediment residue and leachate samples typically around 100 ng of Nd was dried down and treated with aqua regia prior to Nd column chemistry.

Mass balance was checked on two SCo-1 sequential extractions (100 mg and 50 mg), as well as on two samples were there was enough material to also analyze the bulk sediment composition. Elements usually reproduced within 10%, and always with 20% (Supplementary Table S6). Elements hosted mainly in the
silicate phase (Al, Ti) were monitored in leach solutions to assess detrital
dissolution and were not significantly mobilized.

1.4 Analytical Reproducibility

1.4.1 Agilent 5100 ICP-OES

External reproducibility was monitored using certified standards, diluted to
appropriate concentrations for each matrix and calibration line.

1.4.1.1 Residue and bulk sediment samples

The calibration line was made up from lithium-borate fused micro-beads made
from a mixture of USGS rock standards BHVO-2 and SDC-1, dissolved in 2%
HNO₃. External reproducibility and drift were monitored with the following suite of
USGS rock standards: BCR-2, SCo-1, BHVO-2 and SDC-1. They were
processed alongside samples and analysed every 5 to 10 samples during
analytical sessions. Repeated analyses yielded values which were accurate to
within ±3% for Al, Na, Si, Mn, Zn, ±5% for Ba, Fe, Mg, V, Ti, ±6% for Ca, K and
±7% for Sr, n=67. Repeated analysis for Nd was accurate to within ±15% (n=56),
and any solution (sample or standard) analysed at or below ~5 ppb was
considered unreliable and discarded.

1.4.1.2 Leachate Samples

The calibration line was made up of single element standards diluted in a matrix-
matched solution (i.e. diluted in the appropriate ‘blank’ leach solution at the right
concentration to match that of the sample being analysed). Drift was monitored using a 50% calibration line standard made up from single element standards, run every 5 to 10 samples, and external reproducibility was monitored using certified standards – a USGS rock standard, BCR-2, digested in HF, and diluted to match the sample matrix, and a surface water standard SPS-SW2 (Spectrapure Standards, Olso Norway), run either concentrated (in 0.5% HNO₃) or as a 1:10 dilution, diluted with the appropriate matrix solution.

For the NH₄Cl calibration line, repeated analyses on SPS-SW2 (in 0.5% HNO₃) and a 1:10 dilution of SPS-SW2 in matched NH₄Cl matrix were accurate to within ±5% Ba, Fe, Mg, Mn, Si and Sr, ±8% for Ca and Na, and ±14% for Fe, K and Al (n=21). Precision was 5%(RSD) for Al, Ba, Mg, Na, Si, Sr (n=21). Fe, K and Mn were precise to better than 4% (RSD) for SPS-SW2 (n=8) and 15% (RSD) for the 1:10 dilution of SPS-SW2 (n=13). Ti and Nd were below the detection limit in NH₄Cl samples. Nd in the SPS-SW2 standard was accurate to ±1%, (10% (RSD), n=8), but below detection in the 1:10 dilution.

For the weak acid reductive leaches, repeated analysis on a matrix matched dilute BCR-2 standard, reproduced certified values to within ±5% for Ba, Ca, Fe, Mg, Mn, Nd and Sr, and within ±10% for Al, K and ±15 for Ti (n=21). For SPS-SW2 certified values were reproduced within ±5% for Al, Ba, Ca, Fe, Mg, Mn, Si, Sr (n=7). The overall precision was always better than 10% (RSD) for all elements (n=28).
For the AcOH calibration line the matrix matched dilute BCR-2 standard reproduced values to within ±5% for Al, Ba, Ca, Fe, Mg, Na, Nd, and Sr, and within ±8% for K and Mn (n=14). For SPS-SW2, values were accurate to within ±5% for Al, Ba, Ca, Fe, Mg, Mn, Na, Nd, Si and Sr (n=7). The overall precision was better than 5% (RSD, n=21) for all elements apart from Na and Nd, which were better than 10% for the BCR-2 standard and 20% for SPS-SW2. For both the weak acid reductive leach and the AcOH leach, Ti was generally below detection in samples.

For the HCl calibration line, the dilute BCR-2 rock standard and a 1:10 dilution of SPS-SW2 (in 0.1M HCl) were analysed. Several elements (Fe, Mg, Nd) were out of range of the calibration line for the dilute SPS-SW2 (which was generally more dilute than samples), and so the precision and accuracy is not reported for these elements. The 1:10 SPS-SW2 reproduced certified values to within ±10% for, Al, Ba, Ca, K, Mn, Na, Si and Sr (n=15). The diluted BCR-2 standard, reproduced values to within ±3% for Al, Ca, Fe, Mg, Mn, Na, Sr, ±6% for Ba, Nd, and ±10% for Ti (n=22). The overall precision was better than 5% (RSD, n=37), except for elements outside the calibration range.

Na was not measured for the weak acid reductive leach, due to the large amount of Na present in the matrix (as the leach contains Na-EDTA and NaOH). It is noted that Na is concentrated in the sediment residue, and thus when certified values (for SCo-1) are compared to the sum of the different leaching steps and
residue and bulk values, the %Na (relative to the total) extracted in the weak acid reductive leach must be negligible (Supplementary Table S3).

1.4.1.3 Filtered waters

Cation and additional (e.g. Fe, Mn and S) concentrations were measured on acidified waters using a calibration line made of single elemental standards across an appropriate range. External reproducibility was monitored by repeated analysis of suite of certified water standards (SLRS-5, SLRS-6 (National Research Council, Canada) and SPS-SW2 (Spectrapure Standards AS, Oslo, Norway)) and were accurate within ±10% for all reported elements with a precision (RSD) of 5% or better. Al concentrations are not reported but were monitored to check for particulate contamination of the filtered waters, which was not observed in any samples.

1.4.2 Nd isotopic analysis

Nd isotopic analysis was carried out on a Neptune Plus MC-ICP-MS at the University of Cambridge, Department of Earth Sciences, with a CETAC Aridus II introduction system and Jet/X Ni cones in order to maximize sensitivity for small sample sizes, with a 50 μl/min nebulizer. Oxide production was monitored throughout analytical sessions and minimized to below 0.4%. Typically, samples were analysed at a Nd concentration of 20 ppb however for smaller samples sizes (such as the ultrafiltrates), analyses were carried out at lower Nd concentrations, as a separate analytical session with concentration matched standards, to a minimum concentration of 5 ppb.
Long-term external and internal reproducibility was monitored using digested USGS rock standards, with at least one standard analysed per analytical session at the same concentration as samples, and standards were regularly passed through column chemistry at the same time as samples. Rock standards produced values as follows: BHVO-2 $\varepsilon$Nd=6.79±0.18 ($2\sigma$, n=18), BCR-2 $\varepsilon$Nd=-0.09±0.27 ($2\sigma$, n=17), SCo-1 $\varepsilon$Nd=-10.48±0.27 ($2\sigma$, n=8), G-2 $\varepsilon$Nd=-8.09±0.02 ($2\sigma$, n=3). All 4 rock standards are within error of previously published values: BHVO-2 $\varepsilon$Nd=6.75±0.21 ($2\sigma$) (Weis et al., 2005), BCR-2 $\varepsilon$Nd=-0.02±0.23 ($2\sigma$) (Weis et al., 2006), SCo-1 $\varepsilon$Nd =-10.77±0.57 ($2\sigma$) (Hindshaw et al., 2018), G-2 $\varepsilon$Nd=-7.95±0.26 ($2\sigma$) (Weis et al., 2006).

1.5 REE Analysis

Nd concentrations on filtered waters were determined by isotope dilution, alongside the rest of the REE (only Nd concentrations are reported). This method is modified from Greaves et al., 1989 with measurement by ICP-MS after Rousseau et al., 2013 and Skinner et al., 2019. Approximately 10ml of filtered water was spiked with a mixed REE spike, dried, and then passed through cation exchange (Biorad AG50W-X8 200-400μm mesh-size, hydrogen form, resin bed volume 250μl) to remove elements with mass interferences (e.g. Ba oxides) and other matrix ions. Sample/spike ratios were optimised with an uncertainty magnification factor of ~1 and always < 3. Samples were measured on a Thermo Element-XR ICP-MS coupled with an ESI quartz APEX-IR introduction system, with N₂. Oxide generation was monitored and minimised, with oxide and isobaric interferences corrected for offline. REEs concentrations were calculated offline.
following the methods of Skinner et al. 2019, with the monoisotopics and La
determined using an external mixed REE standard with the spiked REE
concentrations used as internal standards to correct for yield. Although the
column chemistry removed ~98% of the Ba present in samples, due to the
concentration of Ba being so much greater than that of La in natural waters, it
was not possible to correct for the isobaric interference of Ba on $^{138}$La. Therefore,
La concentrations are calculated using $^{139}$La, in a similar way to the
monoisotopics, following Skinner et al., 2019. Several samples were measured in
duplicate during separate sessions in order to check instrument reproducibility,
with a 2σ of better than 5%. External reproducibility was monitored using a USGS
BCR-2 rock digest (HF digested) solution diluted to a comparable concentration,
which was spiked and processed using the same method alongside samples,
whose values are summarised in Supplementary Table S1. Two filtered River
Severn (UK) waters were used as an internal standard to check long-term
reproducibility, being processed as separate aliquots at the same time as
samples (Supplementary Table S12). Procedural blanks were processed and
measured alongside samples, typically representing <1% of sample sizes. Thus,
samples were not blank corrected.

Nd concentrations were measured in leachate solutions and residue solutions on
an Agilent 5100 ICP-OES using the highest intensity interference free
wavelength, $\lambda=406.108$ nm, in axial mode, similar to that used for marine
authigenic phases. However as <2 ppb Nd solutions are below the detection limit
of ICP-OES instruments ([Practical Inductively Coupled Plasma Spectrometry],

2019), and samples values were only considered reliable at >~4 ppb, some samples could not be analysed using this method, and analytical errors where generally greater for Nd than for other elements. Therefore, in order to verify Nd concentrations in sediments and sediment leachates and determine the concentrations of all the REEs, two additional methods were applied. Several weak acid reductive leachate solutions were measured directly on a Thermo Element-XR ICP-MS, with a cyclonic spray chamber, using a matrix matched calibration line made up of an REE standard diluted with a blank leach solution. Oxide generation was monitored and minimised using single element REE standards, with oxide and isobaric interferences corrected for offline, and drift was monitored and corrected for using repeat calibration line standards. Reproducibility was monitored using two certified standards: a USGS BCR-2 rock digest solution diluted to a comparable concentration with a blank leach solution, and SPS-SW2 (Spectrapure Standards, Olso Norway), which reproduced certified values within ±10% for all REE, with a 1σ (n=2 measurements) of 4% or better. One suspended sediment sample (CAN17-10, Mackenzie, middle channel, 2017) was chosen to accurately determine the partitioning of the REEs between the different leachate and residue phases using isotope dilution, in the same way as for filtered waters. The HCl, acetic acid and weak-acid reductive leaches and residue were measured in order to determine the partitioning of the REEs between the different phases. REE concentrations within the NH₄Cl leach were below detection and so not reported. 2 additional residue samples were also measured for their REE concentration.
using the same method. The residue and leach solutions were diluted to a comparable concentration, a mixed REE spike added such that the uncertainty magnification factor for spiked elements was \( \sim 1 \) (and always \(<3\)) and passed through cation exchange resin before being analysed in the same way as the water samples. One leachate sample was analysed twice, once directly on the Element-XR in addition to being measured via isotope dilution, with a precision of 10\% (RSD, \( n=2 \)) for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm and 13\% for Er, Yb and Lu.
Supplementary text 2

Mackenzie River Daily Discharge

Daily discharge data plotted in Fig. 2 is retrieved from the ArcticGRO data base (https://www.arcticrivers.org/data, Shiklomanov et al., 2020). Data from 2018 is listed as provisional.

MREE/MREE* HREE/LREE cross plot

Literature data used in Fig. 5 is retrieved from the following publications:

Bayon et al., 2002; Blaser et al., 2016; Charbonnier et al., 2012; Hindshaw et al., 2018; Martin and Haley, 2000; Moiroud et al., 2013; Wilson et al., 2013.

Supplementary text 3

Mass Balance Calculations

The values used to solve equation 1 and 2 are indicated in Table S15 (supplementary data file). Errors are estimated using Monte Carlo methods calculating the unknown for 100,000 values of each variable. Values which are known (measured) are considered to approximate to normal distributions and those which are unknown (and therefore estimated) are considered as uniform distributions in order to reflect the uncertainty in those values, and account for all possibilities at equal probability.

\[
\frac{\text{Nd}}{\text{Fe}}_{\text{sil}}
\]

is taken as the average of the Nd/Fe molar ratio in all riverine suspended and bank sediment residues, which averages to within error of upper continental crust estimates \((\frac{\text{Nd}}{\text{Fe}})_{\text{UCC}} \times 1000 = 0.27\pm0.03\), Rudnick and
Gao, 2014).  

$\left(\frac{\text{Nd}}{\text{Fe}}\right)_{\text{auth}}$ is the largest unknown and therefore considered as a range from the HH leaches from two samples from a small Peel River tributary (CAN18-43, and CAN18-45, therefore n=2), sampled from a uniform distribution. The HH leaches of these samples were considered to represent the authigenic fraction of the source rocks. $f_{\text{Fe,auth}}$ was only determined for the two riverine sample sets in order to avoid any potential for changes in the Nd/Fe ratio due to estuarine processes affecting the calculation.

In order to provide an additional constraint on the $\varepsilon$Nd mass balance calculated above, in particular the integrated $\varepsilon$Nd$_{\text{auth}}$ composition, which is unknown, equation 2 can be combined with equation 1:

$$\varepsilon_{\text{Nd}}^{\text{labile}} \left(\frac{\text{Nd}}{\text{Fe}}\right)_{\text{labile}} = f_{\text{Fe,sil}} \varepsilon_{\text{Nd}}^{\text{sil}} \left(\frac{\text{Nd}}{\text{Fe}}\right)_{\text{sil}} + f_{\text{Fe,auth}} \varepsilon_{\text{Nd}}^{\text{auth}} \left(\frac{\text{Nd}}{\text{Fe}}\right)_{\text{auth}} \quad (S1)$$

where $f_{\text{Fe,auth}} + f_{\text{Fe,sil}} = 1$.

This equation can therefore be solved for $\varepsilon$Nd$_{\text{auth}}$, using the distribution of $f_{\text{Fe,auth}}$ calculated from Equation 2, and then the solution from equation 1 can be refined. Re-solving Equation 1 using the solution of $\varepsilon$Nd$_{\text{auth}}$ from equation S1, the interquartile range from the sum of the two riverine datasets (Middle Channel, 2017 and 2018) refines the estimate of $f_{\text{Nd,auth}}$ to between 11-30%.

Equation S1 is solved for $\varepsilon$Nd$_{\text{auth}}$, using values indicated in the supplementary data file Table S13, and results are given in Table S15. The distribution produced for $\varepsilon$Nd$_{\text{auth}}$ is narrowed to exclude values outside the reasonable
range expected (values calculated outside of the range $\varepsilon_{\text{Nd}_{\text{auth}}} \geq \varepsilon_{\text{Nd}_{\text{labile}}}$ and $\varepsilon_{\text{Nd}_{\text{auth}}} < 10$ are excluded).

Although this represents a refinement of the range from the first calculation, it is noted that the uncertainties and assumptions involved in calculating $f_{\text{Fe,auth}}$ will also propagate to this re-evaluation of $f_{\text{Nd,auth}}$. Resulting probability distributions for calculated values are all positively skewed such that a higher proportion (up to 100%) of Fe or Nd derived from inherited authigenic phases cannot be ruled out.

**Supplementary text 4**

**Dissolved Fe Flux estimates**

Approximate dissolved (<0.2 μm) Fe flux estimates are calculated using the average concentration of dissolved Fe measured at the Mackenzie Middle Channel across both years (181 nM, supplementary data Table S7) and annual discharge (316 km$^3$/yr) from the ArcticGRO data base (https://www.arcticrivers.org/data, Shiklomanov et al., 2020). The resulting Fe flux was calculated to be 0.00006 Tg/yr, representing 0.027% of the estimated labile Fe flux from SPM (0.21 Tg/yr).

Dissolved Fe concentrations in the Mackenzie are similar to or smaller than that measured in other Arctic Rivers (250–650 nM for the Ob and Yenisey 410–7132 nM for the Lena, (Klunder et al., 2012, and references therein)).

5. **Supplementary references**


Rousseau, T.C.C., Sonke, J.E., Chmeleff, J., Candaudap, F., Lacan, F., Boaventura, G., Seyler, P., Jeandel, C., 2013. Rare earth element

https://doi.org/10.1039/C3JA30332B


https://doi.org/10.1016/B978-0-08-095975-7.00301-6


https://doi.org/10.1016/j.gca.2018.10.027


https://doi.org/10.1029/2006GC001283
