Decoupling of dissolved and bedrock neodymium isotopes during sedimentary cycling

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Abstract

and sediments, with implications for the isotopic composition of seawater, and 2) the large scale decoupling between a rapidly exchanging labile reservoir and a silicate-bound reservoir during sediment recycling.

The radiogenic neodymium isotope ratio $^{143}\text{Nd}/^{144}\text{Nd}$ (expressed as ϵNd) has been applied to examine seawater elemental budgets, sedimentary provenance, oceanic water mass source and circulation, large scale geochemical cycling, and continental crust growth rates. These applications are underpinned by the assumption that during sedimentary processing the parent/daughter (samarium/neodymium) ratio is conservative during low temperature fluid related processes. In this study, we report ϵNd data from two streams draining sedimentary formations in the Arctic archipelago of Svalbard. The ϵNd value of the dissolved load is offset from stream suspended sediment samples by up to 5.5 epsilon units. We demonstrate that dissolved load ϵNd values are controlled by the dissolution of labile phases present in the catchment rocks which are isotopically distinct from the silicate residue and account for up to 12 % Nd in the bulk sediment. This study highlights;

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Introduction

Radiogenic neodymium isotopes ($^{143}\text{Nd}/^{144}\text{Nd}$), commonly reported as ϵNd (Goldstein and Jacobsen, 1987), have influenced our understanding of geophysical processes, from planetary differentiation to ocean circulation. Continental growth curves are based on ϵNd values (Taylor and McLennan, 1985) and changes in ocean dynamics and silicate weathering have been inferred from ϵNd measurements (Piepgras and Wasserburg, 1980; Bayon *et al.*, 2009).

On a finer spatial and temporal scale, variations in the ϵNd values of seawater recovered from archives, such as foraminifera (*e.g.*, Vance and Burton, 1999) and Fe-Mn (oxyhydr) oxides (*e.g.*, Bayon *et al.*, 2004), are commonly interpreted as indicating relative contributions of different water masses and associated changes in ocean circulation. The accuracy of conclusions gleaned from these sediment and seawater ϵNd records is however dependent on understanding the processes affecting the Nd concentration and isotopic composition during transport of Nd from rock to seawater *via* rivers and during sediment dissolution in the ocean (*e.g.*, Jeandel *et al.*, 2007).

Many studies have assumed that solutes released during dissolution have the same ϵNd composition as the bulk rocks being dissolved. However, riverine dissolved ϵNd values can be different from both the suspended load and the bedrock

over which the river has flowed (Goldstein and Jacobsen, 1987; Tricca *et al.*, 1999; Andersson *et al.*, 2001; Rickli *et al.*, 2013). Additionally the rare earth element (REE) chemistry of sediment/soil leachates indicates that REE (including Sm and Nd) are mobile and can be fractionated during chemical weathering and diagenesis (*e.g.*, Bock *et al.*, 1994; Viers and Wasserburg, 2004). Goldstein and Jacobsen (1987) proposed that dissolved load ϵNd values are controlled by labile phases but direct evidence has been lacking. In this study we present ϵNd data on the dissolved load, stream suspended sediment and leachates (which access labile phases) of rock and glacial sediment samples in the same catchment to investigate the compositions and decoupling of these reservoirs.

We present data for an Arctic catchment (Svalbard, Supplementary Information) where the bedrock ϵNd and $^{87}\text{Sr}/^{86}\text{Sr}$ data were interpreted as a two component mixture between two sources: Proterozoic sediments derived from Greenlandic basement rocks and Carboniferous to Jurassic sediments derived from Siberian basalts (Hindshaw *et al.*, 2018). Due to recent glaciation, there has been negligible soil development which along with the large ϵNd range in the rocks exposed in the catchment (>12 epsilon units), the well-constrained field setting and its geographic location proximal to deep water formation, makes it an ideal site to evaluate the processes affecting ϵNd during river transport from terrestrial

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rock sources to the ocean. We find that similar to the well-established behaviour of radiogenic Sr (*e.g.*, Blum *et al.*, 1994), the dissolved ϵNd values are distinct from stream suspended sediments. Through sequential extractions of catchment rock and glacial sediment samples we demonstrate that dissolved ϵNd values are controlled by the most readily dissolved components, which are isotopically distinct from the bulk.

Decoupling Water Chemistry from Bulk Rock Compositions

The dissolved load (<0.22 μm) has higher ϵNd (2.0–5.5) and lower $^{87}\text{Sr}/^{86}\text{Sr}$ (0.020–0.028) values (Fig. 1a, Table S-2) compared to the corresponding stream suspended sediment samples (>0.22 μm ; Hindshaw *et al.*, 2018). These differences result in an offset between the dissolved load Sr–Nd array and solid sample array (Fig. 1a), implying that the solid samples contain isotopically distinct phases that are preferentially weathered.

To investigate the compositions of the phases which are most labile and therefore likely to contribute to water chemistry, a range of rock and glacial sediment samples were leached (Supplementary Information, Haley *et al.*, 2008; Chen *et al.*, 2012). The ϵNd values of hydroxylamine hydrochloride (HH) and acetic acid (AA) leachates are always higher than the ϵNd values of the bulk sample (Fig. 1b, Table S-3).

The dissolved load samples define a linear trend bounded by the leachates from the three rock samples containing >1 % bulk Nd in the leachates (Table S-4). A mixing line can be fitted between HH leachate end members R1 and R3, which passes through the dissolved load samples (Fig. 1c), implying that the dissolved load composition is a mixture of these two labile end members. The chemical extraction procedure, which was developed to extract seawater Nd isotopes from authigenic phases in sediment cores (*e.g.*, Haley *et al.*, 2008), appears to target the same labile, end member phases as natural chemical weathering conditions.

The first end member is defined by the leachates from the shale samples R1 and R2 (Fig. 1b). Given that these shales were deposited in a deep water marine environment (Hindshaw *et al.*, 2018), this labile phase is likely an authigenic phase precipitated from seawater. To aid in identifying the source of Nd, we utilise rare earth element (REE) patterns (*e.g.*, Haley *et al.*, 2004; Supplementary Information). When normalised to the bulk REE pattern, the AA and HH leachates of R1 and R2 have a middle REE (MREE) enrichment (Fig. 2, Table S-5), which indicates the REE are hosted in authigenic phosphate minerals and/or Fe–Mn (oxyhydr)oxides (*e.g.*, Goldberg *et al.*, 1963; Sholkovitz *et al.*, 1999; Supplementary Information). The Sm/Nd ratios in the leachate samples (AA: 0.27–0.30; HH: 0.37–0.39) are higher than those of the bulk rock (0.19, typical for shale; McCulloch and Wasserburg, 1978) consistent with leaching of marine precipitates, as these phases preferentially incorporate Sm (Goldstein *et al.*, 1984).

The second end member is defined by the leachates from the sandstone sample (R3, Fig. 1b). The AA and HH leachates removed 91 % Ca and 88 % Sr respectively (Table S-4), with a Ca/Sr mass ratio of 325 (Veizer, 1983), strongly suggesting the presence of a carbonate phase. The sandstone leachates have a Sm/Nd mass ratio (0.20–0.21) typical for carbonates (~0.20, Hua *et al.*, 2013), and a high REE (HREE) enrichment (Fig. 2), typical for complexation with carbonate (*e.g.*, Byrne and Sholkovitz, 1996). This implies that Nd, like Sr, is hosted in the carbonate phase of this rock sample.

Figure 1 Dissolved (<0.22 μm) and solid samples (rock, sediment and stream suspended sediment) form distinct arrays in Sr–Nd space. (a) A linear regression is fitted for the dissolved samples ($r^2 = 0.93$, $p < 0.001$). The linear line for the solid samples is the mixing line between a Greenlandic ($^{87}\text{Sr}/^{86}\text{Sr} = 0.78059$, $\epsilon\text{Nd} = -37.1$) and Siberian ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70626$, $\epsilon\text{Nd} = -0.4$) sediment source with identical Sr/Nd mass ratios (Hindshaw *et al.*, 2018). The four rock and one glacial sediment sample subjected to the leaching procedure are labelled. (b) The isotopic compositions of the leachates, residual and bulk samples. The dissolved load array is bound by leachates of the sandstone (R3) at one end and leachates of the shale samples (R1 and R2) at the other end. (c) The dissolved samples can be fitted with a mixing line between the HH leachate end members. The best fit line uses the concentration and isotopic values measured in R3–HH and R1–HH (Table S-3). The numbers on the mixing line refer to the mass fraction of the sandstone end member in the mixture. Error bars are smaller than symbol size.

Figure 2 REE concentrations of the leachates normalised to bulk. (a) AA leach. (b) HH leach. REE concentrations are normalised against the bulk REE concentrations of the same sample. Note the scale break in (b). The sandstone sample (R3) has a HREE enriched pattern for both leachates. Shale samples R1 and R2 have MREE enriched patterns for both leachates. REE data is reported in Table S-5.

In summary, ϵNd values of the dissolved load are distinct from those of stream suspended sediment sampled at the same time. We attribute this to the preferential leaching of two components found in sedimentary rocks in the catchment; 1) authigenic phosphates and/or Fe-Mn (oxyhydr)oxides, and 2) carbonate. Both phases have chemical and isotopic compositions distinct from the detrital silicate fraction (Fig. 1b).

Implications for Leaching an Isotopically Distinct Labile Phase

Sedimentary rocks contain a mixture of authigenic, detrital and biological components. The results from this study imply that in areas with extensive sedimentary rock cover, weathering of labile phases may dominate the riverine Nd flux, with two important implications. First, ϵNd measurements of bulk rock or the detrital silicate fraction will not represent the continental ϵNd input to ocean water masses. Second, analogous to $^{87}\text{Sr}/^{86}\text{Sr}$, ϵNd released to rivers and seawater will be controlled by the availability of (often) isotopically distinct labile phases *e.g.*, oxides. In weathering-limited regimes, where the availability of labile phases is not limited, ϵNd will be subject to environmental factors, such as discharge and temperature, which determine whether the dissolution of labile phases is promoted or suppressed (West *et al.*, 2005).

This has important implications for studies calculating budgets of seawater Nd isotopes relative to lithological sources, suggesting greater temporal and spatial variability. Using the Arctic Ocean as an example, where 49 % of the land drains shales (Amiotte Suchet *et al.*, 2003), we predict (Supplementary Information) that if a change in climatic or erosional conditions resulted in the weathering regime evolving from transport-limited, where the contribution of labile phases is negligible, to weathering-limited, where the dissolution of labile phases is dominant, then this would shift the ϵNd value of the ocean by 1 epsilon unit in just over 1 τ (Nd residence time; Fig. S-2). This basic calculation only considers the dissolved load. However, if the proportion of sedimentary rock exposed to chemical weathering and the flux of stream suspended sediment were greater immediately after periods of glaciation (Vance *et al.*, 2009), then increased preferential weathering of labile phases from that sediment could occur in the marine environment, providing a climate-linked mechanism to alter

the end member composition of water masses, independent of the source of Nd isotopes to the site of deep water formation, or of the location of deep water formation.

On long geological timescales, we suggest that if a fraction of the dissolved load was derived from a labile phase with a marine origin, then it could act as a “buffer” on seawater compositions. This would result in the geochemical decoupling between a labile sedimentary reservoir, which more readily exchanges with seawater due to rapid dissolution kinetics, and a silicate-bound reservoir, which maintains its composition set by crystallisation, plus radiogenic ingrowth through time. The leachates measured in this study have Sm/Nd ratios >20 % higher than the silicate fraction in the same sample (Table S-3), in agreement with literature values (Shaw and Wasserburg, 1985; Charbonnier *et al.*, 2012). If allowed to evolve 500 Myr, the ϵNd composition of the labile reservoir would become 1.5 epsilon units more radiogenic than the detrital silicate fraction due to ingrowth of ^{143}Nd (Supplementary Information). The exchange of this labile reservoir with seawater would result in seawater with a more radiogenic composition than the geological terranes that surround it, even in the absence of a volcanic fraction within marine sediment, which tends to contribute Nd preferentially to seawater (Pearce *et al.*, 2013; Wilson *et al.*, 2013). Exchange of ϵNd between seawater and labile phases during sediment recycling would cause the composition of terrestrial fine sediment to shift progressively further from bulk silicate rock towards higher ϵNd values over long geological timescales.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1828>.

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