

# Impact of glacial activity on the weathering of Hf isotopes – Observations from Southwest Greenland

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## Abstract

Data for the modern oceans and their authigenic precipitates suggest incongruent release of hafnium (Hf) isotopes by chemical weathering of the continents. The fact that weathering during recent glacial periods is associated with more congruent release of Hf isotopes has led to the hypothesis that the incongruity may be controlled by retention of unradiogenic Hf by zircons, and that glacial grinding enhances release of Hf from zircons. Here we study the relationship between glacial weathering processes and Hf isotope compositions released to rivers fed by land-terminating glaciers of the Greenland Ice Sheet, as well as neighbouring non-glacial streams. The weathered source rocks in the studied area mostly consist of gneisses, but also include amphibolites of the same age (1.9 Ga). Hafnium and neodymium isotope compositions in catchment sediments and in the riverine suspended load are consistent with a predominantly gneissic source containing variable trace amounts of zircon and different abundances of hornblende, garnet and titanite.

Glacially sourced rivers and non-glacial streams fed by precipitation and lakes show very unradiogenic Nd isotopic compositions, in a narrow range ( $\epsilon_{\text{Nd}} = -42.8$  to  $-37.9$ ). Hafnium isotopes, on the other hand, are much more radiogenic and variable, with  $\epsilon_{\text{Hf}}$  between  $-18.3$  and  $-0.9$  in glacial rivers, and even more radiogenic values of  $+15.8$  to  $+46.3$  in non-glacial streams. Although relatively unradiogenic Hf is released by glacial weathering, glacial rivers actually fall close to the seawater array in Hf–Nd isotope space and are not distinctly unradiogenic.

Based on their abundance in rocks and sediments and their isotope compositions, different minerals contribute to the radiogenic Hf in solution with a decreasing relevance from garnet to titanite, hornblende and apatite. Neodymium isotopes preclude a much stronger representation of titanite, hornblende and apatite in solution, such as might result from differences in dissolution rates, than estimated from mineral abundance. The strong contrast in Hf isotope compositions between glacial rivers and non-glacial streams results mostly from different contributions from garnet and zircon, where zircon weathering is more efficient in the subglacial environment.

A key difference between glacial and non-glacial waters is the water–rock interaction time. While glacial rivers receive continuous contributions from long residence time waters of distributed subglacial drainage systems, non-glacial streams are characterized by fast superficial drainage above the permafrost horizon. Therefore, the increased congruency in Hf isotope

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weathering in glacial systems could simply reflect the hydrological conditions at the base of the ice-sheet and glaciers, with zircon weathering contributions increasing with water-rock interaction time.

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## 1. INTRODUCTION

Glacial weathering processes promote high silicate weathering rates over Pleistocene glacial-interglacial cycles (e.g., Vance et al., 2009). Glacial grinding of rock substrate produces fine-grained rock powder with large surface area, which can be exposed to weathering in a range of settings (e.g., Anderson, 2007). In addition to surface area, soil age is an intrinsic factor for silicate-weathering rates, with rates decreasing rapidly with time of exposure (e.g., Taylor and Blum, 1995). Taken together, glacial-interglacial cycles combine to yield high time-integrated silicate weathering rates as reactive soil substrate is produced during glacial periods and weathered effectively in intervening interglacials (Foster and Vance, 2006). These interactions may be reflected in the Pb isotope evolution of seawater in the northwestern Atlantic (Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010). Other approaches to study variations in glacial-interglacial weathering rates, such as oceanic  $^{10}\text{Be}/^{9}\text{Be}$  ratios, on the other hand, suggest little change (von Blanckenburg et al., 2015).

Continental weathering conditions also affect the seawater evolution of Hf isotopes on Pleistocene and longer timescales (Piotrowski et al., 2000; van de Flierdt et al., 2002; Gutjahr et al., 2014; Dausmann et al., 2015, 2017). These variations can, however, also reflect changes in weathered source rocks rather than the degree of weathering congruency (Chen et al., 2012). The information Hf isotopes hold has not been fully accessible to date due to our limited understanding of their behaviour during weathering. Early studies of iron-manganese crusts and nodules, which record ambient seawater isotope compositions for radiogenic isotopes, suggested that the generally incongruent release of Hf isotopes during weathering is diminished during times of continental glaciation (Piotrowski et al., 2000; van de Flierdt et al., 2002). A cause for the incongruency of Hf isotope release is the retention of unradiogenic Hf isotopes in weathering-resistant zircon (Patchett et al., 1984), with more efficient release during glacial times due to glacial comminution of rocks and the production of glacially strained surfaces (Piotrowski et al., 2000; van de Flierdt et al., 2002). This concept has recently been reinforced by observations on the Hf isotope composition in dispersed marine iron-manganese phases extracted from sediments that span the last deglaciation of North America (Gutjahr et al., 2014). In addition, Gutjahr et al. (2014) inferred that a change from a relatively congruent release of Hf isotopes during the Last Glacial Maximum to a more incongruent release shortly afterwards could be linked to the transition from a dominantly cold-based to a warm-based Laurentide Ice Sheet.

A complementary mineralogical control, namely the release of radiogenic Hf from preferentially weathered

accessory minerals with high Lu/Hf ratios, can also affect the incongruency in Hf isotope weathering (Bayon et al., 2006; Godfrey et al., 2007; Chen et al., 2011, 2013a, 2013b). Thus, studies of the dissolved load of rivers specifically invoke preferential weathering of apatite and titanite or garnet, depending on the weathering lithologies (Bayon et al., 2006; Godfrey et al., 2007). Hafnium released during weathering may, hence, become more congruent with increasing soil age, as the accessory minerals are depleted. This mechanism has, however, not been evaluated conclusively to date (e.g., Ma et al., 2010; Bayon et al., 2016). An effect on dissolved Hf from the dissolution of radiogenic accessory minerals, which also carry radiogenic Pb, appears to be at odds with observations from the North Atlantic as there is no co-evolution of seawater Pb and Hf – isotope compositions (Gutjahr et al., 2014).

In addition to glacial activity, mineralogy and soil age, the release of Hf isotopes has also been suggested to depend on run-off conditions and temperature (Bayon et al., 2012, 2016; Rickli et al., 2013). High run-off seems to promote the release of radiogenic Hf, as observed in catchments with different source lithologies in Switzerland (Rickli et al., 2013). Hafnium isotopes in the clay fraction of river and shelf sediments, mostly reflecting released Hf during weathering, are positively correlated with precipitation and temperature in catchments of various sizes and lithology from around the globe (Bayon et al., 2016).

A currently unclear aspect of seawater Hf isotope compositions is the relative overall homogeneity between  $\varepsilon_{\text{Hf}} = -2$  in the Northwest Atlantic and  $\varepsilon_{\text{Hf}} = +6$  in the North Pacific (Rickli et al., 2009; Zimmermann et al., 2009a). This narrow range cannot be easily reconciled with the variable riverine Hf isotope compositions reported thus far (Bayon et al., 2006; Godfrey et al., 2007; Rickli et al., 2013; Chen et al., 2013b; Merschel et al., in press) and a short seawater residence time of Hf (Chen et al., 2013b; Filippova et al., 2017), similar to that of Nd (< 500 yr, Siddall et al., 2008).

In summary, the interplay of environmental parameters – such as soil age, glacial activity, temperature and precipitation – and mineralogical properties of weathered rocks – in particular the availability of specific accessory minerals – is likely to govern the Hf isotope compositions of rivers. But the relative significance of these aspects is not well constrained to date. In this study, we seek to characterise the hydrological and mineralogical controls on the congruency in Hf isotope release in the subglacial and proglacial environment of the Russell and Leverett Glaciers in West Greenland (Fig. 1). To this end, we have characterized the weathered source rocks and derived sediments, and compare them to the dissolved riverine isotope compositions, specifically in glacially fed rivers and non-glacial streams.

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