Quaternary Science Reviews 99 (2014) 97–111

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

Peak Last Glacial weathering intensity on the North American continent recorded by the authigenic Hf isotope composition of North Atlantic deep-sea sediments

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ARTICLE INFO

Article history:
Received 29 January 2014
Received in revised form
30 April 2014
Accepted 16 June 2014
Available online

Keywords:
Authigenic hafnium
Fe–Mn oxyhydroxide
Laurentide Ice Sheet
Incongruent weathering
Zircon effect
Lu-rich accessory minerals
Feldspar weathering
Deglaciation
LGM

ABSTRACT

We have retrieved radiogenic hafnium (Hf) isotope compositions (ε_{Hf}) from authigenic Fe–Mn oxyhydroxides of deep northwest Atlantic sediments deposited over the past 26 ka to investigate the oceanic evidence of changes in dissolved weathering inputs from NE America during the last deglaciation. The extraction of seawater-derived Hf isotopic compositions from Fe–Mn oxyhydroxides is not a standard procedure. Comparisons between the Al/Hf ratios and Hf isotopic compositions of the chemically extracted authigenic phase on the one hand, and those of the corresponding detrital fractions on the other, provide evidence that the composition of past seawater has been reliably obtained for most sampled depths with our leaching procedures. This is endorsed most strongly by data for a sediment core from 4250 m water depth at the deeper Blake Ridge, for which consistent replicates were produced throughout. The Hf isotopic composition of the most recent sample in this core also closely matches that of nearby present day central North Atlantic seawater. Comparison with previously published seawater Nd and Pb isotope compositions obtained on the same cores shows that both Hf and Pb were released incongruently during incipient chemical weathering, but responded differently to the deglacial retreat of the Laurentide Ice Sheet. Hafnium was released more congruently during peak glacial conditions of the Last Glacial Maximum (LGM) and changed to typical incongruent interglacial ε_{Hf} signatures either during or shortly after the LGM. This indicates that some zircon-derived Hf was released to seawater during the LGM. Conversely, there is no clear evidence for an increase in the influence of weathering of Lu-rich mineral phases during deglaciation, possibly since relatively unradiogenic Hf contributions from feldspar weathering were superimposed. While the authigenic Pb isotope signal in the same marine sediment samples traced peak chemical weathering rates on continental North America during the transition to the Holocene a similar incongruent excursion is notably absent in the Hf isotope record. The early change towards more radiogenic ε_{Hf} in relation to the LGM may provide direct evidence for the transition from a cold-based to a warm-based Laurentide Ice Sheet on the Atlantic sector of North America.

1. Introduction

During the glacial cycles of the past 2.7 Ma, northern North America has recurrently been overlain by substantial continental ice in the form of the Laurentide Ice Sheet (LIS) (Dyke and Prest, 1987; Clark and Pollard, 1998; Lisiecki and Raymo, 2007). The LIS alone stored as much as 56–76 m of sea level equivalent during the LGM (Paterson, 1972; Peltier, 1994; Carlson and Clark, 2012). Despite its importance for northern hemisphere Pleistocene climate the areal extent and volume of the LIS during non-peak glacial conditions is not well understood. Furthermore, its growth and retreat should have generated variable runoff fluxes into the adjacent ocean basins, but these too are not well constrained. This lack of knowledge regarding intermediate-sized ice sheet evolution is largely due to loss of geomorphological and geochemical

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http://dx.doi.org/10.1016/j.quascirev.2014.06.022
0277-3791/

evidence of these intermediate climate- and ice sheet states on land. As a result, the evolution of North American physicochemical weathering conditions and chemical runoff fluxes are not very well known for most of the recent Pleistocene geological history, although it is evident from the marine isotopic budgets of elements such as Sr that chemical weathering fluxes varied significantly on glacial–interglacial timescales (Vance et al., 2009).

In contrast to incomplete continental Pleistocene sedimentary sequences of continental North America, marine sediments in the northwest Atlantic adjacent to the LIS should have recorded an undisturbed and continuous geochemical LIS runoff history. Trace metals transferred in solution to the marine realm are scavenged from seawater and incorporated into authigenic phases (Bruland and Lohan, 2003). The isotopic compositions of some of these elements provide clues as to the conditions under which weathering and erosion took place. For example, the release of Pb during incipient chemical weathering of freshly eroded rocks is highly incongruent, meaning that its isotopic composition reflects that of more soluble minerals and of more loosely bound radiogenic Pb as a consequence of α-recoil processes rather than that of the bulk rocks. This is particularly true in recently deglaciated areas (Erel et al., 1994; Harlavan et al., 1998). The incongruent release is manifested in more radiogenic Pb isotopic compositions of the early Holocene North American runoff compared with corresponding bulk crustal Pb of the source rocks (e.g., Gutjahr et al., 2009; Crocket et al., 2013). The resultant seawater Pb isotope records archived in authigenic Fe–Mn oxyhydroxides of marine sediments of the last glacial–interglacial transition provided records of spatially and temporally resolved variations in runoff fluxes to the northwest Atlantic (Gutjahr et al., 2009; Kurzweil et al., 2010) and the Labrador Sea (Crocket et al., 2012). The pronounced radiogenic Pb isotope excursions facilitated the determination of early Holocene peak chemical weathering rates in the interior of northeast America and provided new constraints on the opening of the major eastern runoff route to the North Atlantic via the St. Lawrence seaway during the Younger Dryas (Kurzweil et al., 2010).

Hafnium is another radiogenic trace metal isotope system that is released incongruently during chemical weathering (Patchett et al., 1984; Piotrowski et al., 2000; van de Flierdt et al., 2002). Lutetium-176 decays to ^{176}Hf with a half life of 37.2 Ga (Scherer et al., 2001). Lutetium is a rare earth element (REE) whereas Hf is a high field strength element (HFSE) resulting in significantly different chemical affinities and partition coefficients into major and trace mineral phases during formation of continental crust. Just as radiogenic Pb isotopes trace preferential weathering of uranium- and/or thorium-rich mineral phases in recently deglaciated continental areas, Hf isotopes trace preferential weathering of Lu-rich and/or Lu-poor mineral phases (Bayon et al., 2006, 2012). The radiogenic Hf isotope ratio (^{176}Hf/^{177}Hf) is usually reported in the ε_{Hf} notation as deviation from the chondritic uniform reservoir (CHUR):

$$\varepsilon_{Hf} = \left[\frac{\left[{}^{176}\mathrm{Hf}/{}^{177}\mathrm{Hf}_{\mathrm{sample}}\right]}{\left[{}^{176}\mathrm{Hf}/{}^{177}\mathrm{Hf}_{\mathrm{CHUR}}\right]} - 1\right] \times 10^4$$

with ^{176}Hf/^{177}Hf$_{\mathrm{CHUR}} = 0.282772$ (Blichert-Toft and Albarède, 1997). Similarly, Nd isotopes are expressed as ε_{Nd} values relative to ^{143}Nd/^{144}Nd$_{\mathrm{CHUR}} = 0.512638$ (Jacobsen and Wasserburg, 1980).

Hafnium is highly depleted in open ocean seawater, reaching concentrations as low as 0.04 pmol/kg in surface waters of the Southern Ocean (Rickli et al., 2010; Stichel et al., 2012b). In contrast, surface water concentrations of up to 4.2 pmol/kg have been found in low salinity waters in the Arctic Ocean originating from riverine inputs (Zimmermann et al., 2009a). The majority of published open seawater Hf concentrations are below 1.5 pmol/kg (e.g., Godfrey et al., 2009; Rickli et al., 2009; Zimmermann et al., 2009b; Stichel et al., 2012a). Efficient removal of Hf in estuaries contributes to the low concentrations in seawater (Godfrey et al., 2008). Several publications discussing the Hf speciation and behaviour in seawater proposed a residence time for Hf longer than that of Nd (White et al., 1986; Godfrey et al., 1997, 2008). In contrast, despite the relative Hf isotopic similarity in the various ocean basins, recent water column work suggests a short residence time of Hf in seawater based largely on the chemical behaviour and scavenging intensity, as well as the lack of enrichment in dissolved deep water Hf concentrations along the flow paths of deep water masses in the Atlantic (Rickli et al., 2009; Rickli et al., 2010, 2014; Chen et al., 2013a). The latter view implies that the deep marine ε_{Hf} signature is mainly controlled by proximal (intra-basin) weathering contributions largely independent of the origin of prevailing deep water masses.

Since a large proportion of continental Hf is stored in the mineral zircon, which is hardly accessible during non-glacial chemical weathering (cf. Rickli et al., 2013), the corresponding continental runoff signal is offset to more radiogenic ε_{Hf} signatures than the bulk crustal Hf isotope signal. Albarède et al. (1998) coined the term *seawater array* for this systematic offset towards more radiogenic ε_{Hf} for a given ε_{Nd} in seawater-derived hydrogenetic ferromanganese deposits than in bulk terrestrial rocks. The seawater array was confirmed in subsequent studies using hydrogenetic Fe–Mn crusts (e.g. Piotrowski et al., 2000; David et al., 2001) and direct seawater measurements (e.g., Godfrey et al., 2009; Rickli et al., 2009; Zimmermann et al., 2009b; Stichel et al., 2012a). More recently, chemical weathering of either lutetium-rich mineral phases or rather unradiogenic feldspars were proposed to contribute significantly to the observed shift (Bayon et al., 2006, 2012; Chen et al., 2011). Some authors also argued that the offset towards more radiogenic ε_{Hf} of seawater or at least some level of decoupling between hydrogenetic ε_{Hf} and ε_{Nd} (van de Flierdt et al., 2004) is controlled by significant contributions of hydrothermal Hf characterised by highly radiogenic mantle-like isotope signatures (White et al., 1986; Bau and Koschinsky, 2006). While hydrothermal inputs may indeed contribute to the Hf budget of seawater, a strong continental source is clearly required in order to explain the Hf isotopic differences between the ocean basins (van de Flierdt et al., 2007; Chen et al., 2013b). Therefore, seawater-derived ε_{Hf} in northwest Atlantic sediments is expected to reflect changes glacial weathering conditions in North America given the Hf residence time well below the average ocean mixing time (cf. Piotrowski et al., 2000; van de Flierdt et al., 2002).

This study investigates the Hf isotope evolution of northwest Atlantic deep water during the last glacial–interglacial transition. Seawater-derived colloidal or truly dissolved Hf is incorporated into the authigenic Fe–Mn oxyhydroxide phase of marine pelagic sediments (Chen et al., 2012). Since Hf is depleted both in seawater and in marine authigenic Fe–Mn oxyhydroxides, the extraction of a pure seawater-derived Hf phase from sediments is less straightforward than for example for Nd, Pb, or Th (Bayon et al., 2002; Gutjahr et al., 2007; Robinson et al., 2008; Basak et al., 2011). Our findings demonstrate both the potential but also the limitations associated with the extraction of a seawater Hf isotope signature from marine drift sediments. Following a critical assessment of the chemical and isotopic composition of the chemically extracted authigenic fraction of Hf, the isotopic records are compared with previously published authigenic Pb and Nd isotope records from the same sediment cores (Gutjahr et al., 2008, 2009). In combination with these other records, it is possible to constrain whether variations in deep water ε_{Hf} have been controlled by chemical weathering trends alone, by changes in provenance of deep water masses, by periods of enhanced continental runoff, or even by