Glacial weathering and the hafnium isotope composition of seawater

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Received 18 September 2001; received in revised form 30 January 2002; accepted 4 February 2002

Abstract

The Hf isotope composition of seawater does not match that expected from dissolution of bulk continental crust. This mismatch is generally considered to be due to retention of unradiogenic Hf in resistant zircons during incomplete weathering of continental crust. During periods of intense glacial weathering, zircons should break down more efficiently, resulting in the release of highly unradiogenic Hf to the oceans. We test this hypothesis by comparing Nd and Hf isotope time series obtained from NW Atlantic ferromanganese crusts. Both isotope systems show a decrease associated with the onset of northern hemisphere glaciation. The observed changes display distinct trajectories in εNd–εHf space, which differ from previously reported arrays of bulk terrestrial material and seawater. Such patterns are consistent with the release of highly unradiogenic Hf from very old zircons, facilitated by enhanced mechanical weathering. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hf-177/Hf-176; zircon; seawater; isotope geochemistry; ferromanganese composition

1. Introduction

The isotope composition of Nd in pristine seawater precipitates, such as hydrogenous ferromanganese crusts, reflects the dissolved isotope composition of Nd in ambient seawater [1,2]. This in turn has varied in response to changes in inputs and mixing, the evolution of which can be monitored by time-resolved sampling of crusts. The flux of hydrothermal Nd is negligible because of very strong particulate scavenging of rare earth elements near vents [3,4]. Therefore, the ultimate sources of Nd in the oceans today are dominated by inputs from weathering of continental crust. Consequently, the Nd isotope composition of seawater is sensitive to the amount of detrital input and the source provenance. The dependence on the style of weathering is thought to be small [5–7]. Recently some evidence has been presented for incongruent weathering effects on Nd [8–10], but it is not yet clear whether these effects are significant for the dissolved Nd isotope composition of seawater.

Less use has been made of Hf isotopes as a
tracer in seawater, because at present the inputs are not well defined and understood. The roles of hydrothermal fluxes and incongruent weathering are particularly unclear. The data obtained from ferromanganese crusts/nodules and deep-sea clays display an offset to higher \(^{176}Hf/^{177}Hf\) for a given \(^{143}Nd/^{144}Nd\) when compared with the corresponding isotope composition of bulk continental rocks, consistent with either incongruent weathering or hydrothermal contributions [11]. Hydrothermal crusts carry highly radiogenic (MORB-like) Hf isotopes, indicating that hydrothermal Hf does indeed enter the ocean to some extent [12]. However, no Hf isotope data are available so far for seawater profiles or vent fluids to test or quantify this. Furthermore, the Hf isotope compositions recorded in ferromanganese crusts from the central Pacific Ocean have been remarkably constant for the past 10 Myr [15,16] and do not show any correspondence with independent estimates of changes in arc volcanism or ridge activity. Therefore, the most likely cause of the high \(^{176}Hf/^{177}Hf\) of seawater is that the normal erosion of the continents involves incongruent weathering [14]. That is, the Hf isotope composition of river waters should be more radiogenic relative to the bulk composition of their source rocks.

Lu and Hf are strongly fractionated between muds and sands due to the preferential concentration of Hf (\(\sim 1%\) by weight) in chemically resistant zircons [6,11,17]. These detrital zircons have low Lu/Hf and low \(^{176}Hf/^{177}Hf\). They reside mainly in sands on the continents and continental shelves and can only enter the deep oceans via turbidites. Such zircons remain mostly intact and do not release their unradiogenic Hf to deep water. The more radiogenic Hf of the remaining (non-zircon) fraction in the source rocks is incorporated in less resistant minerals. Therefore, Hf is probably preferentially supplied to the oceans either as suspended fine particulates or in dissolved form [6,17]. Because of analytical difficulties there are no direct river and seawater Hf isotope measurements with which these theories could be tested. However, by using ferromanganese crusts one can study the changes in seawater Hf isotope composition that took place as a function of time adjacent to continental regions that underwent a big change in weathering style.

If the retention of zircon on the shelf areas is responsible for the offset of \(\delta_{Hf}\) in seawater, a change in the style of weathering (more intense mechanical weathering) should result in a more efficient breakdown of zircons and consequently larger amounts of unradiogenic Hf would be released to the ocean. Therefore during times of intense physical erosion such as during glacial weathering the Hf isotope composition of seawater should be driven towards the bulk rock composition and lead to seawater Hf and Nd isotope compositions that track bulk continental crust more closely. Here we test this model by using isotope records of ferromanganese crusts from the NW Atlantic, proximal to the areas where drastic changes in weathering regime accompanied the onset of northern hemisphere glaciation (NHG).

2. Samples and methods

Ferromanganese crusts ALV539 and BM-1969.05 were dredged from the New England Seamount and the San Pablo Seamount (35°36′N, 58°47′W, \(\sim 2700\) m depth and 39°00′N, 60°57′W, \(\sim 1800\) m depth, respectively) approximately 120 km SE of the edge of the North American continental shelf. Both locations are close to the pathway of the Deep Western Boundary Current, which is the southern extension of North Atlantic Deep Water (NADW). The isotope compositions for Be, Pb, Nd and Hf of both crusts have already been studied intensively [14,18–21]. To complete the data set we performed additional Hf isotope analysis for BM1969.05 because the upper 2 Myr were missing in the previous work [14], as deduced from Nd isotope measurements on the same aliquots. Nine samples from the surface down to 5 mm depth (3.1 Ma) were analysed for their Hf isotope composition (Table 1). The sampling was done using a computer-controlled drilling device. Between 10 and 15 mg of materials were used in each analysis. Chemical separation of Hf followed the two-column procedure of Lee et al. [16]. Measurements were carried out on a
Nu Plasma MC-ICPMS. Repeated analyses of the JMC475 Hf standard gave an average $^{176}$Hf/$^{177}$Hf of 0.282139 ± 0.0018 ($n = 56$). The integrity of our time series was checked by measuring Pb isotopes in the uppermost sample (0–0.5 mm). The $^{206}$Pb/$^{204}$Pb of 19.233 ± 0.002 obtained this way shows good agreement with the previously reported ratio for the surface of this crust ($^{206}$Pb/$^{204}$Pb = 19.240 ± 0.004 [21]).

3. Discussion

3.1. Previous work

There is still controversy about the cause of the major changes in Pb, Nd and Hf isotopes in the NW Atlantic seawater. A general decline in $^{207}$Pb/$^{206}$Pb, $\varepsilon_{\text{Nd}}$ and $\varepsilon_{\text{Hf}}$, all starting around 3–2 Ma, occurs in the records of both crusts. Possible explanations include major palaeoceanographic changes caused by the closure of the Panama Gateway, intensification of NADW flow, changes in water mass contributions (higher Labrador Seawater component in NADW), and changes in the amount and/or provenance of material delivered to the North Atlantic Ocean [10,14,18,20–25].

The scope of our study is not to provide a solution for the (mis)matches in the variations of Pb, Nd and Hf isotope records but to further investigate the potential of combined Hf and Nd isotopes in ferromanganese crusts to trace changes in the continental weathering style [13,14].

Vervoort et al. [17,26] showed that Hf and Nd isotopes for nearly all terrestrial samples (oceanic basalts, sediments, continental basalts, granitoids and juvenile crustal rocks) form a single array (Fig. 1). To a first-order approximation, Hf and Nd isotope systems behave coherently in the crust and the mantle [26]. Subsequent variations within the array are due to Lu–Hf and Sm–Nd fractionations in certain crust and mantle reservoirs but none of these rather local features results in large-scale decoupling of the Hf and Nd systems [26]. Generally speaking, Hf and Nd isotopes in old, crustal rocks (post 2.7 Ga) with low Sm/Nd and Lu/Hf ratios plot at the lower (radiogenic) end of the terrestrial array while young and juvenile rocks with high Sm/Nd and Lu/Hf ratios plot at the upper (radiogenic) end of the terrestrial array.

Albarède et al. [13] have shown that seawater Nd and Hf isotope compositions are roughly correlated along an array that is distinct from the terrestrial array (Fig. 1). This so-called seawater array is defined by surface scrapings of ferromanganese crusts and nodules from the Pacific, Indian and Atlantic oceans (Fig. 1). The residence time of both Nd and Hf is on the order of or slightly shorter than the global ocean mixing time [15,16,27–32]. Therefore, a general provinciality between the three deep ocean basins can be observed. The samples of the more radiogenic upper part of the seawater array are from the Pacific Ocean and the least radiogenic values of the lower part are from the North Atlantic Ocean [13] (Fig. 1). This feature is a simple function of the age of the surrounding continents/source areas. The Atlantic Ocean is mainly sourced by Proterozoic and Archaean cratons in Canada and Greenland whereas the Pacific Ocean is rather dominated by young, arc-derived material. The offset in $\varepsilon_{\text{Hf}}$ to more radiogenic values compared to the values of the terrestrial array is relatively small for the Pacific Ocean but increases towards

<table>
<thead>
<tr>
<th>Depth (mm)</th>
<th>Age (Ma)</th>
<th>$^{176}$Hf/$^{177}$Hf</th>
<th>$\varepsilon_{\text{Hf}}$</th>
<th>$\varepsilon_{\text{Nd}}$</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td>± 2o S.E.</td>
<td>± 2o S.E.</td>
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<tr>
<td>0.0-0.5</td>
<td>0.15</td>
<td>0.282823 ± 0.02</td>
<td>1.80 ± 0.76</td>
<td></td>
</tr>
<tr>
<td>0.5-1.0</td>
<td>0.46</td>
<td>0.282841 ± 0.02</td>
<td>2.45 ± 0.59</td>
<td></td>
</tr>
<tr>
<td>1.0-1.5</td>
<td>0.77</td>
<td>0.282826 ± 0.02</td>
<td>1.93 ± 0.50</td>
<td></td>
</tr>
<tr>
<td>1.5-2.0</td>
<td>1.08</td>
<td>0.282866 ± 0.02</td>
<td>3.33 ± 0.65</td>
<td></td>
</tr>
<tr>
<td>2.0-2.5</td>
<td>1.39</td>
<td>0.282890 ± 0.02</td>
<td>4.16 ± 0.79</td>
<td></td>
</tr>
<tr>
<td>2.5-3.0</td>
<td>1.70</td>
<td>0.282898 ± 0.02</td>
<td>4.44 ± 1.15</td>
<td></td>
</tr>
<tr>
<td>3.0-3.5</td>
<td>2.01</td>
<td>0.282841 ± 0.02</td>
<td>2.42 ± 0.63</td>
<td></td>
</tr>
<tr>
<td>3.5-4.0</td>
<td>2.31</td>
<td>0.282867 ± 0.02</td>
<td>3.34 ± 0.37</td>
<td></td>
</tr>
<tr>
<td>4.0-5.0</td>
<td>2.78</td>
<td>0.282855 ± 0.02</td>
<td>2.95 ± 0.45</td>
<td></td>
</tr>
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</table>

\(a\) Be ages calculated with growth rate of 1.62 ± 0.10 mm/Ma defined by $^{10}$Be/$^{9}$Be ratios [19].

\(b\) Repeated analyses of the JMC475 Hf standard gave an average ratio $^{176}$Hf/$^{177}$Hf of 0.282139 ± 0.0018 ($n = 56$); to compare the values with Hf isotopic measurements of [14] all ratios were normalised to their reported JMC475 value of 0.282161 ± 0.0018.

\(c\) Calculated with $^{176}$Hf/$^{177}$Hf$_{\text{CHUR}}$ = 0.282772 [47].
the Atlantic values. This decoupling of Nd and Hf isotopes in seawater is thought to be caused by the retention and preservation of zircon on the shelf areas. As a first approximation, the seawater array can be regarded as a zircon-deficient equivalent of the terrestrial array.

New and published data for BM1969.05 and ALV539 time series are shown in Fig. 1, where they plot at the least radiogenic end of the seawater array. They are among the most extreme examples showing the decoupling between Hf and Nd isotopes and define distinct curved trends within the seawater array (Fig. 1b,c).

3.2. Changes in the weathering style

The pronounced curvatures of the NW Atlantic ferromanganese crust time series (Fig. 1b,c) can be explained by a change in weathering style. The records start with a relatively radiogenic Hf isotope composition that would correspond to the ‘normal’ weathering effect of a large portion of Hf released from minerals that are not very resistant. There is a decrease in $\varepsilon_{\text{Nd}}$ in crust ALV539 by about 1 $\varepsilon$ unit between 3.5 and 2.1 Ma. The Hf isotopes show little change during the same period (Fig. 1b). Furthermore, no systematic relation-
ships can be observed between $\varepsilon_{\text{Nd}}$ and $\varepsilon_{\text{Hf}}$ prior to 1.7 Ma for BM1969.05 (Fig. 1c). However, between about 2 Ma and the present both crusts show a distinct decrease in $\varepsilon_{\text{Hf}}$ by 2.5–4 $\varepsilon$ units, while $\varepsilon_{\text{Nd}}$ during that same time interval only decreased by $\sim$0.5 $\varepsilon$ units. This timing is similar to changes of other climate indicators. For example, there is a controversial debate on deep ocean circulation changes associated with the onset of NHG. Several arguments have been presented, ranging from a general increase in NADW production [33,34], or an increase in Labrador Sea Water contribution [25], to the concept of weaker NADW production [35,36]. However, it is very unlikely that the decrease in Hf isotopes in NW Atlantic seawater, starting $\sim$2 Ma, is a result of ocean circulation changes, because in this case it should have started simultaneously with the changes in Nd and Pb isotopes.

The beginning of increased $\delta^{18}$O variations and the first major occurrence of ice-rafted detritus in the North Atlantic was at 2.5–2.4 Ma [37,38], and an increase in dropstone abundances in sediment cores from the Arctic Ocean started around 1.7 Ma [39]. This correspondence with the timing of the change in Hf isotopes provides support for the hypothesis that northern hemisphere ice growth and the accompanying changes in weathering style were responsible for the changes in Hf isotopes in ALV539 and BM1969.05.

In accordance with Piotrowski et al. [14], we suggest that more intense mechanical weathering has facilitated more efficient breakdown of usually very resistant zircons. Although glaciers do not influence the total chemical denudation rates, they may yield compositionally distinctive chemical fluxes to the oceans. Two important factors may be: (1) the disruption of mineral lattices by grinding which increases dissolution rates and (2) the increase of surface area of mechanically destroyed minerals [40]. These processes make it very likely that glacial sediments are more easily weathered. It is important to mention that physical erosion and chemical weathering are interrelated processes, which means that physical erosion is the essential precondition to make trace elements in robust minerals, such as Hf in zircons, chemically accessible. In contrast, studies on the surface chemistry of zircons weathered over a long time in tropical areas (e.g. Amazon basin) suggest that these zircon grains are very robust to pure chemical weathering [41].

The more complete breakdown of zircons would greatly affect the Hf isotope composition of continental runoff and of seawater without a significant change in Nd isotopes. This is because zircons contain the majority of the Hf budget in a rock (about 1% or $10^4$ ppm Hf in zircon) but much less Lu (usually 10–100 ppm) and other rare earth elements. If also Nd would have been affected by incongruent weathering to any large extent, the isotope time series should not show the observed curvature during the past 3 Myr (Fig. 1b,c). The trend in Nd isotopes can be better explained by increased net erosional inputs from the old surrounding continents [21,24,25].

The Hf isotope composition of old zircons derived from the continental crust is extremely unradiogenic. Isotope measurements in 3.6–3.8 Ga old single zircon grains from Greenland and north-western Canada yielded $\varepsilon_{\text{Hf}}$ values as low as $-88$ [26,42]. The more complete destruction of the old resistant zircons by glacial weathering entails a change from incongruent weathering prior to $\sim$2 Ma (release of radiogenic Hf from easily weatherable minerals solely) to more congruent weathering thereafter (release of a more bulk rock-like Hf isotope composition to the oceans because Hf from zircons is partly included in the dissolved material). Hence the data of the crusts are driven away from the seawater array towards the bulk crust data array (Fig. 1).

3.3. Changes in the source terrain

Another interpretation that may be considered is that the changes in Hf isotope composition, observed in NW Atlantic ferromanganese crust time series, reflect changes in the source terrain. To fit the observed data in ALV539 and BM1969.05, the new source area would have to be characterised by lower (less radiogenic) $\varepsilon_{\text{Nd}}$ values and lower (less radiogenic) $\varepsilon_{\text{Hf}}$ values as is typical for old continental crust. The problem with this interpretation lies in the amplitude of changes in Nd and Hf isotopes. It is evident
from the less steep slope of the seawater array (Fig. 1) that the bulk of the materials delivered to the ocean shows the tendency to be more radiogenic in Hf relative to Nd when compared with typical crustal materials (Fig. 1). While terrestrial rocks display a range in $\varepsilon_{\text{Nd}}$ of $\sim 30$ units and a range in Hf isotopes of $\sim 50$ units (Nd:Hf $\approx 1:2$), manganese crusts and nodules exhibit only a range of $\sim 10$ units, both in Nd and in Hf isotopes (Nd:Hf $\approx 1:1$). Both arrays in Fig. 1 are a function of age and lithology. While the terrestrial array represents the whole range of mantle and crustal rocks, the seawater array is the equivalent to the zircon-free part of the same rock suite. The smaller degree of overall variation in $\varepsilon_{\text{Nd}}$ and $\varepsilon_{\text{Hf}}$ in seawater is due to homogenisation in the oceans. Obviously, if the weathering and erosion processes have remained the same, any changes towards an older source terrain should result in a shift of the data on the seawater array towards lower $\varepsilon_{\text{Nd}}$ and $\varepsilon_{\text{Hf}}$ values. However, the Nd isotopes in both crusts show continuous shifts towards lower values ($0.5$--$1$ unit changes during the past $2$ Ma Fig. 1b,c) but are accompanied by much more drastic shifts in the Hf isotopes ($3$--$4$ units in the same time interval, Fig. 1b,c), which is not expected from a simple change of source regions. Solely changing the source area towards old continental crust without the accompanying change in the weathering mechanism is unlikely to be responsible for the observation in these two ferromanganese crusts.

Another important point to mention is that the radiogenic isotope compositions of BM1969.05 and ALV539 may have been derived from different water masses. While ALV539 (2700 m water depth) definitely grew from NADW or a precursor of it, BM1969.05 may have been sourced by a different (intermediate) water mass (1800 m water depth). This might also explain the observed difference in the fine structure of the two time series [20]. The Hf data of BM1969.05 are overall more radiogenic than those of ALV539 and a clear trend prior to $1.7$ Ma is missing. However, besides these differences there is remarkable agreement between the Hf, Nd (and Pb) isotope trends since the onset of NHG. These similar trends point to a common process, e.g. a change in the style of weathering associated with the onset of enhanced physical erosion as described above. Such fundamental changes are likely to be visible in every water mass sourced in the regions of Canada and Greenland and should consequently be monitored by both crusts even if they grew from mixtures of different water masses.

### 3.4. Evidence from Pb isotopes

Assuming that the breakdown of zircon minerals plays a key role in controlling the Hf isotope composition of ALV539 and BM1969.05, we can do some simple model calculations for the zircon-derived dissolved Pb component in seawater to check our hypothesis.

Incongruent weathering also affects Pb isotopes, but in a completely different way. The first Pb fraction released during the initial stage of weathering of a fresh granitic rock has higher $^{206}\text{Pb}/^{204}\text{Pb}$, higher $^{208}\text{Pb}/^{204}\text{Pb}$ and lower $^{207}\text{Pb}/^{206}\text{Pb}$ than its bulk composition [10,43,44]. This is because $^{206}\text{Pb}$ and also $^{208}\text{Pb}$ are loosely bound in U- and Th-rich minerals and grain boundaries due to radiation damage originating from the decay of $^{238}\text{U}$ and $^{232}\text{Th}$. Intense physical erosion during glacial periods causes increased exposure of fresh, previously unweathered rock surfaces and thus favours the release of radiogenic Pb. It has been inferred by von Blanckenburg and Nå-
gler [10] that this is the main reason for the drastic mismatch between the Pb isotope composition of deep water in the Northern Atlantic (present-day NADW has a $^{206}\text{Pb} / ^{204}\text{Pb} \simeq 19$ [22]) and that of the nearby continental landmasses (Archaean crust from Labrador, Greenland, and the Proterozoic parts of Greenland show bulk $^{206}\text{Pb} / ^{204}\text{Pb}$ between 13 and 16 [39]). If the changes in Pb isotope composition over the past few million years reflect the breakdown of minerals enriched in U such as zircon, we can calculate the average age of these zircons. Zircon incorporates almost no common lead and therefore its $^{204}\text{Pb} / ^{206}\text{Pb}$ ratio is effectively zero. The correlation between $^{207}\text{Pb} / ^{206}\text{Pb}$ and $^{204}\text{Pb} / ^{206}\text{Pb}$ for ALV539 (Fig. 2, MSWD for the linear fit: 0.44) defines a $^{207}\text{Pb} / ^{206}\text{Pb}$ intercept at zero $^{204}\text{Pb} / ^{206}\text{Pb}$ that corresponds to an age of $1.68^{+0.19}_{-0.20}$ Ga. This age is probably biased to low values because the dominant leachable Pb in crustal rocks is labile $^{206}\text{Pb}$ from U-rich lattice damaged sites. However, even as a minimum value it is consistent with the presence of large outcrops of Precambrian crust in the area bordering the North Atlantic. The data for crust BM1969.05 (Fig. 2, MSWD = 0.40) do not define such a precise intercept, but the resulting age, $1.30^{+0.31}_{-0.39}$ Ga, is similar.

One can take this a step further and calculate the $\varepsilon_{\text{Hf}}$ value of a hypothetical ‘pure zircon component’. There have certainly been sources other than zircons contributing to the dissolved Hf and Pb in the North Atlantic but nevertheless this value is a useful semi-quantitative test of the hypothesis that the changes in Hf isotopes in seawater have indeed been dominated by zircon destruction. Linear extrapolation of the $\varepsilon_{\text{Hf}}$ vs $^{204}\text{Pb} / ^{206}\text{Pb}$ plot of ALV539 to $^{204}\text{Pb} / ^{206}\text{Pb} = 0$ yields an $\varepsilon_{\text{Hf}}$ value of $-100 \pm 20$ (MSWD = 1.43) if the uppermost 2.25 mm (0.75 Myr) are omitted (Fig. 3). This youngest portion shows no clear relationship between Hf and Pb isotopes, probably due to the complex processes involved in the more intense breakdown of the zircons themselves and other silicates, rather than just the initial release of loosely bound radiogenic Pb. The $\varepsilon_{\text{Hf}}$ of $-100 \pm 20$ is similar to reported Hf isotope measurements in single grains of zircon from Greenland (3.81 Ga, $\varepsilon_{\text{Hf}}(0) = -83$ to $-87$ [26]) and north-western Canada (3.60 Ga, $\varepsilon_{\text{Hf}}(0) = -82$ to $-88$ [42]) and is consistent with an Archaean crustal residence age.

4. Concluding remarks

The presented lines of evidence support the conclusion that the offset in Hf relative to Nd isotope composition in seawater is caused by incomplete breakdown of zircon, an effect that is lessened during more intense physical erosion. Average continental crust of old landmasses such as the Canadian shield or Greenland, which are the main source regions for detritus supply to the NW Atlantic Ocean, host a large amount of very unradiogenic Hf, which is released to the ocean mainly during periods of intense mechanical weathering such as NHG. Therefore, the combination of Nd and Hf isotopes in seawater at locations which are directly sourced by continental regions should be a powerful tool to assess changes in style and intensity of continental weathering in the past, which have been related to major climatic changes.

However, with our restricted data set we cannot ultimately rule out the possibility that the trends observed in ALV539 and BM1969.05 are – at least partly – due to changes in the source areas. Further work on other suitable locations or on
other promising weathering tracers (e.g. Os isotopes \cite{45,46}) is necessary to demonstrate conclusively that incongruent weathering of Hf is responsible for the observed decoupling of Hf and Nd in NW Atlantic deep water.

Acknowledgements

We are very grateful to Alex Piotrowski and Friedhelm von Blanckenburg for discussion and comments on an earlier version of this paper. The final version of this paper greatly benefited from thorough and constructive reviews of Bernhard Peucker-Ehrenbrink and an anonymous reviewer. Yoshihiro Asahara is thanked for assistance with the Hf chemistry. This research was supported by the Swiss National Fonds and the ETH.

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