Controls on the incongruent release of hafnium during weathering of metamorphic and sedimentary catchments

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Abstract

It is well established that Hf weathers incongruently such that the isotopic compositions in seawater are offset from those of Nd relative to the correlation defined by bulk lithologies of the continental crust. Here we study this process in detail with new records of the seasonal variability of isotope compositions and concentrations of Hf and Nd in four Swiss rivers. The water has been filtered at a pore size of 0.45 μm and therefore represents the truly dissolved and the colloidal pool of both elements. The studied rivers drain metamorphic (gneissic) or sedimentary (mixed carbonate/siliciclastic) lithologies. The dissolved isotope data are compared to the isotope compositions and concentrations of the suspended load and different fractions of the actual source rocks in the respective catchments, as well as to concomitant changes in the aqueous chemistry of the major elements.

Dissolved Nd concentrations span similar ranges for all rivers, whereas Hf concentrations are one order of magnitude lower in the rivers that drain gneissic catchments compared to those draining sedimentary rocks. This primarily results from the retention of most of the Hf in the gneissic zircons, as indicated by the Hf budget of the gneisses, whereas Hf in the sedimentary catchments is readily weathered from fine detrital silicates.

Large differences are found between the dissolved Hf isotope compositions of the rivers and those of the suspended load and the source rocks, consistent with the release of Hf from a radiogenic rock fraction during weathering. In the metamorphic catchments this primarily reflects that fact that zircons are barely accessible for weathering. The zircon-free portion of the rocks appears to weather congruently as the riverine Hf isotope compositions are similar to the zircon-free portion of the gneisses, rather than being distinctly more radiogenic. Leaching experiments performed to understand the riverine Hf budget in the sedimentary catchments reveal that the carbonate fraction of the sedimentary rocks is extremely radiogenic, yielding Hf isotope compositions up to ε_{Hf} of +208. However, the Hf concentrations in the carbonate fractions are too low to dominate the riverine Hf budget, which is instead controlled by the weathering of detrital silicate minerals.

Two of the catchments, a metamorphic and a sedimentary one, show relatively systematic changes towards more radiogenic dissolved Hf isotope compositions as discharge increases. This suggests that continental runoff conditions could be a relevant parameter for the control of the seawater Hf isotope composition, whereby more congruent weathering is achieved during low discharge when Hf is increasingly derived from weathering-resistant unradiogenic minerals.
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1. INTRODUCTION

The interplay between physical and chemical weathering is of particular interest because it appears to be important for the processes that control the long-term carbon cycle (e.g., Raymo and Ruddiman, 1992; West et al., 2005; Vance et al., 2009). While some radiogenic isotopic systems, such as Rb–Sr and U–Th–Pb, have been used extensively to investigate weathering processes (e.g., Blum and Erel, 1997; Harlavan and Erel, 2002), coupled Hf and Nd isotopes have been relatively neglected, yet potentially offer greater insight. Variable Lu/Hf ratios in rock forming minerals result in variable Hf isotope compositions due to the decay of ^{176}Lu to ^{176}Hf over time. The Hf isotope compositions of river waters reflect this because they are derived from the integrated Hf budget of weathered minerals. Thus, Hf isotopes in the dissolved load of rivers have the ability to track the preferential weathering of some key mineral phases. Combined with Nd isotopes, this may have the potential to quantify the distinction between times of less intense weathering, when Hf-rich, low Lu/Hf zircon is largely resistant to dissolution, from periods of intense physical erosion, such as during glaciation, when zircons suffer more effective physical breakdown and are thus possibly more readily weathered (Piotrowski et al., 2000; van de Flierdt et al., 2002). This in turn could potentially clarify the relationships between the intensity of chemical weathering and its controlling factors – namely physical weathering vs climatic controls – through Earth history. However, this approach, and especially its "groundtruthing" through observations in the present day weathering environment, has scarcely been explored because of the technical difficulties associated with the low concentrations of Hf in aqueous solutions at the Earth's surface.

Hints at how this could be done come from global Nd–Hf isotope systematics, which can essentially be described by two linear arrays. The global distribution of seawater isotope compositions (Godfrey et al., 2009; Rickli et al., 2009; Zimmermann et al., 2009a,b; Stichel et al., 2012a), also recorded in authigenic marine sediments (White et al., 1986; Godfrey et al., 1997; Albarède et al., 1998; David et al., 2001), is offset towards more radiogenic Hf from the global silicate earth array or terrestrial array (Vervoort et al., 1999, 2011). Though it has been suggested that the shift of seawater from the terrestrial array might be due to the addition of radiogenic Hf to the ocean from hydrothermal systems (White et al., 1986; Bau and Koschinsky, 2006), whereas Nd is strongly scavenged into hydrothermal sediments (Michard et al., 1983; Halliday et al., 1992), subsequent work has found no indication for radiogenic Hf contributions to seawater from hydrothermal vents (Firdaus et al., 2011). Rather it appears that weathering of the continental crust is the dominant input of Hf to seawater, though with the usual caveats that a significant portion of riverine Hf is trapped in estuaries (Godfrey et al., 2008) and that there are further external sources including the interaction of seawater with continental shelf sediments (Zimmermann et al., 2009a) and mafic ocean islands (Rickli et al., 2010; Stichel et al., 2012b), as well as the partial dissolution of dust (Rickli et al., 2010). Thus, in recent years a variety of studies have concluded that the offset between the seawater and terrestrial array mainly results from the incongruent behaviour of Hf during continental weathering (Bayon et al., 2006, 2009; van de Flierdt et al., 2007).

In terms of incongruent weathering of Hf isotopes, the focus has been on zircons (Albarède et al., 1998; Piotrowski et al., 2000) due to their high Hf concentrations ($\sim$1.7 wt.%) (Hoskin and Schaltegger, 2003), unradiogenic Hf isotope compositions and their resistance to weathering. However, there is also evidence that even the zircon-free crust weathers incongruently. River dissolved Hf isotope compositions and those of leached parent material from the Vosges mountains (France) suggest that the dissolved Hf in the rivers is dominated by the weathering of trace minerals such as apatite and titanite, which are characterised by high Lu-Hf ratios and radiogenic Hf isotope compositions (Bayon et al., 2006). This finding is supported by observations on the Hf isotope compositions of marine sediments (Chauvel et al., 2008; Bayon et al., 2009; Carpentier et al., 2009; Vervoort et al., 2011) and a model, which estimates the Hf isotope composition of the zircon-free crust from U–Pb ages and Hf isotope compositions of riverine zircons (Chen et al., 2011). These studies confirm that congruent weathering of the zircon-free crust would yield less radiogenic Hf isotope compositions than observed in seawater.

In this study we investigate the seasonal variability in Hf and Nd isotope composition and concentrations in filtered waters ($<$0.45 μm) of four Swiss rivers, which drain mixed carbonate/siliciclastic and gneissic catchments. We adopt the term "dissolved" for the elemental concentrations and isotope compositions in the filtered waters, noting that the filtrate will contain a truly dissolved and a colloidal fraction of Hf and Nd. Dissolved isotope compositions are compared to those in the suspended matter and the weathered parent rocks. We aim to constrain the relationship between (1) the weathered lithology, the riverine chemistry and further environmental parameters and (2) the congruency in Hf weathering and its dissolved concentrations. The findings deepen our current understanding of the behaviour of Hf isotopes during weathering, and contribute to a sounder interpretation of records of past seawater Hf isotope compositions. Hafnium and neodymium isotope compositions are expressed in ε_{Hf} and ε_{Nd} units, which are the deviations of the ^{176}Hf/^{177}Hf and ^{143}Nd/^{144}Nd ratios in samples from those of the Chondritic Uniform Reservoir (CHUR) of 0.282785 (Bouvier et al., 2008) and 0.512638 (Jacobsen and Wasserburg, 1980) in parts per 10,000.

2. SAMPLING AND METHODS

2.1. Geological setting

The four rivers in this study drain different catchments within Switzerland (Fig. 1). The Verzasca is a high mountain river with a small catchment (186 km^2) that has eroded a narrow V-shaped valley into crystalline bedrock. Bedrock outcrops and thin soil layers dominate the catchment's

surface. In the catchment of the Ticino (1515 km^2) the main valley consists of cultivated alluvial flood plains covered with extensive soil horizons, flanked on both sides by high mountains. The two other rivers, the Birs (911 km^2) and the Saane (1861 km^2), represent meandering river systems. The land use in both catchments is mainly agriculture and forestry.

The Verzasca and the Ticino drain catchments within the metamorphosed (amphibolite-facies) Pennine units of the central Alps (Fig. 1a), where mica-rich gneisses of granitic and sedimentary origin dominate the bedrocks. Apart from the mapped small outcrops of amphibolites and marbles in the catchment of the Verzasca, there are also frequent lenses of amphibolites, eclogites and marbles occurring in the side-valleys Val d' Efra and Val Frasco. Additionally boudins and megaboudins of meta-peridotite and meta-rodinites

outcrop in these valleys (Evans and Trommsdorff, 1974; Pfiffner and Trommsdorff, 1998). The precise total extent of such outcrops cannot be estimated, as a detailed map is not available to date. In the catchment of the Ticino, there are also minor occurrences of amphibolites, metamorphosed peridotites and marbles and calcareous schists ("Bündnerschiefer"). Evaporites occur in the northern part of the catchment of the Ticino.

The Birs is located in the northern part of Switzerland and drains the Swiss Jura Mountains (Fig. 1b). The bedrock consists largely of marine Mesozoic sediments, which are dominated by limestones, but also include marly lithologies and some claystones. In addition, there is a significant proportion of Tertiary siliciclastic marine and freshwater deposits of the Alpine foreland basin (Lower Freshwater
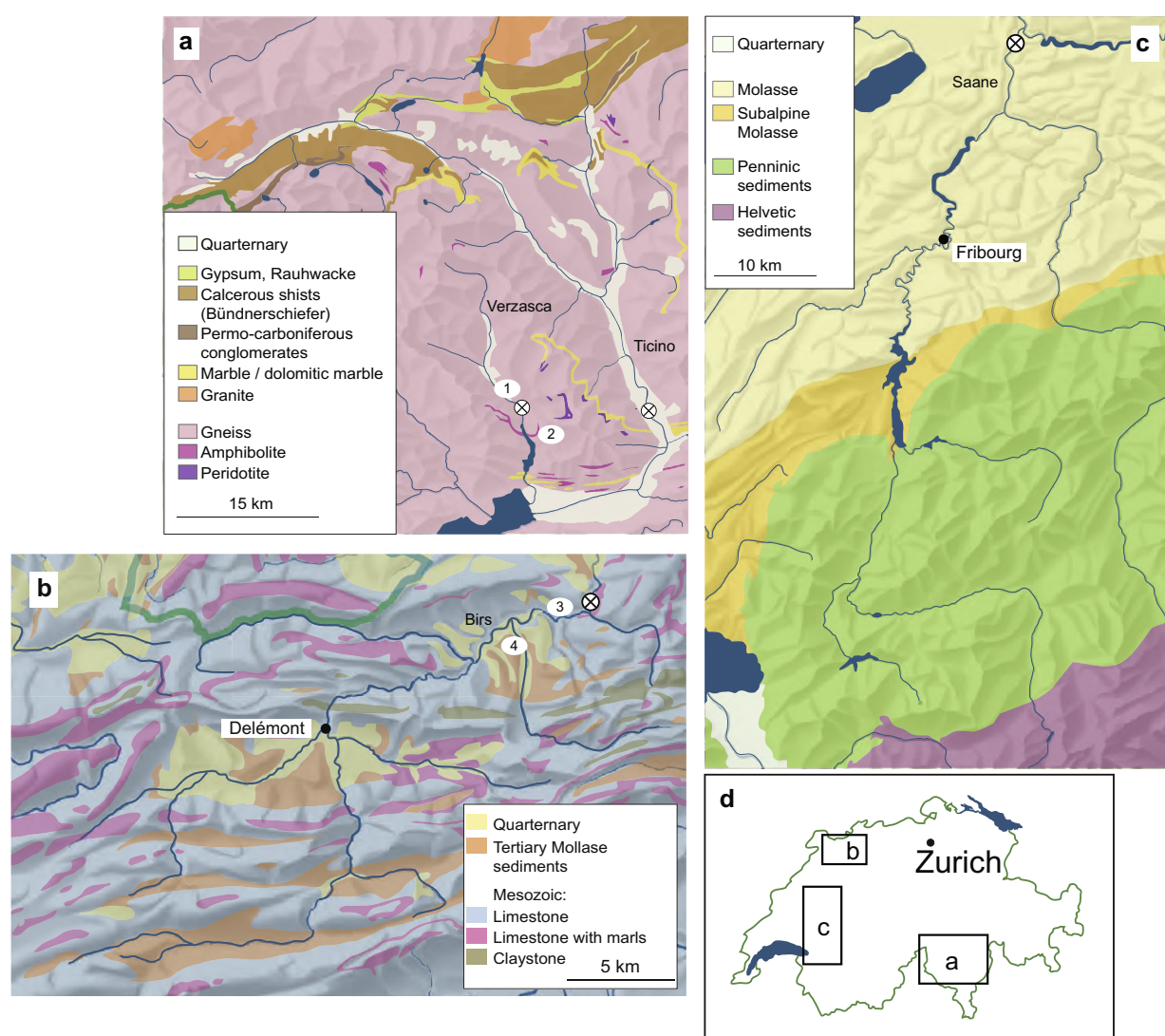

Fig. 1. Geological maps of the four river catchments: (a) the Verzasca and the Ticino, (b) the Birs and (c) the Saane. (d) illustrates the geographical positions of the catchments within Switzerland. Crosses indicate the sampling locations. The gneiss boulders in the Verzasaca were sampled at location 1, the amphibolite at an outcrop at location 2. The limestone samples in the catchment of the Birs were sampled at location 3, the carbonate sandstone at location 4. For a more detailed description of the lithologies within the geological units of (b) and (c) see Section 2.1. The maps are based on the Atlas of Switzerland 3 (2010).

Molasse, Upper Marine Molasse). The catchment of the Saane covers a variety of different sedimentary lithologies (Fig. 1c). The mountainous part of the catchment drains sedimentary units of the Penninic depositional realm, and includes marine turbidites (Flysch), marls and limestones. In the lowlands the river flows through sliliciclastic marine and freshwater deposits (Lower Freshwater Molasse, Upper Marine Molasse), consisting of carbonate-rich sandstones and claystones.

2.2. Sampling

2.2.1. River waters and suspended matter

Each of the four rivers was sampled 10 times between March 2004 and July 2005, and the sample locations and field campaigns were the same as those of a previously published study on Si isotopes (Georg et al., 2006). Sample locations were chosen close to monitoring stations of the Swiss Federal Office for the Environment (FOEN) to ensure that changes in discharge for each sampling point are well documented. Twenty to forty litres of river water were collected close to the riverbank and filtered through 0.45 μm Millipore nitrocellulose filters (142 mm diameter) at the sampling site. The filtered water was collected in acid pre-cleaned 20 l canisters and the water was acidified with suprapure HCl to a pH between 2 and 3. The corresponding filters covered with suspended load were stored in individual polyethylene bags. Concentration measurements of the main cations and trace elements for each sample were performed by ICP-MS at ACME Analytical Laboratories Ltd. in Vancouver, Canada. Trace element data are reported in the Appendix, whereas major elements have been published in the prior study on Si isotopes (Georg et al., 2006).

2.2.2. Rock samples

A set of four rock samples was collected from the catchment of the Birs for isotopic analysis (Fig. 1b). Three of these rocks represent the major Mesozoic sedimentary units in the catchment, including the Hauptrogenstein (Bajocian, sample C2), the Rauracien coral limestones and oolites (Oxfordian, sample C1) and the Sequan limestones (Oxfordian, sample C3) (Koch et al., 1983; Bitterli-Brunner et al., 1984). As a representation of the Tertiary Molasse sediments a carbonate sandstone (Oligocene, "Meeressand", sample S1) has been analysed. This selection does not represent the full spectrum of outcropping lithologies, but is a basic framework to study the relationship between Hf and Nd isotopes in the weathered source rocks and in the river. Furthermore the leaching experiments (Section 2.4.4) yield constraints on the significance of the detrital fraction and the authigenic pool (carbonate minerals, FeMn-oxides, as well as marine phosphates) for the Hf and Nd budget of sedimentary rocks, which by extension can be used to characterise marls and claystones. Due to the diversity of sedimentary rocks in terms of age and type it was not feasible to sample a representative suite of rocks in the Saane catchment. For the Saane there is thus only the comparison with the suspended sediment, which is likely to integrate a signal of the weathered rocks in the catchment in terms of Nd iso-

topes (e.g., Goldstein et al., 1984) but is potentially influenced by sedimentary sorting with respect to its Hf isotope composition (e.g., Patchett et al., 1984).

Five metamorphic rocks were sampled in the catchment of the Verzasca. Four of them were typical large gneiss boulders (G1–G4) collected in the riverbed of the Verzasca. The fifth is a fresh amphibolite (A1) sampled at an outcrop (Fig. 1a). Due to the similar catchment lithologies of the Verzasca and the Ticino (see Section 2.1), the gneisses sampled near the Verzasca are inferred to be representative of the catchment of the Ticino as well.

2.3. Correction for wet depositional and road salt input

The characteristics of the four rivers in terms of their major element chemistry have been outlined in Georg et al. (2006). Chlorine contributions from road salts rendered the use of Cl^- concentrations in the river and elemental ratios in the rain inadequate for atmospheric corrections. So Georg et al. (2006) corrected for atmospheric contributions to the dissolved riverine load by comparing riverine elemental fluxes to precipitation fluxes. However, it is noted that Na/Cl in the rain next to sampling areas as well as in road salts is ∼1, and a Na^+ correction that approximately corresponds to the Cl^- concentrations observed in the river should also be made. Georg et al. (2006) corrected Na^+ contributions from precipitation not considering the contributions from road salts. The weathering-derived Na^+ fluxes are re-evaluated here using average elemental Na/Cl ratios in rain at neighbouring sites to the sampling locations in order to correct for the Na^+ contributions from rain and road salt, whereas for the other elements the volumetric correction of Georg et al. (2006) is applied. All major elemental ratios throughout the text and in the figures are corrected for precipitation and road salts and reflect the weathering of the source rocks.

2.4. Chemical processing and blanks

2.4.1. River water

A detailed description of the chemical methods used to separate and purify Hf from the samples is given in Rickli et al. (2009). Samarium, neodymium and hafnium concentrations were obtained on 1–2 l sample aliquots by isotope dilution. An appropriate amount of tracer enriched in ^{178}Hf was added in 200–350 μl of 2 M HF together with a mixed $^{149}Sm/^{150}Nd$ tracer in 250–500 μl of 2 M HNO_3, and the samples were left for 5 days of equilibration. The larger sample fractions (18–38 l) were processed for the determination of Hf and Nd isotope compositions. Hafnium and neodymium were pre-concentrated from the water samples by co-precipitation with ferric hydroxide in the clean laboratory at ETH Zurich. Subsequently they were chromatographically purified as summarised in Section 2.4.5.

Observed procedural blanks for isotopic determinations were 28 pg for Hf and 33 pg for Nd. This corresponds to <0.5% of the Hf in the samples of the Birs and the Saane, and to < 3.5% for the reported samples of the Verzasca and the Ticino. All except one sample from the Ticino were very low in Hf concentrations (corresponding to less than

0.9 ng in 40 l) and it was not possible to measure their Hf isotope compositions. Neodymium isotope blanks are <0.1% of the smallest river water sample analysed. Isotope dilution blanks corresponded to <0.2% for Nd and <5.2% for Hf. No blank corrections were applied to the isotopic and concentration determinations.

2.4.2. River suspended matter

A selection of the collected suspended matter samples was processed to characterise the Hf and Nd isotope composition of the suspended load of the four rivers. Several filters from a single sampling event were placed in acid pre-cleaned 60 ml porcelain crucibles and heated stepwise to 550 °C in an oven to oxidise the nitrocellulose. The suspended matter, ranging between approximately 20 and 90 mg in mass, was subsequently transferred into Teflon vials in 10 ml of 2 M HCl. After evaporation to dryness, 4 ml of concentrated HF and 1 ml of concentrated HNO_3 were added and the samples were digested for 5 days in a pressurised bomb. Following digestion, Hf and Nd were chromatographically purified as summarised in Section 2.4.5.

A blank was obtained by processing four blank nitrocellulose filters in the same way as the samples. The observed blank was 73 pg for Hf and 1.35 ng for Nd. For both elements this was <0.3% of the smallest sample size and hence no blank corrections were applied.

2.4.3. Metamorphic rocks

The gneisses and the amphibolite were first crushed in a jaw crusher. Subsequently rock fragments were milled in an agate mill for 4 min, producing rock powders with grain sizes between approximately 50 and 100 μm. The rock powders were digested using two different methods, namely a hot plate digestion (HP) and a digestion in a pressurised bomb (PB). HP digestion was performed at 140 °C for 3 days in 4 ml concentrated HF and 1 ml concentrated HNO_3, while the PB digestion was performed for 5 days using the same acids. For isotopic determinations 100 to 200 mg of rock powder were digested in the bomb and 500 mg during HP digestion. For the determination of concentrations 40–60 mg of rock powder was spiked for Hf and Sm/Nd and subsequently digested using both digestion methods.

The two different digestion methods were applied to yield two significant pieces of information. On the one hand the contrast in Hf concentrations and isotopes between both methods allows quantification of the significance of zircons for the Hf budget of the rocks, as zircons do not dissolve during HP digestion. On the other hand a comparison of the Hf isotope composition observed in the HP digests with the river dissolved Hf isotope compositions will allow an assessment of the magnitude of incongruent weathering of Hf from the zircon-free crust in the sampled metamorphic catchments. Such incongruent weathering of the zircon-free crust has been proposed to occur in igneous catchments of the Vosges Mountains (Bayon et al., 2006). The hot-plate digestion, however, is not meant to reflect the natural weathering process as it will dissolve all non-zircon bound Hf, and will not weight the contributions of the variable minerals according to their relative weathering rates. To mimic weathering suitable leaching protocols have to be designed,

which yield sufficient Hf for isotopic analysis. In the case of the sampled gneisses – and possibly many felsic rocks – this will be hampered by the very low non-zircon bound Hf concentrations of 35–42 ng Hf per g of rock (see Section 3.3.1).

To test the potential significance of phosphates for the Hf budget of the Verzasca and the Ticino a weak leach in 0.5 M HNO_3 was performed for 24 h on ~4 g of crushed rock powder of the gneisses and the amphibolite. This approach is identical to the first leaching step performed by Bayon et al. (2006) in terms of leaching agent, molarity and leaching time. Bayon et al. (2006) concluded that most of the phosphates were dissolved during this initial leaching step, before using higher molarities during later steps.

Following digestion or leaching, Hf and Nd were chromatographically purified as summarised in Section 2.4.5. Procedural blanks for isotope compositions and concentrations were <0.1% for Nd and <0.4% for Hf. No blank corrections were applied.

2.4.4. Sedimentary rocks

In order to investigate the Hf and Nd contributions from pure carbonate, FeMn-oxides, phosphates and silicates to the dissolved budget of the Birs, Hf and Nd isotope compositions and concentrations were measured on bulk sedimentary rocks, as well as on leached fractions. The leaching experiments and bulk measurements were performed on rock powders. Rock fragments of the sedimentary rocks were produced with a hammer and subsequently fragments were milled as outlined for the metamorphic rocks. Sample sizes corresponded to 50–70 mg for concentration determinations, to 280–670 mg for bulk isotope measurements, and to between 2 and 6 g for isotopic measurements of leached fractions.

The primary leach series, referred to as the *acetate series*, aims to de-convolve the contributions to the Nd and Hf budget from carbonate, FeMn-oxides and the detrital fraction, consisting of silicates and potentially phosphates. For these series we report a complete set of Hf and Nd isotopes and concentrations, excluding the Hf isotope composition of the FeMn fraction, which proved to be very poor in Hf. The carbonate was leached with 0.5 M sodium acetate and 0.5 M acetic acid, whereas FeMn-oxides were leached using a buffered mixture of 0.05 M hydroxylamine hydrochloride, 15% acetic acid and 0.01 M EDTA (Gutjahr et al., 2007). The detrital fraction was digested in 4 ml of concentrated HF and 1 ml of concentrated HNO_3 at 140 °C on a hotplate to yield isotope compositions of the more readily weathering non-zircon bound portion of the detrital Hf.

A second leach series, referred to as the *HCl series*, aims to characterise the significance of phosphates for the Nd and Hf budget of the rocks. The reported data include all Hf and Nd concentrations as well as the Hf isotope composition of the intital HCl leach in 1 M HCl. The series first uses 1 M HCl to leach carbonate, FeMn-oxides and potentially phosphates. 1 M HCl has been used as the last most aggressive reagent in a leaching series to extract phosphorus from marine sediments and will dissolve authigenic/biogenic and detrital apatite (Ruttenberg, 1992). Subsequently the series continues as the acetate series, whereby any remaining FeMn-oxides are leached before the final

digestion of the residue. Comparing the results from both leach experiments will help constrain the significance of carbonate, FeMn-oxides, phosphates and silicates for the REE and Hf budget of the rocks.

For isotopic analyses Hf and Nd were enriched from the leaching solution by co-precipitation with ferric hydroxide, whereas the smaller isotope dilution samples were dried down and re-dissolved for column chemistry. The samples for bulk isotope and concentration determinations were first dissolved in 6 M HCl to dissolve carbonate. Subsequently the silicates were digested in HF and HNO_3 (as above) and, after evaporation to dryness, recombined with the dissolved carbonate fractions in HCl.

The leached fractions and the bulk samples were chromatographically purified as summarised in Section 2.4.5. Blanks for bulk and leached samples corresponded to <0.5% for Nd and Hf isotope and Nd concentration measurements. For Hf concentrations blanks were usually <1%, excluding three very depleted samples where they reached up to 3.8%. No blank corrections were applied.

2.4.5. Chromatographic separation of Hf and Nd

The separation of Hf and Nd for the determination of isotope compositions used a combination of three ion exchange columns. These were: a (a) cation exchange column (AG50W-X8, 2.7 or 7 ml resin bed) allowing for the separation of rare earth elements (REEs, including Nd) and high field strength elements (HFSE, including Hf) from each other and the remaining matrix (Patchett and Tatsumoto, 1980), (b) an Eichrom Ln spec column to separate Hf from the other HFSE (Ti, Zr) but also from the REEs (Münker et al., 2001) and (c) an Eichrom Ln spec column to separate Nd from the other REEs (Pin and Zalduegui, 1997). For the ferric hydroxide precipitates of the river waters and the carbonate leachates the cation exchange column (column a) was used first followed by the individual purification of Hf and Nd (column b, c). All other samples were first processed following Münker et al. (2001, column b), resulting in a pure Hf fraction ready for mass spectrometric analysis and a REE fraction for subsequent purification of Nd following Pin and Zalduequi (1997, column c). In many cases the REE fraction collected from column (b) still contained a large amount of matrix elements and was therefore first processed through a 1.4 ml cation exchange column before the final separation of Nd.

The separation of Hf and Nd for the determination of concentrations by isotope dilution was achieved on 1.4 ml cation exchange resin following Patchett and Tatsumoto (1980). The HFSE and the REE fractions were not processed further, since Sm, Nd and Hf all have sufficient interference-free isotopes to allow the determination of concentrations without further separation steps. In the case of Nd this, however, involves a deconvolution of the Sm and Nd contributions on mass 150, which corresponds to the enriched Nd isotope of the spike.

2.5. Mass spectrometry

Hafnium and neodymium isotope compositions and concentrations of river waters and river suspended matter were measured on a Nu Plasma MC-ICPMS at ETH Zurich. Igneous rocks and sedimentary rocks (leachates/bulk rocks) were measured for their isotope compositions on a Nu Plasma MC-ICPMS (GEOMAR, Kiel) and/or on a Neptune MC-ICPMS (University of Bristol). Hafnium and neodymium concentrations of these rocks and leachates were determined on the Neptune instrument in Bristol. As a convention 2 SD external reproducibility is reported for isotopic measurements (see Sections 2.5.1 and 2.5.2) and 1 SD external reproducibility for measured concentrations (see Section 2.5.3). Natural variability of any observation, e.g. the dissolved isotope compositions observed in the Birs, is reported as average ±1 SD.

2.5.1. Hafnium isotopes

Measured Hf isotope compositions were corrected for mass bias using a $^{179}Hf/^{177}Hf$ ratio of 0.7325 and applying an exponential mass fractionation law. Minor interference corrections (<4ε_{Hf}) on the measured ^{176}Hf intensity were applied by monitoring ^{172}Yb (respectively, ^{173}Yb in Bristol) and ^{175}Lu. All data were normalised to the accepted literature value for JMC 475 of 0.282160 (Nowell et al., 1998; Vervoort and Blichert-Toft, 1999) using the average value obtained during the respective session. The external reproducibility of the $^{176}Hf/^{177}Hf$ ratios was estimated from repeated measurements of JMC 475 solutions in the course of a measuring session ($n = 9$–38). Dilutions (10, 20 or 50 ppb) and integration times of the measured JMC 475 solutions were adapted for the samples of the corresponding session. Estimated reproducibility depends mainly on sample size and to some degree on the MC-ICPMS in question and ranges between ±0.2ε_{Hf} for rock samples and ±1.5 to 1.7ε_{Hf} for the most depleted river and carbonate leach samples (2 SD, Tables 1–3). Duplicate measurements performed on gneisses on the Nu instruments (Kiel) and Neptune (Bristol) mass spectrometers agree within the analytical uncertainty (Table 2). These replicates are either complete replicates, including two separate digestions (G2, G4), or replicate measurements of independently purified stock solutions (G1, G2).

To assure the integrity of the data the $^{178}Hf/^{177}Hf$ ratios (corrected for mass bias using $^{179}Hf/^{177}Hf$) were monitored for all samples. The measured ratios are natural within the external reproducibility of the data, as deduced from repeated measurements of JMC 475.

2.5.2. Neodymium isotopes

Neodymium isotope compositions measured on the Nu Instrument MC-ICPMS (Zurich, Kiel) were corrected for mass bias to $^{146}Nd/^{144}Nd$ of 0.7219 applying an exponential mass fractionation law. All data were normalised to the accepted literature value for JNdi-1 of 0.512115 (Tanaka et al., 2000) using the average value obtained during the respective session. External reproducibility, estimated from repeated measurements of 50 ppb JNdi-1 solutions in the course of a measuring session, was <0.33ε_{Nd} ($n = 13$–21, 2 SD).

Neodymium isotope determinations on the Neptune instrument (Bristol) followed the procedures outlined in Vance and Thirlwall (2002). Mass bias corrected ratios were normalised to the $^{143}Nd/^{144}Nd$ of the La Jolla standard

Table 1

Hafnium and neodymium isotope compositions and concentrations in the four sampled Swiss rivers. The reproducibility of Nd concentrations is better than 1% (1 SD). For the Hf-rich Saane and Birs the reproducibility of Hf concentrations corresponds to 3%, for the Ticino and the Verzasca to 14% (1 SD).

River	Sample	Hf (pmol/l)	Nd (pmol/l)	Hf/Nd	Sm/Nd	ε_{Hf}	Internal repro. ±2 SEM	External repro. ±2 SD	ε_{Nd} ±0.3, 2 SD
Birs	Mar 04	4.04	22.10	0.183	0.226	−4.31	±0.43	±0.63	−
Dissolved, <0.45 μm	May 04	1.65	20.00	0.083	0.223	−	−	−	−9.34
	Aug 04	2.93	39.84	0.073	0.221	−	−	−	−9.50
	Oct 04	1.91	20.61	0.093	0.232	−2.06	±0.42	±0.65	−9.49
	Jan 05	1.04	25.94	0.040	0.219	−1.78	±0.42	±0.65	−9.55
	Feb 05	2.83	26.19	0.108	0.216	−2.02	±0.42	±0.65	−9.15
	Mar 05	3.65	67.24	0.054	0.213	−0.36	±0.22	±0.65	−9.21
	May 05	2.26	33.88	0.067	0.218	−1.56	±0.27	±0.65	−8.97
	Jun 05	5.28	168.29	0.031	0.212	−2.30	±0.23	±0.63	−9.91
	Jul 05	2.25	36.71	0.061	0.215	−3.57	±0.23	±0.63	−9.17
Suspended, >0.45 μm	Jan 05	−	−	−	−	−9.82	±0.25	±0.59	−9.90
Saane	Mar 04	3.54	40.24	0.088	0.263	+5.45	±0.41	±0.63	−8.41
Dissolved, <0.45 μm	May 04	1.32	19.25	0.069	0.273	+3.82	±0.69	±1.13	−8.81
	Aug 04	0.98	19.04	0.051	0.232	+4.87	±0.33	±0.65	−7.82
	Oct 04	1.35	19.78	0.068	0.257	+5.97	±0.41	±0.65	−8.30
	Jan 05	1.61	20.86	0.077	0.269	+5.26	±0.35	±0.65	−8.11
	Feb 05	2.12	32.87	0.065	0.252	+4.62	±0.38	±0.65	−8.11
	Mar 05	1.74	33.27	0.052	0.251	+4.21	±0.27	±0.63	−8.21
	May 05	1.98	40.77	0.049	0.253	+5.34	±0.27	±0.63	−8.35
	Jun 05	1.68	43.09	0.039	0.241	+3.29	±0.27	±0.63	−8.65
	Jul 05	1.22	20.54	0.059	0.244	+4.99	±0.55	±0.63	−8.33
Suspended, >0.45 μm	Jan 05	−	−	−	−	−6.53	±0.18	±0.59	−8.98
Ticino	May 04	0.31	86.44	0.0035	0.261	−1.59	±0.99	±0.94	−9.11
Dissolved, <0.45 μm	Aug 04	0.10	69.75	0.0014	0.248	−	−	−	−9.32
	Oct 04	0.09	9.94	0.0086	0.249	−	−	−	−8.52
	Jan 05	0.08	14.01	0.0055	0.218	−	−	−	−9.13
	Feb 05	0.07	11.99	0.0058	0.213	−	−	−	−9.18
	Mar 05	0.12	19.60	0.0062	0.241	−	−	−	−8.52
	May 05	0.07	31.05	0.0023	0.232	−	−	−	−9.28
	Jun 05	0.11	26.77	0.0040	0.267	−	−	−	−8.81
	Jul 05	0.05	14.77	0.0035	0.245	−	−	−	−9.10
Suspended, >0.45 μm	Aug 04	−	−	−	−	−5.83	±0.24	±0.63	−9.58
Verzasca	Mar 04	0.76	48.76	0.0155	0.213	+2.82	±1.20	±1.46	−8.73
Dissolved, <0.45 μm	May 04	0.35	52.46	0.0066	0.290	+1.26	±0.92	±1.46	−8.51
	Aug 04	0.42	61.48	0.0068	0.292	+1.60	±0.78	±0.94	−8.41
	Oct 04	0.23	18.94	0.0121	0.163	−	−	−	−8.46
	Jan 05	0.13	16.97	0.0075	0.296	+2.82	±2.12	±1.46	−7.93
	Feb 05	0.14	14.56	0.0098	0.300	−4.18	±2.05	±1.46	−8.11
	Mar 05	0.28	38.53	0.0072	0.296	+2.68	±1.06	±1.46	−8.26
	May 05	0.12	26.06	0.0047	0.291	+5.05	±1.70	±1.46	−8.47
	Jun 05	0.24	46.46	0.0052	0.296	+3.49	±0.92	±1.46	−8.32
	Jul 05	0.22	20.55	0.0105	0.488	−0.29	±1.20	±1.46	−8.29
Suspended, >0.45 μm	Aug 04	−	−	−	−	−4.75	±0.24	±0.62	−8.73

of 0.511856 using the average value obtained during the session. External reproducibility estimated from repeated measurements of 50 ppb La Jolla solutions over the course of the measuring session was $0.12\varepsilon_{Nd}$ ($n = 16$, 2 SD). Duplicate measurements on Nu instrument (Kiel) and Neptune (Bristol) agree within the analytical uncertainty (Table 3). These duplicates represent complete leaching repeats of sedimentary rocks.

2.5.3. Isotope dilution measurements of Hf, Sm and Nd

For Hf as well as for Sm/Nd an iterative routine was developed to correct the ratios used for mass bias corrections for the contributions from the spikes. The spiked Hf ratio $^{178}Hf/^{179}Hf$ was normalised to a natural $^{179}Hf/^{177}Hf$ ratio of 0.7325 using an exponential law. In an analogous manner the spiked $^{150}Nd/^{144}Nd$ and $^{149}Sm/^{147}Sm$ ratios were normalised to a natural $^{146}Nd/^{145}Nd$ of 0.482639.

Replicate processing and measurement of different aliquots of a Saane river sample indicates that for the Hf-rich Saane and Birs rivers the Hf concentrations are reproducible within 3% ($n = 4$, 1 SD). For the Hf poor Verzasca and Ticino the reproducibility is estimated to be 14% ($n = 10$, 1 SD). Neodymium concentrations of river waters are reproducible within 1% ($n = 4$, 1 SD).

Table 2
Hafnium and neodymium isotope compositions and concentrations in four gneiss samples and an amphibolite sample from the catchment of the Verzasca. Nitric refers to the 24 h leach in 0.5 M HNO_3, HP and PB to hotplate and pressurised bomb digestion, respectively. Elemental ratios are given as molar ratios. Isotope compositions given in italics were obtained on a Nu Plasma MC-ICPMS in Bristol, all other data were obtained on a Neptune MC-ICPMS in Kiel.

Sample	Hf Nitric (ppb)	Hf HP (ppb)	Hf PB (ppm)	Nd Nitric (ppm)	Nd HP (ppm)	Nd PB (ppm)	Hf/Nd Nitric ($\times 10^{-3}$)	Hf/Nd HP ($\times 10^{-2}$)	Sm/Nd Nitric	Sm/Nd HP	Sm/Nd PB	ε_{Hf} Nitric	int ±2 SEM	ext ±2 SD	ε_{Hf} HP	int ±2 SEM	ext ±2 SD	ε_{Hf} PB	int ±2 SEM	ext ±2 SD	ε_{Nd} HP	int ±2 SEM	ext ±2 SD	ε_{Nd} Nitric	int ±2 SEM	ext ±2 SD
A1	2.66	352.3	1.45	0.58	14.7	12.4	3.72	1.94	0.224	0.195	0.09	+4.07	±0.50	±0.81	+4.86	±0.49	±0.38	+1.30	±0.11	±0.30	–	–	–	BD	±0.11	±0.25
G1	0.26	34.6	3.72	1.4	23.7	23.4	0.15	0.12	0.341	0.196	0.13				+5.48	±0.64	±0.38	−7.41	±0.14	±0.30	−8.30	±0.08	±0.12	+0.30	±0.11	±0.30
G1 replicate																		−7.12	±0.32	±0.20						
G2	0.42	41.8	4.40	1.0	21.3	26.1	0.36	0.16	0.355	0.181	0.14				−1.38	±0.53	±0.38	−5.73	±0.11	±0.30	−8.56	±0.08	±0.12	−8.09	±0.12	±0.25
G2																		−5.93	±0.35	±0.20				−8.25	±0.11	±0.25
G2 replicate																		−6.00	±0.18	±0.20						
G3	0.40	38.3	3.46	1.1	13.3	25.9	0.30	0.23	0.373	0.187	0.11				−1.64	±0.42	±0.38	−5.07	±0.08	±0.30	−8.31	±0.16	±0.12	−7.84	±0.09	±0.25
G4	0.21	42.1	5.47	2.5	36.1	21.5	0.07	0.09	0.248	0.201	0.21				+19.61	±0.54	±0.38	−8.24	±0.08	±0.30	−8.34	±0.06	±0.12	−8.29	±0.12	±0.25
G4 replicate																		−8.53	±0.14	±0.20						

Pooled gneiss leach, G1 to G4: ε_{Hf} Nitric = +62.65 ±1.20 (±0.81).

Replicate determinations of Hf concentrations in the BCR-2 rock standard, consisting of four separate hotplate digestions, which were processed and measured twice, yielded a value of 5.016 ppm ($n = 8$, 1 SD = 0.3%). This is consistent with the reported Hf concentration in the literature (e.g., Nebel et al., 2009).

3. RESULTS

3.1. Major element chemistry of the four rivers

The major element composition of the collected samples, as well as the long-term data we refer to (Binderheim-Bankey et al., 2000), were corrected for wet depositional input as well as road-salt contribution as outlined in Section 2.3. For Na^+, average weathering-derived fluxes correspond to ∼26%, ∼24%, ∼39%, ∼81% of the Na^+ concentrations observed in the Birs, the Saane, the Ticino and the Verzasca, respectively. Long-term average dissolved solid contents (calculated as the sum of Ca^{2+}, Mg^{2+}, Na^+, K^+, Si, HCO_3^-, SO_4^{2-}, NO_3^-) range between 16 mg/l for the Verzasca and 410 mg/l for the Birs. In the Saane and the Ticino the total dissolved solids are 330 and 180 mg/l, respectively. The Birs, Saane, and Ticino display similar compositions with respect to the major cations and Si, and the order of molar concentrations is as follows: $[Ca^{2+}] > [Mg^{2+}] > [Na^+] + [K^+] > [Si]$. The cation abundances in the Verzasca show a different succession: $[Si] \approx [Ca^{2+}] > [Na^+] + [K^+] > [Mg^{2+}]$, documenting the dominance of silicate weathering in this catchment. The molar Ca/Na ratios, corrected for atmospheric contributions and road salt, reflect the relative contributions from carbonate and silicate weathering, and average long term values are ∼33 for the Birs, ∼39 for the Saane, ∼17 for the Ticino and ∼3 for the Verzasca. For comparison, molar Ca/Na ratios in rivers draining pure carbonates are ∼50, whereas rivers in pure silicate catchments are characterised by a Ca/Na ratio of ∼0.4 (Gaillardet et al., 1999a). As outlined in Georg et al. (2006), a correction for gypsum dissolution should be applied for the Saane and the Ticino, which reduces the Ca/Na ratios to ∼36 and ∼11, respectively. Calcium/sodium ratios in the Birs and the Saane indicate predominant contributions from carbonate weathering as expected from the catchment lithologies. The Ca/Na ratio in the Ticino suggests that carbonate weathering also strongly influences the riverine chemistry, which likely reflects the occurrence of calcareous schists in the northern part of the catchment. The Verzasca indicates the largest contributions from silicate weathering, but potentially still a contribution of ∼5% from carbonate weathering assuming end-member Ca/Na ratios as cited above. This will be evaluated further in Section 4.2.1.

3.2. Dissolved and suspended Hf, Sm and Nd in the rivers

Dissolved Hf concentrations show marked differences between the different catchments (Table 1 and Fig. 2). The Ticino and Verzasca, which drain predominantly gneissic rocks, display very low Hf concentrations that do not exceed 0.3 pmol/l for the Ticino and 0.8 pmol/l for the

Table 3
Bulk and fraction specific Hf and Nd isotope compositions and concentrations in three Mesozoic shallow marine limestones (C1–C3) and a Molasse carbonate sandstone (S1) from the catchment of the Birs. Elemental ratios are given as molar ratios. A detailed description of the two leaching series, referred to as the acetate and HCl series, is given in Section 2.4.4. The concentrations in the fractions are given as ng of an element per mg of bulk sample. Isotope compositions given in italic were obtained on a Nu Plasma MC-ICPMS in Kiel, all other data were obtained on a Neptune MC-ICPMS in Bristol.

	Hf (ppm)		Nd (ppm)		Hf/Nd		Sm/Nd		ε_{Hf}	int.	ext.	ε_{Hf}	int.	ext.	ε_{Nd}	int.	ext.	Replicate ε_{Nd} ±0.12, 2 SD
	Acetate series	HCl series	Acetate	HCl	Acetate	HCl	Acetate	HCl	HCl	±2 SEM	±2 SD	Acetate	±2 SEM	±2 SD	Acetate	±2 SEM	±2 SD	
S1																		
1st leach	0.015	0.020	4.83	6.82	0.0026	0.0024	0.158	0.169	+6.64	±0.51	±0.81	+5.58	±0.48	±0.38	*−8.94*	*±0.09*	±0.25	−8.87
FeMn	0.010	0.017	1.95	0.18	0.0043	0.0782	0.195	0.157	−			+3.91	±0.85	±0.38	*−8.94*	*±0.10*	±0.25	−9.30
Detrital	0.417	0.470	1.43	1.26	0.2362	0.3006	0.169	0.168	−			−13.75	±0.21	±0.20	*−11.70*	*±0.12*	±0.25	
Bulk calculated	0.443	0.507	8.21	8.26	0.0436	0.0496	0.169	0.168				−12.39	−	±0.33	−9.36	−	±0.23	
Bulk measured	0.492/0.590		8.34		0.0476/0.0571		0.167					−11.32	±0.18	±0.20	−9.74	±0.07	±0.12	
C1																		
1st leach	0.003	0.003	7.01	7.45	0.0004	0.0003	0.204	0.195	+176.23	±0.37	±0.38	+208.07	±0.77	±0.81	*−9.36*	*±0.09*	±0.25	−9.12
FeMn	0.003	0.004	0.19	0.06	0.0122	0.0554	0.217	0.178	−			−	−	−	*−9.02*	*±0.10*	±0.25	−9.22
Detrital	0.047	0.042	0.25	0.16	0.1483	0.2190	0.141	0.138	−			−2.34	±0.33	±0.20	*−11.39*	*±0.08*	±0.25	
Bulk calculated	0.053	0.049	7.45	7.67	0.0057	0.0052	0.202	0.194				−	−	−	−9.39	−	±0.25	
Bulk measured	0.051/0.061		7.65		0.0053/0.0064		0.192					+26.20	±0.36	±0.20	−9.21	±0.10	±0.12	
C2																		
1st leach	0.003	0.005	4.20	4.71	0.0006	0.0009	0.209	0.206	+94.37	±0.29	±0.38	+126.65	±0.99	±0.81	*−9.81*	*±0.11*	±0.25	−9.92
FeMn	0.003	0.006	0.19	0.08	0.0148	0.0575	0.248	0.161	−			−	−	−	*−9.79*	*±0.06*	±0.25	−9.92
Detrital	0.058	0.065	0.29	0.37	0.1612	0.1424	0.116	0.130	−			+2.15	±0.29	±0.20	*−11.78*	*±0.10*	±0.25	
Bulk calculated	0.065	0.075	4.68	5.15	0.0112	0.0118	0.205	0.200				−	−	−	−9.95	−	±0.24	
Bulk measured	0.075/0.104		4.91		0.0123/0.0171		0.198					+6.48	±0.24	±0.20	−10.04	±0.09	±0.12	
C3																		
1st leach	0.001	0.001	4.82	5.02	0.0002	0.0002	0.198	0.193	+86.84	±1.33	±1.67	+75.03	±0.90	±0.81	*−7.63*	*±0.10*	±0.25	−7.26
FeMn	0.001	0.001	0.02	0.01	0.0415	0.0753	0.200	0.188	−			−	−	−	*−7.78*	*±0.39*	±0.25	−7.84
Detrital	0.006	0.002	0.03	0.01	0.1968	0.1813	0.198	0.198	−			+0.57	±2.79	±1.67	*−11.15*	*±0.12*	±0.25	
Bulk calculated	0.009	0.005	4.87	5.04	0.0015	0.0008	0.197	0.193				−	−	−	−7.64	−	±0.25	
Bulk measured	0.006/0.017		4.92		0.0009/0.0028		0.192					+18.30	±0.50	±0.20	−7.64	±0.09	±0.12	

Verzasca, yielding averages of only 0.1 and 0.3 pmol/l. In contrast, the Birs and Saane rivers show maxima of 5.3 and 3.5 pmol/l, and averages of 2.8 and 1.8 pmol/l, respectively. While these average Hf concentrations differ by a factor of 25 between the most and the least depleted river, average Nd concentrations are very similar between all rivers, spanning a range from 29 pmol/l in the Saane to 46 pmol/l in the Birs.

The average dissolved Nd isotope composition of the four rivers is very similar and ranges between $\varepsilon_{Nd} = -9.4$ for the Birs and $\varepsilon_{Nd} = -8.3$ for the Saane (Table 1 and Fig. 2). The seasonal variability is very limited, remaining within $1\varepsilon_{Nd}$ unit for all rivers. The suspended loads of the rivers are slightly less radiogenic than the dissolved loads by 0.4–0.7ε_{Nd} units. Dissolved Sm/Nd ratios show only minor temporal variability for the Birs, Saane and the Ticino (1 SD < 0.02) but the variation is more pronounced for the Verzasca (1 SD = 0.08).

In contrast to Nd, Hf displays large isotopic differences between the dissolved load of the four rivers, from an average of $-2.2\varepsilon_{Hf}$ for the Birs to $+4.8\varepsilon_{Hf}$ for the Saane (Table 1 and Fig. 2). The seasonal variability in each river is also larger, and encompasses a range of 3.9ε_{Hf} units for the Birs (-4.3 to -0.4), 2.6ε_{Hf} units for the Saane ($+3.3$ to $+6$) and 9.2ε_{Hf} units for the Verzasca (-4.2 to $+5.1$). The low concentrations in the Ticino allowed only one Hf isotope measurement at a reasonable blank to sample ratio (1.7% blank contribution) and no constraints on its temporal variability are thus available. The measured Hf isotope composition of the Ticino is $\varepsilon_{Hf} = -1.6$ and is within the range observed for the Verzasca. A significant shift to more radiogenic Hf isotope compositions of the dissolved load compared with the suspended load is observed for all rivers. In the gneissic catchments the difference between the average dissolved Hf isotope composition and the suspended load is 4.3 and 6.5ε_{Hf} units for the Ticino and the Verzasca, respectively. In the catchments of the Birs and the Saane, which are dominated by sedimentary lithologies, this difference is larger and amounts to 7.6 and 11.3ε_{Hf} units, respectively.

3.3. Comparison of Hf, Sm, and Nd in the weathered parent rock to the riverine dissolved and suspended load

3.3.1. Igneous rocks from the catchment of the Verzasca

For simplicity we term data measured on bomb digests as "bulk concentrations/isotopes" and data obtained on hotplate digests as "soluble" components. In addition, to make all statements clear, we add PB for pressurised bomb digestion and HP for hotplate digestion as an index (e.g. $\varepsilon_{Hf\text{-}PB}$). As outlined in Section 2.4.3 the hotplate digestion does not reflect the natural weathering process, as different minerals of the rocks will weather at different rates.

Measured rare earth element concentrations vary between 12.4 ppm Nd for the bomb digestion of the ampibolite and 36.1 ppm Nd for the hot plate digestion of gneiss G4. The different digests of the same rock display a variation of up to ∼20% for A1, G1 and G2 (Table 2). For G3 and G4 the variation is even greater but still within a factor of 2. Bomb-digestion does not yield systematically

higher REE concentrations than hotplate digestion and the variations thus reflect inhomogeneity of rock powders, with variable proportions of REE-enriched trace minerals. In contrast, the soluble concentrations of Hf are consistently much lower than the bulk concentration, corresponding to <1% of the bulk concentrations in the case of the gneisses and to 22% for the amphibolite. In absolute terms, gneissic soluble Hf concentrations are below 42 ppb, roughly 1/10 of the corresponding amphibolite concentration. Whereas the Nd concentrations obtained from the nitric leaching experiments on the gneisses are substantial, ranging from 1 to 2.5 ppm, the corresponding Hf concentrations are extremely low, not exceeding 0.42 ppb. As for the HP digestion, the nitric leach of the amphibolite also shows much higher Hf concentrations than observed for the gneisses, yielding a concentration of 2.6 ppb.

The gneisses show homogenous Nd isotope compositions with an average ε_{Nd} of -8.3 (Table 2 and Fig. 3). Hotplate and bomb digests of rock samples are identical within error. This gneissic Nd isotope composition is similar to the suspended and dissolved isotope composition in the Verzasca ($\varepsilon_{Nd} = -8.7$ and -8.3 ± 0.2, 1 SD, respectively) but more radiogenic than the Ticino (suspended $\varepsilon_{Nd} = -9.6$, dissolved $\varepsilon_{Nd} = -9.0 \pm 0.15$, 1 SD). The amphibolite is significantly more radiogenic in Nd than the gneisses yielding a value of $\varepsilon_{Nd} = +0.3$.

The gneisses show relatively large variations in their bulk Hf isotope composition ranging between $\varepsilon_{Hf\text{-}PB} = -8.5$ and -5.1 (Table 2 and Fig. 3). The amphibolite is more radiogenic, yielding an isotope composition of $\varepsilon_{Hf\text{-}PB} = +1.3$. For all rocks the soluble portion is clearly more radiogenic than the bulk: the difference corresponds to 3.7ε_{Hf} for the amphibolite and to between 3.4 and 28.6ε_{Hf} units for the gneisses. The Hf isotope compositions of the river suspended loads of the Verzasca ($\varepsilon_{Hf\text{-}PB} = -4.8$) and the Ticino ($\varepsilon_{Hf\text{-}PB} = -5.8$) are near the radiogenic end of the range observed for the bulk gneisses. On the other hand, the riverine dissolved Hf isotope composition ($\varepsilon_{Hf} = -0.3$ to $+5.1$) is generally similar to the range observed for the soluble Hf isotope compositions of the sampled rocks ($\varepsilon_{Hf\text{-}HP} = -1.6$ to $+5.5$, one value as high as $+19.6$). The riverine dissolved Hf was, however, significantly less radiogenic in February 2005 ($\varepsilon_{Hf} = -4.2$).

The nitric leach of the four gneisses had to be combined for one single isotope measurement due to the low Hf concentrations in the leachates. The pooled sample shows a very radiogenic isotope composition of $\varepsilon_{Hf} = +62.7$, which is much more radiogenic than the observed soluble gneissic isotope compositions that do not exceed $+19.6$. The isotope composition of the amphibolite leachate ($\varepsilon_{Hf} = +4.1$), however, is virtually identical to the soluble amphibolite fraction ($\varepsilon_{Hf\text{-}HP} = +4.9$).

3.3.2. Sedimentary rocks from the catchment of the Birs

In order or characterise the purity of the limestones and the carbonate sandstone the weights of the detrital fractions were determined after dissolution of the carbonate and the FeMn fractions. For the carbonate sandstone S1 this residual fraction corresponds to 13 wt.%, for the limestones C1 and C2 to 1.2 and 1.3 wt.%, respectively. C3 is so pure that
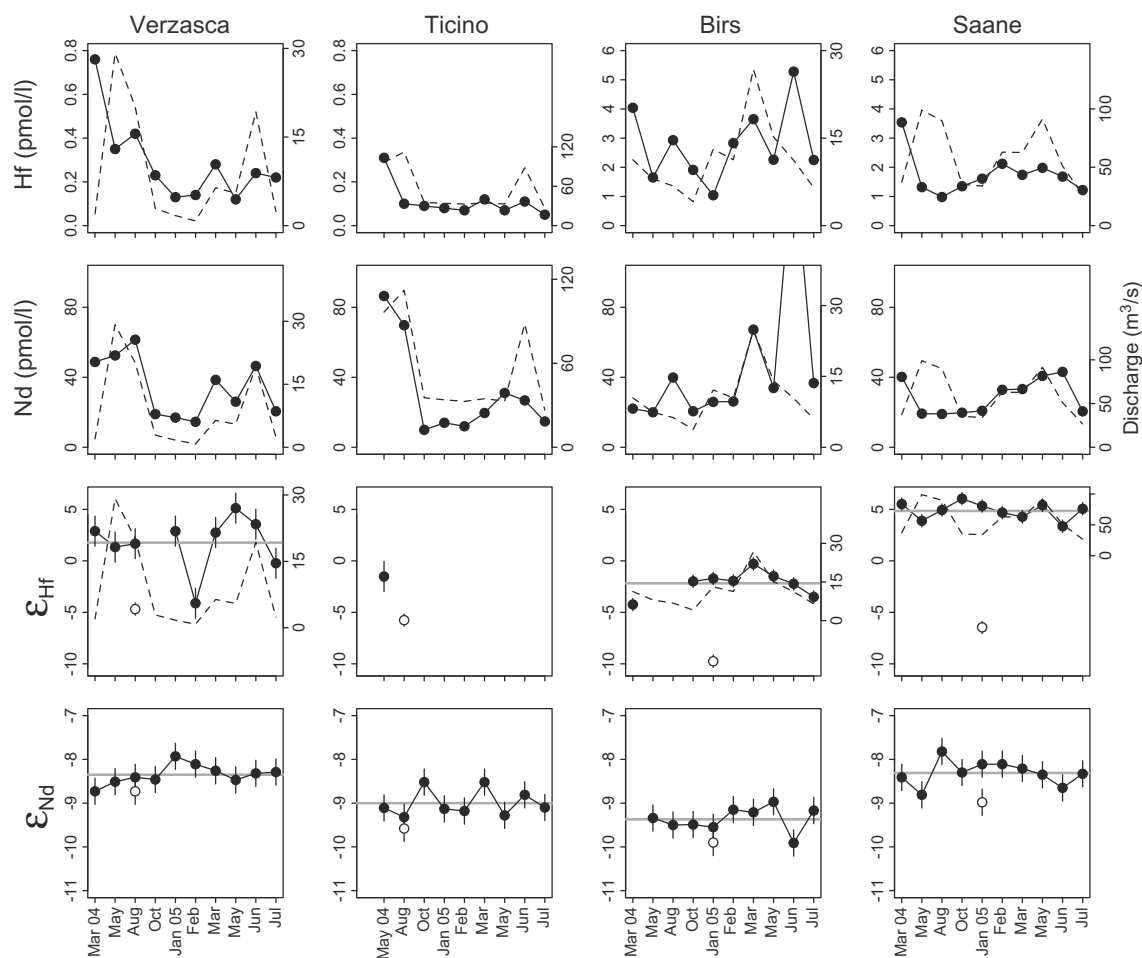
Fig. 2. Hafnium and neodymium concentrations and isotope composition in the Verzasca, Ticino, Birs and Saane between March 2004 and July 2005. Open circles represent the isotope composition of the suspended load (>0.45 μm), solid circles the dissolved concentrations and isotope compositions (<0.45 μm). The grey lines in the graphs for Hf and Nd isotope compositions represent average dissolved compositions and dashed lines indicate discharge.

the residue could not be weighed. These carbonate contents have been confirmed through coulometric determinations of the inorganic carbon content of the samples, which are consistent with the carbonate contents derived from the residual weights after leaching.

For clarity and simplicity we discuss the Nd mass balances of the rocks based on the leached sample aliquots, calculating the bulk as the sum of the fractions, which agrees with the measured bulk Nd concentrations within 5% (Table 3). Also "ppm" always refers here to ng per mg of bulk sample, rather than the concentration in a leached fraction itself.

The Nd concentrations of the bulk rocks range between 5 ppm for C3 and 8.3 ppm for S1 (Table 3). The acetate leaching series indicates that Nd is predominantly associated with the carbonate fraction, exceeding 90% in C1–C3 and corresponding to 59% in S1. The Nd contained in the FeMn fraction ranges between 0.5% and 4% for C1–C3, and corresponds to 24% in S1. Comparing the Nd concentrations in the FeMn fraction from the acetate leaching ser-

ies with the HCl series shows that the 1 M HCl leach dissolved a large portion of the FeMn fraction. This is particularly evident for S1, where the 1 M HCl leach yields 6.8 ppm Nd compared to the 4.8 ppm Nd in the acetate leach. C1 and C2, however, also show a clear effect, and the HCl series of both rocks contain less than half as much Nd in their FeMn fraction as in the acetate series. The detrital fraction contains fairly similar amounts of Nd for both leaching series, agreeing in terms of their fractional contribution to the bulk within 2.1%. In the case of S1 the detrital fraction corresponds to 15.3% (HCl series) to 17.4% (acetate series) of the bulk Nd. For the limestones the detrital fraction contains a maximum of 7% of the bulk Nd for C2.

The leached authigenic carbonate and FeMn fractions are isotopically indistinguishable in each rock and vary between $\varepsilon_{Nd} = -7.5$ in C3 and -9.9 in C2 (Fig. 4). The detrital fraction is consistently less radiogenic, yielding values of ε_{Nd} between $= -11.1$ and -11.8. Only for S1, however, does the detrital Nd have a significant effect on the bulk Nd isotope composition, whereas for C1–C3 the bulk Nd
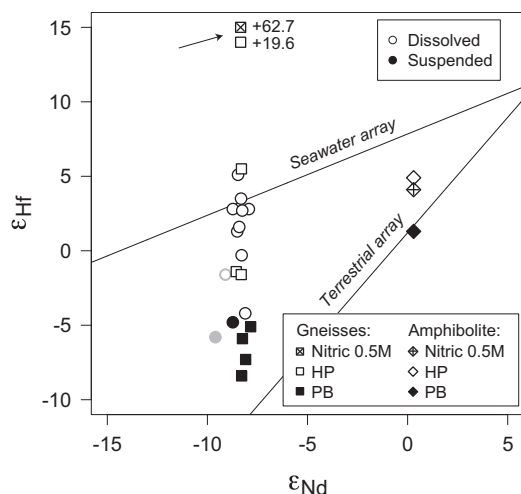
Fig. 3. Hafnium and neodymium isotope compositions from the catchments of the Verzasca and the Ticino. The suspended and dissolved compositions of the Verzasca are given in black, the Ticino data are given in grey. The riverine dissolved Hf isotope compositions are similar to the soluble Hf of the gneisses (hot plate digests, HP). The bulk Hf isotope compositions of the gneisses (pressurised bomb digests, PB) are in turn isotopically similar to those of the suspended load. The nitric acid leach of the gneisses (combined sample) is highly radiogenic in its Hf isotope composition, whereas the nitric leach of the amphibolite is virtually identical with its soluble fraction. Errors are smaller than the symbol sizes (see Tables 1 and 2). For reference the terrestrial array (present day array, Vervoort et al., 2011) and the seawater array (Albarède et al., 1998; David et al., 2001; van de Flierdt et al., 2007) are also shown.
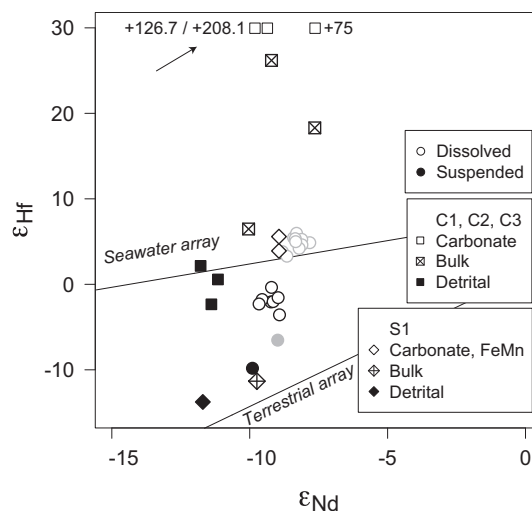

Fig. 4. Hafnium and neodymium isotope compositions in the catchment of the Birs (in black). The riverine dissolved Hf isotope compositions are similar to the detrital fraction of the sampled sedimentary rocks, whereas the dissolved Nd shows a closer affinity with the carbonate-derived Nd. In addition, the dissolved and suspended isotope composition of the Saane are given in grey. Analytical uncertainties are smaller than symbol sizes (see Tables 1 and 3). For reference the terrestrial array (present day array, Vervoort et al., 2011) and the seawater array (Albarède et al., 1998; David et al., 2001; van de Flierdt et al., 2007) are also shown.

isotope composition is identical to the corresponding carbonate fraction. The suspended and average dissolved riverine Nd isotope composition in the Birs ($\varepsilon_{Nd} = -9.9$ and -9.4 ± 0.3, respectively) is similar to the authigenic isotope composition of the rocks but distinct from their detrital fraction.

As for Nd, the mass balance for Hf is discussed based on the leached sample aliquots, comparing the bulk concentrations with those in the sum of the three fractions. Replicate determinations of bulk concentrations consistently indicate that the sediment powders are not homogenous with respect to their Hf concentrations, but show variations within a factor of 1.4 for S1, C1 and C2 and within a factor of 2.8 for C3 (Table 3). As will become clear in next paragraph this is likely to reflect slightly variable detrital contributions to the different sample aliquots. The Hf isotope balance is not fully constrained for the limestones C1–C3 due to missing isotope compositions of the Hf-poor FeMn fractions. The isotope balance of S1 is not entirely consistent as the calculated bulk isotope composition calculated as the sum of the three fractions is $1\varepsilon_{Hf}$ lower than the measured bulk isotopic composition. This observation also supports sample heterogeneity.

Bulk Hf concentrations of the limestones C1–C3 are low and do not exceed 0.1 ppm, which is in contrast to the much higher concentration of 0.49–0.57 ppm of S1 (Table 3). The Hf budget in all four rocks is dominated by the detrital fraction. Both leaching series yield very similar contributions of

the detrital fractions to the bulk Hf budget, agreeing to within 4% for S1, C1 and C2. For S1 this fraction constitutes an average of 93%, for C1 and C2 87 to 88%. C3 is extremely depleted in Hf, with a bulk concentration ranging between 0.005 and 0.017 ppm. It also shows variable contributions of the detrital fraction to the bulk varying between 52% (HCl series) and 71% (acetate series). The acetate series data show that the Hf contributions from carbonate and FeMn-oxides are fairly similar in each rock, whereby each fraction accounts for less than 6% of the bulk in S1, C1 and C2 and for ~15% in C3.

The isotopic contrast between the detrital and the carbonate fraction is very large, corresponding to $19.3\varepsilon_{Hf}$ units for S1 and to more than $70\varepsilon_{Hf}$ units for the limestones (Table 3). Both, the 1 M HCl and the acetate/acetic acid leach of the limestones produced highly radiogenic Hf isotope compositions, in excess of $\varepsilon_{Hf} = +75$. For C1 and C2 the Hf isotope composition of the acetate leach is more than 30 units more radiogenic than the 1 M HCl leach, whereas for C3 it is 12 units lower. S1 shows similar isotope compositions in the 1 M HCl leach, the acetate leach and the FeMn-oxide fraction, varying between $\varepsilon_{Hf} = +3.9$ and $+6.6$.

The dissolved isotopic composition in the Birs ($\varepsilon_{Hf} = -4.3$ to -0.4) is isotopically similar to the detrital fraction of the limestones ($\varepsilon_{Hf} = -2.3$ to $+2.2$) and clearly less radiogenic than their carbonate fraction ($\varepsilon_{Hf} = +75$ to $+208.1$). The suspended Hf isotope composition in the river ($\varepsilon_{Hf-PB} = -9.8$) is in turn similar to the bulk composition of S1 ($\varepsilon_{Hf-HP} = -11.3$).

4. DISCUSSION

4.1. Controls on the dissolved Hf and REE concentrations in the rivers

In principle, there are two main factors that control the concentrations of trace elements, such as Hf and the REEs, in rivers. On one hand the dissolved concentration can be related to the availability of an element in the weathered minerals. On the other hand these trace elements are generally insoluble and a variety of chemical characteristics of a river will affect its ability to maintain a specific element in solution (e.g., Gaillardet et al., 2003). We explore both factors – availability and solubility – for the analysed rivers.

4.1.1. Lithological controls on dissolved Hf, Sm and Nd concentrations

The Hf concentrations in the Ticino and the Verzasca are extremely low, not exceeding 0.8 pmol/l. Hafnium/neodymium elemental ratios in the weathered bulk rocks range between 0.10 and 0.22, and are thus much higher than the dissolved ratios of 0.001–0.009 in the Ticino and the ratios of 0.005–0.016 in the Verzasca (Tables 1 and 2 and Fig. 5a; all elemental ratios are expressed as molar ratios). This documents the fact that Hf is strongly depleted in the river relative to the REEs, compared to the weathered rocks. However, the hotplate digests of the gneisses, which dominate the two catchments, show similar, indeed even lower, Hf/Nd ratios than those in the rivers, spanning a range between 0.001 and 0.002. This suggests that the low dissolved Hf concentrations in the Ticino and the Vercasca largely result from the fact that Hf is almost entirely locked up in zircons and thus hardly released into the hydrosphere. This interpretation is also consistent with the observations of the isotope compositions detailed in Section 4.2.1. A plausible cause of the apparently extreme proportion of Hf in zircons for the gneisses (>98.6% of the bulk Hf) is the alpine amphibolite-facies metamorphism (~40–25 Ma, Nagel et al., 2002), during which zircons may have sequestered Hf and Zr from the surrounding rocks.

The outcrops of amphibolite are minor in the catchment of the Verzasca and its contribution to the dissolved Hf is in principle unlikely to be relevant, despite the fact that its soluble Hf concentration is about 10 times larger than for the gneisses. However, it may be that, together with the ultramafic-/mafic lenses and megaboudins, the Hf contributions from the non-gneissic litholgies to the riverine budget are still relevant, which will be further discussed in Section 4.2.1.

Comparing dissolved Hf/Nd ratios in the Birs, which typically range between 0.031 and 0.108, with the bulk source rocks reveals that only S1 is characterised by a comparable ratio of 0.048–0.057 (Table 3). While the carbonates are much lower, ranging between 0.001 and 0.017 (Tables 1 and 3, Fig. 5b). Hafnium thus seems enriched relative to the REEs in the river compared to the sampled source rocks. We further evaluate this finding in Section 4.2.2 using Hf/Nd ratios and Hf and Nd isotopes in the leached rock fractions and in the river. In contrast to the Verzasca and the Ticino, there is thus no major depletion of Hf relative to Nd during the transfer of the elements into the river. On one hand this is likely to reflect the fact that Hf is available in readily weathering minerals and not locked up in zircons (though zircons may nevertheless be of some significance for the Hf budget of Tertiary Molasse sediments). On the other hand, there may also be favourable chemical conditions allowing Hf to remain in solution in the Birs, as will be discussed in the following section.

4.1.2. Riverine chemical controls on the dissolved Hf, Sm and Nd concentrations

A variety of chemical parameters can affect the concentrations of trace metals in a river. These include the pH, the abundance of suitable ligands to form soluble complexes, the abundance of organic or inorganic colloids that can keep trace elements in solution (although not truly dissolved), and the concentration of suspended river sediment onto which trace metals can adsorb. Dissolved Nd concentrations in rivers are to a fair degree controlled by pH, whereby increasing pH leads to a decrease in concentrations (Deberdt et al., 2002). The four rivers analysed here show similar Nd concentrations at similar pH, ranging between 6.7 for the Verzasca, 7.8 for the Ticino and 8.2 for the Saane and the Birs (Georg et al., 2006). The measured Nd concentrations agree with typical concentrations observed in other rivers in this pH range (Deberdt et al., 2002). Hafnium on the other hand displays large differences between the Verzasca/Ticino and the Birs/Saane, implying that pH is not an important controlling parameter for dissolved Hf concentrations.

An important difference between the metamorphic and the sedimentary catchments is the much larger abundance of carbonates in the sedimentary catchments, and hence of HCO_3^- in solution. Hafnium is thought to exist predominantly as hydrolysed species in solution due to its high polarising power (Turner et al., 1981), and it would thus seem unlikely that carbonate complexes are significant in controlling dissolved Hf concentrations. In agreement with this, the Ticino is characterised by similarly low Hf concentrations as the Verzasca, in spite the fact that it has much higher HCO_3^- concentrations (reflecting the weathering of carbonate containing "Bündnerschiefer" in the northern part of the catchments), on average 985 μmol/l compared to 59 μmol/l observed in the Verzasca (Binderheim-Bankey et al., 2000).

The data for all four rivers indicate that Hf is most likely primarily present in colloidal form. This is supported by the observed elemental relationships between Hf and REEs and, depending on the river, with Al or Mn. The relevant correlation coefficients are summarised in Table 4. It has been shown that REEs are predominantly associated with inorganic and organic colloids in rivers, and that only a small proportion is present in truly dissolved form (Ingri et al., 2000; Deberdt et al., 2002). Aluminium is also associated with the colloidal load and positive correlations between Al, REE, and dissolved organic carbon (DOC) have been reported (Dupré et al., 1999; Ingri et al., 2000). A possible explanation for the variable Hf concentrations observed in the four analysed rivers may thus simply be varying contents of DOC. The long term data sets shows
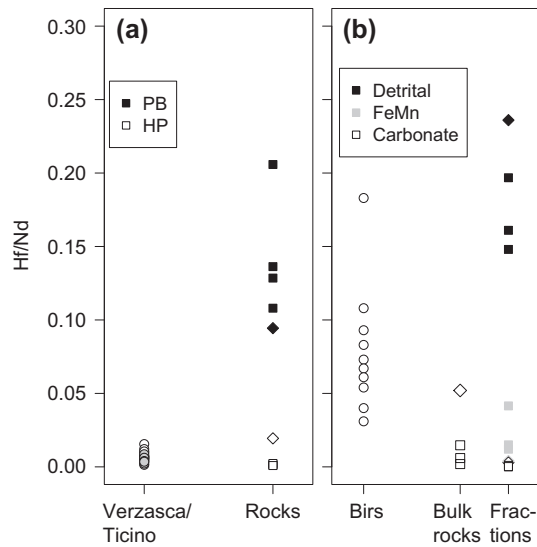
Fig. 5. Hf/Nd ratios in the source rocks and the river in the metamorphic catchment of the Verzasca and Ticino (a) and the Birs (b). (a) The riverine dissolved ratios in the Verzasca (white circles) and the Ticino (grey circles) are similar to, but slightly higher than, the soluble portion of the gneisses (hot plate digests, HP), and much lower than the bulk Hf/Nd ratios (pressurised bomb digests, PB). The diamond represents the sampled amphibolite. (b) Riverine dissolved ratios in the Birs are higher than the bulk ratios of the sampled source rocks, suggesting that no major depletion of Hf relative to the REEs occurs during weathering of these rocks. The elemental ratios in the different rock fractions are also indicated. The diamond represents the carbonate sandstone S1.

average DOC concentrations of 0.4, 1.2, 2.1 and 2.6 mg C/l for the Verzasca, the Ticino, the Saane and the Birs, respectively (Binderheim-Bankey et al., 2000). These average DOCs correlate well with the average Hf concentrations of the rivers ($r^2 = 0.84$), suggesting that the concentration of DOC could be an important parameter in controlling dissolved Hf concentrations.

Further support for an association of Hf with colloids is provided by the relationship of Hf concentrations and discharge for the Verzasca and the Ticino. Elements associated with colloids tend to increase as discharge increases, together with DOC (e.g., Ingri et al., 2000), while major

Table 4
Correlation coefficients (r) for Hf concentrations with Al, Mn, Sm, Nd and discharge in the four sampled rivers. The sample of the Verzasca taken in March 2004 yields very high Hf concentrations at low discharge (see Fig. 6a) and thus does not follow the general pattern. The reason for this is unclear. Two correlation coefficients are indicated in each row for the Verzasa, whereby the first value includes this unusual sample and the second one does not. Significant correlations at the 5% confidence level are given in bold.

	Birs	Saane	Verzasca	Ticino
Al	−0.04	0.52	0.17/**0.65**	**0.90**
Mn	0.18	−0.28	−0.06/0.43	**0.79**
Nd	**0.76**	**0.82**	0.67/**0.88**	**0.78**
Sm	**0.76**	**0.83**	0.45/**0.83**	**0.80**
Discharge	0.28	0.17	0.15/**0.76**	0.57

elements are typically diluted with increasing discharge (e.g., White and Blum, 1995). Such a relationship is observed for the Verzasca and the Ticino (Fig. 6, see Appendix for correlation coefficients of major elements with discharge). For the Birs the relationship between elemental concentrations and discharge is less systematic. The concentrations of elements associated with clays are diluted as discharge increases in the Birs (e.g., K, Mg, Li) while Ca, Hf and REEs do not show systematic changes with runoff. This possibly reflects increasing relative contributions from carbonate weathering with discharge, which will be further discussed in Section 4.2.2. The Saane shows little systematic behaviour with discharge for all elements.

For a particle reactive element such as Hf it may also be expected that a suspension-rich river is depleted due to the adsorption of Hf onto suspended sediment. Such a relationship is, however, not observed in our data. The Ticino is poorer in suspended load, yielding typical suspended
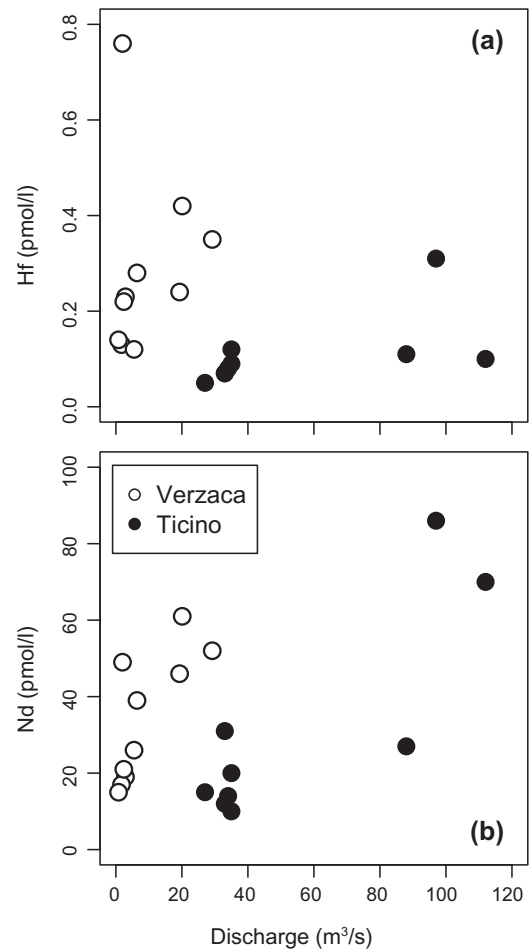

Fig. 6. Hafnium (a) and neodymium (b) concentrations as a function of discharge in the metamorphic catchment of the Verzasca and the Ticino. Hafnium and neodymium concentrations increase more or less consistently with discharge in the Verzasca and Ticino, supporting an association of these elements with colloids. There is, however, little systematic behaviour observed with discharge in the two catchments that are dominated by sedimentary rocks (not shown).

concentrations between 2.0 and 11.0 mg/l (25% and 75% quartile), than the Birs and the Saane, which yield concentrations between 12.7 and 39.9 and between 9.3 and 39.8 mg/l, respectively (Binderheim-Bankey et al., 2000). For the Verzasca no data are available, but the concentration of suspended load is probably similar to or even lower than that of the Ticino. Possibly such a relationship is not observed due to the colloidal association of Hf. Truly dissolved Hf may indeed decrease with suspended load, whereas colloidal Hf may hardly be affected by surface adsorption.

4.2. Incongruent weathering of Hf isotopes

The reason for the mostly congruent weathering of Nd as compared to the incongruent weathering of Hf has been discussed by Bayon et al. (2006). Samarium and neodymium are both REEs and behave in a very similar manner, resulting in little fractionation of Sm/Nd ratios between most minerals. The Lu/Hf system, on the other hand, consists of Lu – a heavy REE – as the parent isotope and Hf – a HFSE – as the daughter isotope. The variation in Lu/Hf ratios between minerals is much larger and hence the potential for incongruent weathering. In accordance with this we find very small differences between dissolved and suspended Nd isotopes in all four rivers. We thus focus on the discussion of the incongruent weathering of Hf here, noting that in spite of the generally congruent weathering of Nd some incongruent weathering effects have been reported during the weathering of glacial tills (e.g., Andersson et al., 2001; von Blanckenburg and Nägler, 2001) and to some extent during the weathering of granitic rocks as observed in the Strengbach catchment of the Vosges mountains, where small isotopic differences between the suspended an dissolved load of the draining rivers most likely result from preferential weathering of apatite (Tricca et al., 1999; Aubert et al., 2001). The metamorphic and the sedimentary catchments will be discussed one after another in Sections 4.2.1 and 4.2.2.

4.2.1. The metamorphic catchment of the Verzasca

It has previously been suggested that the incongruent weathering of Hf has two components. On the one hand there is the strong isotopic contrast between zircons and the zircon-free crust, which inevitably leads to a preferential release of radiogenic Hf into the hydrosphere (Albarède et al., 1998; van de Flierdt et al., 2007). On the other hand the zircon-free crust has also been suggested to weather incongruently due to the presence of readily weathering highly radiogenic trace minerals, such as apatite and titanite (Bayon et al., 2006). The dissolved Hf in the Verzasca is isotopically similar to the soluble fraction of the gneisses. These isotope compositions, in fact, either encompass most of the riverine dissolved compositions of this study – excluding one distinctly unradiogenic observation – or are even more radiogenic (G4, Fig. 3). The release of distinctly radiogenic Hf is thus not clearly visible in this catchment and the zircon-free crust appears to weather more or less congruently. On a finer scale there is, however, a general co-variation of dissolved Hf isotope compositions with Ca/K ratios (Fig. 7). The possible rea-

sons for this relationship, which will be discussed below, include variable contributions from the weathering of (i) trace calcite, (ii) Ca-rich phases in the gneisses, possibly including phosphates and/or (iii) mafic/ultramafic (mega-) boudins and lenses.

(i) As mentioned before the average dissolved Ca/Na ratio in the Verzasca is ∼3. Rewriting Eq. (1) below, which describes the Ca/Na ratio in a mixture of the contributions of silicate (Ca/Na$_{silicate}$ ∼0.4) and carbonate weathering (Ca/Na$_{carbonate}$ ∼50, Gaillardet et al., 1999a), as Eq. (2) suggests that at a ratio of Ca/Na ∼3 in the Verzasca 85% of the Ca could be calcite derived. (Analogous equations will be used in Section 4.2.2 when calculating Hf and Nd contributions from silicate and carbonate weathering in the Birs).

$$(Ca/Na)_{mix} = f_{sil} \times (Ca/Na)_{sil} + (1 - f_{sil}) \times (Ca/Na)_{carb}$$

$$= \frac{Ca_{sil} + Ca_{carb}}{Na_{sil} + Na_{carb}} \qquad (1)$$

$$(Ca/Na)_{mix} = \frac{1 + \frac{Ca_{carb}}{Ca_{sil}}}{\frac{Na_{sil}}{Ca_{sil}} + \frac{Na_{carb}}{Ca_{carb}} \times \frac{Ca_{carb}}{Ca_{sil}}} \qquad (2)$$

Variable contributions from the weathering of trace calcite could thus, in principle, control the variations in the dissolved Ca/Na and the Ca/K ratios, in which case the relationship between dissolved Ca/K ratios and Hf isotopes would hint at calcite as the main source for the radiogenic Hf. In an environment of active erosion, it is also plausible that very low calcite contents of rocks can be significant for the release of Ca, as in such a case calcite is supplied through continuous exposure of fresh rocks (e.g., White et al., 1999). However, the Verzasca has very low HCO$_3^-$ concentrations ranging between 30 and 113 μmol/l, which argues against significant contributions from trace calcite. The HCO$_3^-$/Na ratio, corresponding to 2.4 ± 0.6, is well within the range of the estimate for pure silicate weathering of 2 ± 1 deduced by the study of small catchments (Gaillardet et al., 1999a). Hence, it seems unlikely that calcite could contribute to the observed relationship, also because such trace calcite is unlikely to be relevant for the Hf budget of the river.

(ii) and (iii) are currently under-constrained hypotheses. The nitric acid leachates of the gneisses indicate that phosphates in these rocks are unlikely to be a very significant source for dissolved Hf. Although the leached fraction is very radiogenic, yielding an ε$_{Hf}$ of +62.7, it constitutes only 0.5–1.1% of the soluble fraction (Table 2). Variable phosphate weathering may thus contribute to the observed co-variation of dissolved Hf isotope compositions with Ca/K ratios, but is unlikely to be the sole factor.

Several arguments suggest that lenses of amphibolites and eclogites, as well as boudins and megaboudins of meta-peridotites and meta-rodingites, could be significant sources of radiogenic riverine Hf, despite their limited occurrence in the catchment. In contrast to the gneisses, the Hf budget of these rocks is not expected to be controlled by zircons. This is consistent with the observed soluble Hf concentration in the amphibolite of 352 ppb, which exceeds the soluble concentrations of the gneisses by a factor of
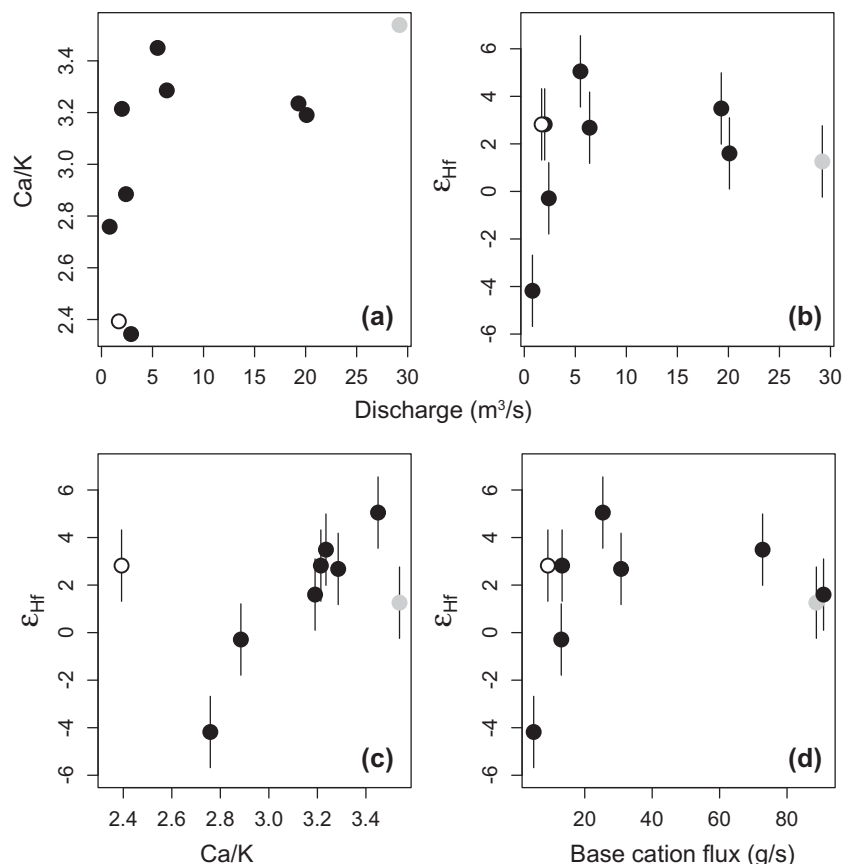
Fig. 7. Relationships between discharge, Ca/K ratios, and Hf isotope composition in the Verzasca (a–c). Increasing discharge leads to less congruent weathering of Hf isotopes, which is discussed in Section 4.2.1. Samples that do not follow the co-variation of Ca/K ratios with Hf isotopes were taken in May (grey) and October 2004 (white). (d) displays the relationship between base cation flux and Hf isotope compositions, which is very similar to the relationship between discharge and Hf isotope composition.

8–10. In addition, these rocks, in particular the meta-rodignites, are rich in Ca, which is consistent with the trend towards more radiogenic dissolved Hf isotope compositions as Ca/K ratios increase. Yet, such contributions cannot dominate the riverine Hf budget, as in this case the dissolved Nd isotopes should deviate from the gneissic Nd isotope composition towards more radiogenic Nd isotopic compositions as observed for the amphibolite.

In summary, it seems plausible that variable contributions from phosphates and ultramafic/mafic rocks contribute to the seasonal variations in dissolved Hf isotope composition. It is, however, not clear whether the phosphates or the ultramafic/mafic rocks exert a stronger control and whether there are further Ca-rich silicate minerals in the gneisses that are involved in releasing radiogenic Hf.

Dissolved Hf isotope compositions and Ca/K ratios in the catchment seem to be influenced by discharge (Fig. 7). As discharge increases Ca/K ratios tend to get higher and more radiogenic dissolved Hf is observed. The release of Hf therefore appears to be sensitive to the fluid residence time, whereby a longer residence time leads to a more congruent release of Hf. Since there is a strong positive correlation between discharge and base cation flux in this catchment ($r^2 = 0.97$, see Appendix) the relationship be-

tween base cation flux and Hf isotopes is very similar to the relationship between discharge and Hf isotopes. This implies that high chemical weathering rates, as reflected in high base cation fluxes, correspond to less congruent weathering of Hf. The relationship, however, is not linear but resembles a logarithmic function that yields relatively homogenous isotopes above a base cation flux of approximately 20 g/s. The data also suggest that at very high chemical weathering fluxes weathering may generally become more congruent again.

As discussed before "dissolved" Hf is likely to be mostly present in colloidal form. Hence, there are in principle two options, which can explain Hf isotope variability in the river. Either Hf is released through the weathering of minerals and subsequently transported in association with colloids, in which case the riverine Hf isotope composition is a true weathering signal. On the other hand, Hf isotope variability could simply imply a change in the nature of the colloids, for instance from a more organic association (whereby the Hf is originally derived from weathering) to a fine detrital association that possibly in part consists of primary minerals. Therefore it is not fully assessed as yet if the observed Hf isotope variability reflects a true weathering signal. However, we note, that the relationship between DOC

contents and Nd concentrations for instance in the Kalix river (Ingri et al., 2000) does not imply that the Nd is organic in origin, but instead suggest that as DOC increases the weathering derived Nd is more successfully kept in solution, which may also apply for Hf.

Sedimentary sorting in rivers can lead to depletion of Zr in the suspended matter relative to the bulk rocks, reflecting the preferential settling and deposition of zircons (Dupré et al., 1996; Gaillardet et al., 1999b). Measured Hf isotope compositions of suspended matter of the Verzasca and the Ticino are isotopically very similar to the bulk rocks of the catchment and sorting has little effect on the suspended Hf isotope compositions (Fig. 3). This possibly reflects the fact that the rivers are close to their source and sorting is not sufficiently efficient over such short distances.

4.2.2. The sedimentary catchment of the Birs
4.2.2.1. Hf and Nd budget of the rocks.
The leaching experiments on the sedimentary rocks provide a tool to elucidate the sources of the dissolved Hf and Nd in the Birs. Although the leaching results are robust in general, they leave a few questions open, as will be seen shortly. The sedimentary fractions that need to be looked at are diverse and consist of: (1) a carbonate fraction, (2) FeMn-oxides, (3a) authigenic and biogenic phosphates, (3b) detrital phospates and (4) silicates. Previous work has shown that the leaching of marine sediments in sodium acetate buffered with acetic acid will dissolve fraction (3a), but not fraction (3b) (Ruttenberg, 1992), which implies that the carbonate fraction leached in this study can potentially contain contributions from authigenic and biogenic phosphates depending on their availability in the sediments. The 1 M HCl leach on the other hand will also dissolve detrital phosphates (Ruttenberg, 1992). Using this information the results of the leaching experiments can be summarised as follows.

Hafnium and neodymium show very opposed distributions in the sampled sedimentary rocks. Whereas Nd is associated strongly with the carbonate phase (59% for S1, >90% for C1–C3), Hf is mostly in the detrital phase (>87% for S1, C1 and C2). Since there is little difference in the Hf and Nd concentrations of the detrital phases between the two leaching series, it can be concluded that detrital phosphates are not very significant for the Hf and Nd bugets of these sediments. The Hf and Nd budget of the detrital phase, therefore, has to be dominated by silicates. For both elemental budgets FeMn-oxides are of a subordinate significance, although the results obtained for S1 indicate that as the detrital proportion in a rock increases Nd also becomes more significant in FeMn-oxide fraction.

4.2.2.2. The Hf isotope composition of the leached carbonate.
As noted before, the carbonate fraction of the limestones is extremely poor in Hf, and at the same time very radiogenic. Although it cannot be precluded that these values are influenced by the leaching of marine phosphates in the rock, they may well be derived from carbonate itself due to the high REE/Hf ratios observed in this fraction leading to fast ingrowth of radiogenic ^{176}Hf over time. This can be evaluated only qualitatively since there are no Lu concentrations available for the measured carbonate fraction. Assuming a typical (average) Lu/Nd ratio in shallow marine carbonates of 0.0178 (Nothdurft et al., 2004) and an approximate age of 150 Ma, the calculated Hf isotope composition of the carbonate fractions of C1–C3 corresponds to an ε_{Hf} in excess of ∼380, which is even higher than the observations. The calculation is based on a simple model for the evolution of the Hf isotope composition of CHUR (van de Flierdt et al., 2007) and the assumption that the carbonates have formed at 150 Ma from congruently weathered 1.45 Ga old crust, the age of which is estimated by the Nd isotope composition of the catchment.

The 1 M HCl and the acetate leach produced markedly different Hf isotope ratios, which possibly has a number of different causes (Table 3). In the case of C1 and C2, where the acetate leach is 30 units more radiogenic than the 1 M HCl leach, the 1 M HCl may have etched relatively unradiogenic clays. For S1 the 1ε-unit more radiogenic value observed in the 1 M HCl leach could reflect dissolution of some detrital apatite. The two values, however, are in near agreement within the analytical reproducibility. The 12ε-units less radiogenic isotope composition in the acetate leach of C3 relative to the 1 M HCl leach is difficult to explain, given that it is a very pure limestone.

4.2.2.3. Hypothetical mixtures between leached carbonate and detritus.
Using mixing relationships between the detrital pool, the Nd and Hf budget of which has been shown to be dominated by silicates, and the carbonate pool of S1, C1 and C2, which potentially includes contributions from marine phosphates, we try to constrain the sources of dissolved Hf and Nd in the Birs (Fig. 8). This approach neglects the contributions of FeMn-oxides because such contributions are likely not very significant for dissolved Nd given the mass balance of the sampled rocks, and because they will only dissolve under specific, namely reducing, conditions. The mixing calculations use the specific concentrations of the fractions of Hf and Nd based on their concentrations per gram sample and the approximate weights of the fractions (see Section 3.3.2). These mixing considerations lead to three significant observations. First, it is evident that the extremely low Hf/Nd ratios of 0.0002–0.0026 in the carbonate fractions imply that the addition of detritus with much higher Hf/Nd ratios of 0.148–0.236 and much less radiogenic Hf isotope compositions will exert the dominant control on the bulk Hf isotope composition and the Hf budget of the mixture (Fig. 8a). Second, the dissolved Hf/Nd ratios in the Birs suggest that detrital sediment contributes approximately 10–30% of the dissolved elements. This estimate is derived from the mixing curves of S1 and C2. If end-member Hf/Nd ratios for the carbonate and silicate fraction similar to C1 are more typical in the catchment, detrital contributions of up to 50% are implied. Third, the Nd isotope composition of the river is consistent with relatively low contributions of detrital Nd (Fig. 8b).

The first and the third observation translate into robust conclusions: (1) Riverine Hf is largely derived from the detrital pool since otherwise the river would be much more radiogenic in its Hf isotope composition. For all three
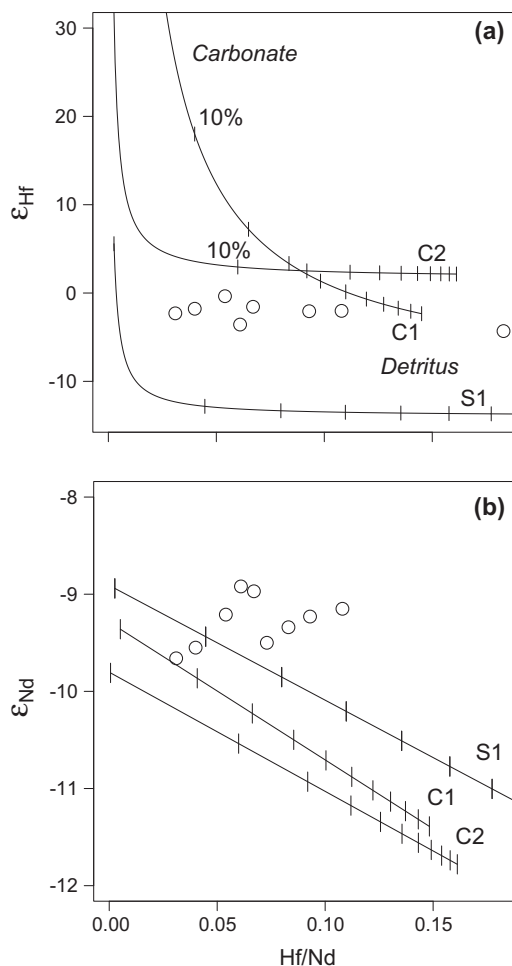
Fig. 8. Hypothetical mixtures of variable detrital rock fractions with variable carbonate fractions for the rocks C1, C2 and S1 sampled in the catchment of the Birs. Observed isotope ratios and Hf/Nd ratios in the river are indicated as circles. Ticks on the mixing lines represent increasing contribution of detritus in steps of 10 wt.%. (a) The Hf isotope composition of the hypothetical mixtures will be dominated by the detrital contribution due to the very low Hf concentrations (low Hf/Nd) in the carbonate fractions. (b) Nd concentrations in both fractions are similar and hence detrital admixture has a gradual effect on the bulk Nd isotope composition.

hypothetical mixtures of detritus and carbonate (S1, C1, C2) even a detrital contribution of 10 wt.% implies that between 90.5 and 99.4% of the Hf is of detrital origin. (2) Dissolved Nd on the other hand is largely carbonate derived. A detrital contribution of 10 wt.% to the river dissolved buget would result in a detrital Nd fraction of only 18–37% for the three rocks S1, C1 and C2.

The second observation is not consistent with the weight proportions of the detritus in the analysed sedimentary rocks. These are less than 1 wt.% for C3, 1.2 and 1.3 wt.% for C1 and C2 and 13 wt.% for S1, which is far too low for many observed ratios in the river. This discrepancy is further evaluated in the following section using major elemental ratios in the river to estimate the contributions from carbonate and silicate weathering to the river.

4.2.2.4. Using Ca/Na and Hf/Nd ratios to constrain the contributions from carbonate and silicate weathering to the Hf and Nd budget of the Birs. The disparity between the abundance of detritus in the sampled rocks and the apparent proportion in the river deduced from dissolved Hf/Nd ratios may result from a sampling bias, as detritus-rich sediments are underrepresented in our sampling suite (Fig. 1b). A few complementary coulumetric determinations of inorganic carbon in marls and claystones of the catchment convert to carbonate contents of 55% (Sequan marls), 63% (Oxfordian marl) and 14.5% (Opalinus clay). If the riverine-dissolved Hf/Nd reflects an unaltered weathering ratio such carbonate-poor rocks must contribute much to the dissolved Hf and Nd budget, a hypothesis which can be tested using the dissolved Ca/Na ratio in the river. Assuming a riverine dissolved Ca/Na ratio of 50 for a carbonate weathering end-member and 0.4 for a silicate end-member (Gaillardet et al., 1999a) and average Hf/Nd ratios for both end-members from the leaching experiments (Table 3), a range of Hf/Nd ratios in the river between 0.05 and 0.12 ratios is calculated, in reasonable agreement with the observations, ranging between 0.03 and 0.18 (Table 1). Re-using these considerations, a very rough estimate for the dissolved Hf and Nd of carbonate origin can be obtained. These estimates are rough because the end-member Hf/Nd ratios are not well constrained, but the estimated carbonate contribution to the elemental budgets is very sensitive to the chosen values. Nevertheless, the agreement between the calculated mixing line in Hf/Nd vs Ca/Na (as outlined above) and the regression to the dissolved Hf/Nd ratios suggests that these estimates are meaningful (Fig. 9). At the observed maximal dissolved Ca/Na ratio of 40 during this study ~80% of the dissolved load reflects carbonate weathering. At this sampling event the dissolved Hf/Nd ratio was 0.054 in which case ~83% of the Hf and ~29% of Nd is silicate derived. For the lowest observed Ca/Na ratio of 15 contributions from carbonate weathering correspond to ~30%. At this sampling event the Hf/Nd ratio corresponded to 0.108, implying a silicate contribution to the dissolved Hf and Nd budget of ~92% and ~58%, respectively. Interestingly, the suggested change in contributions to the Hf budget from carbonates on the order of ~10% (although a larger maximum change is implied in more extreme Hf/Nd ratios during other sampling events) does not cause a very large variability in the dissolved Hf isotope composition, which ranges between $\varepsilon_{Hf} = -4.3$ and -0.3. This likely indicates that the contributions from unradiogenic carbonates of relatively young Tertiary sediments (such as S1) impede larger variations, which would possibly result if all carbonate were as radiogenic as observed for the Mesozoic limestones.

4.2.2.5. Relationship between discharge, base cation flux, major elemental ratios and Hf isotopes and its implication. The dissolved Hf isotope composition in the Birs shows a very similar relationship with discharge, base cation flux and major elemental ratios as previously discussed for the Verzasca (Fig. 9). In the case of the Birs, Ca/Na ratios and Hf isotope compositions in general co-vary, and increase with discharge. For this catchment the most
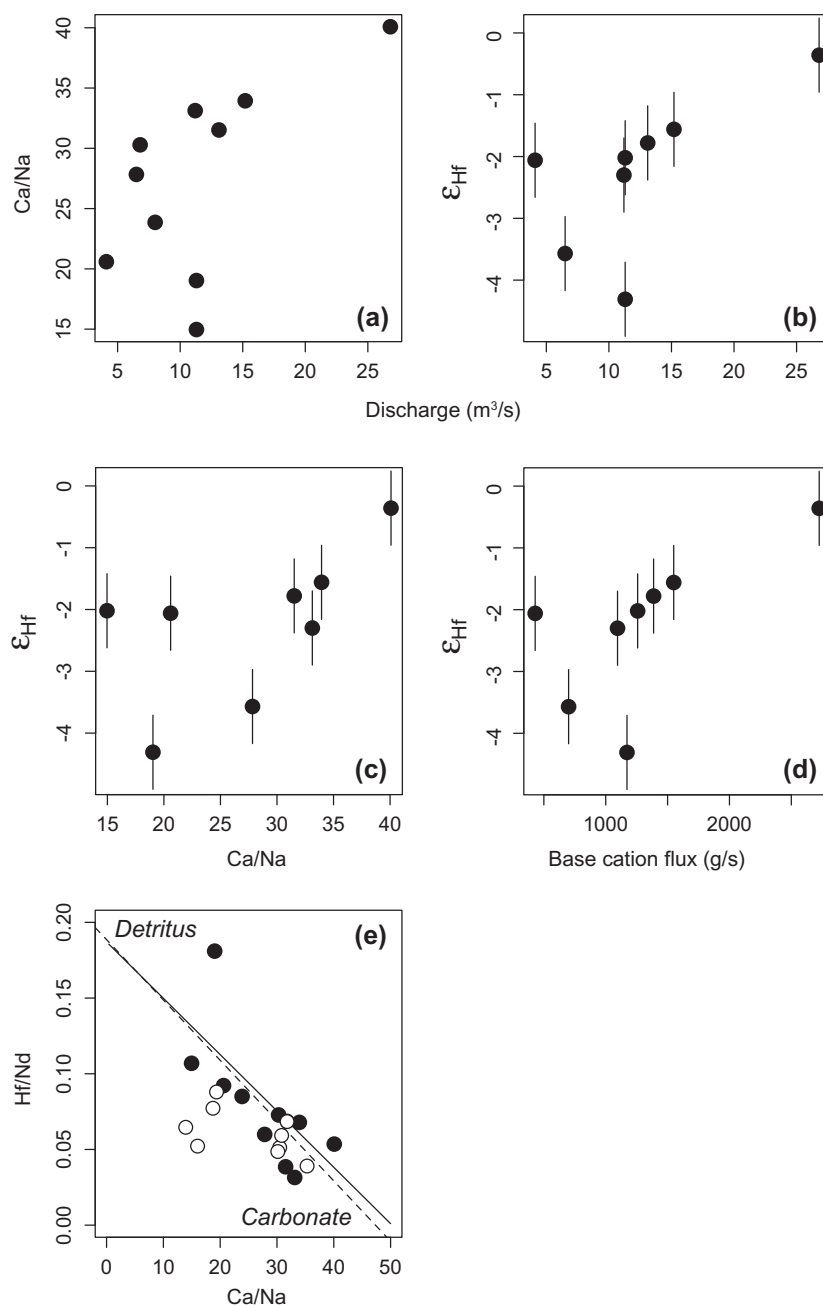
Fig. 9. Relationships between discharge, Ca/Na ratios, and Hf isotope composition in the Birs (a–c). Increasing discharge leads to less congruent weathering of Hf isotopes, which is likely to reflect increasing contributions from carbonate weathering. (d) Displays the relationship between base cation flux and Hf isotope composition which is very similar to the relationship between discharge and Hf isotope composition. (e) Shows the negative correlation between riverine Hf/Nd and Ca/Na ratios (filled circles) observed in the Birs indicating that the Hf/Nd ratios in the river are well explained by variable contributions from carbonate and silicate weathering. Mixing of both end-members (solid line) as outlined in Section 4.2.2 is in good agreement with the linear regression to the observed dissolved Hf/Nd ratios in the Birs (dashed line). Furthermore the observed Hf/Nd ratios in the Saane (open circles) also seem largely controlled by mixing of carbonates and silicates.

plausible interpretation is that the contributions from carbonate weathering increases with discharge and leads to more radiogenic dissolved Hf isotope compositions. This is consistent with the radiogenic Hf isotope composition of the measured carbonate fractions, and is also supported by the negative correlation between Ca/Na ratios and Hf/Nd ratios in the river. As for the Verzasca, base cation fluxes are primarily governed by discharge ($r^2 > 0.99$), resulting in nearly identical relationships between base cation flux and Hf isotope compositions on the one hand, and discharge and Hf isotope compositions on the other.

Dissolved Hf/Nd ratios in the Saane are also consistent with variable contributions from carbonate and silicate weathering (Fig. 9e). The overall smaller Hf isotopic variability (ε_{Hf} = +3.3 to +6), and the fact that there is no systematic variation of Hf isotope compositions with dissolved Ca/Na ratios, possibly reflects the diverse depositional ages of the rocks, which may lead to a less systematic distinction between the Hf isotope composition of the carbonate fraction and the silicate fraction in the catchment.

5. CONCLUSIONS

The data presented in this study show that Hf concentrations in rivers draining metamorphic rocks, such as the Verzasca and the Ticino, can be extremely low (usually <0.4 pmol/l), whereas rivers strongly influenced by carbonate weathering, such as the Birs and the Saane, can yield relatively high concentrations of 1–5 pmol/l. In principle, two factors must be considered to explain these observations. On the one hand the concentrations can be directly linked to the availability of Hf in readily weathering minerals. On the other hand, the concentrations may reflect stability in solution governed by riverine chemistry. In those catchments studied here the primary control is exerted by lithology. The release of Hf from the metamorphic rocks is hampered as a result of the dominance of zircons in the Hf budget of the weathered gneisses, leading to very low dissolved Hf concentrations. The Hf in the sedimentary catchments is, in contrast, to a large degree associated with fine detrital material that is easily altered during weathering and releases the contained Hf. Dissolved Hf/Nd ratios in the analysed rivers are thus reflecting hardly altered original weathering ratios, suffering little fraction in the river due to variable stability of both elements in solution. The contrast in dissolved Hf concentrations between the catchments does therefore not need to invoke a chemical factor such as variable amounts of DOC, which potentially can keep trace elements in solution.

The data obtained on the metamorphic catchments confirm incongruent weathering and release of Hf isotopes to the weathering solutions as previously reported by Bayon et al. (2006). In the catchment of the Verzasca and the Ticino this primarily reflects the fact that zircons are barely accessible for weathering. The zircon-free portion of the rocks is weathered relatively congruently as the riverine Hf isotope compositions are similar to the soluble portion of the gneissic Hf, rather than being distinctly more radiogenic. However, we observe that there is a relatively large Hf isotope variation in the Verzasca (ε_{Hf} = −4.2 to +5.1), whereby more radiogenic Hf isotope compositions are observed at higher Ca/K ratios. Although the origin of this variation is not well constrained as yet, we suggest that it may reflect variable contributions from phosphates or Ca-rich silicate minerals of the gneisses and/or variable contributions from mafic/ultramafic lenses and (mega-) boudins in the catchment.

The leaching experiments performed on sedimentary rocks from the sedimentary catchment of the Birs have revealed that actual weathering of carbonate is not the true source of Hf in the river. The carbonate fractions of the relatively pure limestones are extremely radiogenic in their Hf isotope compositions as a result of high Lu/Hf ratios. The amount of Hf released from the weathering of carbonate is, however, not significant for the riverine Hf buget, which is dominated by the release of Hf from the detrital fraction. Similar to the Verzasca, we also observe for the Birs that the most congruent weathering in Hf isotopes occurs during periods of low discharge, when the Hf contributions from carbonate weathering are lowest.

Although the Verzasca and the Birs drain very different lithologies, a key control on the congruency of Hf isotope weathering seems to be discharge. During periods of high discharge the fluid residence time and hence the interaction of the fluid with the minerals is shortened, which seems to lead to increased contribution from readily weathering radiogenic minerals. This may indicate that past seawater Hf isotope variability could be related to changes in the hydrological cycle and runoff from the continents, rather than reflecting a zircon grinding effect as previously proposed (Piotrowski et al., 2000; van de Flierdt et al., 2002).

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.10.019.

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