## Hf – Hafnium

### Introduction

Hafnium is a member of group 4 of the periodic table, along with Ti and Zr. It has an atomic number of 72, an atomic mass of 178, one oxidation state (+4) and five naturally occurring isotopes ($^{176}Hf$, $^{177}Hf$, $^{178}Hf$, $^{179}Hf$ and $^{180}Hf$), of which the latter is the most abundant at 35.44% of the total mass, followed by $^{178}Hf$ and $^{177}Hf$ at 27.08% and 18.39% respectively.

The geochemical properties of Hf and Zr are very similar since the ionic radius of Hf (71 pm) is almost identical to that of Zr (72 pm). All Zr minerals contain Hf and pure Hf minerals are not commonly known. The concentration of Hf in minerals rarely exceeds Zr with the exception of certain types of thortveitite $(Sc,Y)_2Si_2O_7$. Zircon $(Zr,Hf)SiO_4$, and baddeleyite $ZrO_2$, are the most important sources of Hf and usually contain up to 2%. However, some Norwegian zircon minerals have been found to contain 20% Hf (Wedepohl 1978). Hafnium is predominantly lithophile in its behaviour, occurring in oxides and silicates as the $Hf^{4+}$ ion.

In general, igneous and metamorphic rocks contain very small amounts of Hf. Ultramafic rocks typically contain <1 mg kg$^{-1}$, mafic rocks up to 2 mg kg$^{-1}$ and intermediate rock types between 2 and 4 mg kg$^{-1}$. Kimberlite, carbonatite and alkali-rich lava are commonly enriched with Hf, typically >8 mg kg$^{-1}$, compared to the upper continental crustal average of 5.8 mg kg$^{-1}$ (McLennan and Taylor 1999). Granitic rock types tend to contain the highest concentrations of Hf; Taylor (1964) suggests an average of 4 mg kg$^{-1}$. Alkaline intrusions from the Lovozero Massif (Kola peninsula, Russia) have yielded Hf concentrations in excess of 100 mg kg$^{-1}$ (Wedepohl 1978). Vlasov (1966) observes that there is no marked accumulation of Hf in sedimentary rocks and, with the exception of carbonates, all sedimentary rock types contain similar concentrations of Hf, typically 2.5 to 6.5 mg kg$^{-1}$.

Hafnium may be used as a pathfinder for Zr mineralisation. Elevated Hf values indicate the presence of felsic rocks, especially intrusive masses.

The Hf content in soil ranges from 1.8 to 18.7 mg kg$^{-1}$, depending on the parent rock type (Kabata-Pendias 2001). Loess averages 11.4 mg kg$^{-1}$ Hf (McLennan and Murray 1999).

The resistate nature of Hf minerals limits the concentration of Hf in natural water. In very acid solutions (pH≤1), Hf is present as $Hf(OH)^{3+}$, whilst at higher pH, $Hf(OH)_2^{2+}$ is the only species present in solution in the absence of other stabilising ligands. This complex is very stable and resistant to protonation (Hagfeldt *et al.* 2004). Complexes with sulphates, fluorides and chlorides may be poorly soluble in aqueous solution, but complexation with natural organic materials may increase the concentrations of Hf in natural freshwater. Hafnium is generally present in natural water at concentrations less than 0.1 µg l$^{-1}$. The average abundance in river particulates is 6 mg kg$^{-1}$ (McLennan and Murray 1999).

Sewage is the main anthropogenic source of Hf, and typically contains about 3 mg kg$^{-1}$ (Kabata-Pendias 2001). Hafnium is used in the production of electric light bulb filaments, X-ray cathode tubes, reactor control rods, as alloys with Ti, Nb, Ta, and Fe, and in the ceramics industry. Several investigations during the 1960s and 70s demonstrated that Hf concentrations were not elevated in areas of industrial activity, and it appears that geological sources of Hf are more important than anthropogenic ones (Wedepohl 1978).

Hafnium has no known biological function. Very little information is available concerning its toxicity, but it is generally regarded as being of low toxicity. No negative environmental effects have been reported. However, because insufficient data are available on the effect of Hf on human health, it should be regarded as potentially toxic.

Table 34 compares the median concentrations of Hf in the FOREGS samples and in some reference datasets.

Table 34. Median concentrations of Hf in the FOREGS samples and in some reference data sets.

| *Hafnium (Hf)* | *Origin – Source* | *Number of samples* | *Size fraction mm* | *Extraction* | *Median mg kg$^{-1}$* |
|---|---|---|---|---|---|
| Crust[1)] | Upper continental | n.a. | n.a. | Total | 5.3 |
| **Subsoil** | **FOREGS** | **790** | **<2.0** | **Total (ICP-MS)** | **5.30** |
| **Topsoil** | **FOREGS** | **843** | **<2.0** | **Total (ICP-MS)** | **5.55** |
| Soil[2)] | World | n.a. | n.a | Total | 5 |
| **Water** | **FOREGS** | **807** | **Filtered <0.45 µm** | | **0.004 (µg l$^{-1}$)** |
| Water[3)] | World | n.a. | n.a. | | 0.004 (µg l$^{-1}$) |
| **Stream sediment** | **FOREGS** | **848** | **<0.15** | **Total (XRF)** | **8.32** |
| **Floodplain sediment** | **FOREGS** | **743** | **<2.0** | **Total (XRF)** | **4.51** |
| Stream sediment[4)] | Canada | 26 227 | <0.18 | Total (INAA) | 6 |

[1)]Rudnick & Gao 2004, [2)]Koljonen 1992, [3)]Ivanov 1996, [4)]Garret 2006.

## Hf in soil

The median Hf content is 5.3 mg kg$^{-1}$ in subsoil and 5.55 mg kg$^{-1}$ in topsoil, with a range from <0.2 to 20.8 mg kg$^{-1}$ in subsoil and up to 21.2 mg kg$^{-1}$ in topsoil. The average ratio topsoil/subsoil is 1.080.

Hafnium substitutes for Zr in all its minerals, especially in zircon. This leads logically to a very strong correlation; the observed correlation coefficient Zr-Hf is 0.97 in subsoils, and 0.96 in topsoils. Further, the Hf distribution maps are almost identical to the corresponding Zr maps.

Low Hf values in subsoil (<3.79 mg kg$^{-1}$) occur in central Finland, in small parts of south Poland and north-east Germany, in central Hungary, and in mainly calcareous regions of north-eastern and south-eastern France, southern Spain, northern Italy and Greece.

The subsoil Hf map shows high values (>7.06 mg kg$^{-1}$) in south-western Norway and Sweden, and in north-central Sweden, all related to crystalline rocks, where zircon is normally abundant. A large zone with high Hf values extending from southern England over north-western France into central Germany is related to (a) Quaternary loess deposits rich in weathering-resistant heavy minerals, (b) palaeofluviatile deposits (palaeoplacers) and (c) palaeoshorelines of the Ypresian sea (Lower Eocene) (Salpeteur *et al*. 2005). Further, anomalies occur in the Bohemian Massif, Hungary, Slovenia and most of Croatia (in residual soils on karstified carbonate rocks, palaeofluviatile deposits and loess), and the Roman Alkaline Province. In Spain, point anomalies occur in the central Iberian Massif (Pedroches batholith), Asturias and Galicia (intermediate intrusive rocks of the Iberian Massif). Two isolated anomalous points appear in south-east-Poland, possibly related to Quaternary loess.

The topsoil Hf map is very similar, but elevated values are also present in Lithuania and Estonia, where it is presumed to be agrogenic in origin; formerly imported phosphate fertilisers from the Kola peninsula were rich in zircon (Hf-carrier) and, thus, contribute to higher topsoil Hf values in agricultural soil. Hf is also higher in topsoil in the eastern Pyrenees.

Hafnium has a very strong correlation with Zr both in subsoil (0.97) and topsoil (0.96). In subsoils, Hf also has a good correlation (>0.4) with most REEs, Y, Nb, Ta and Ti, a weak correlation (>0.3) with Eu, Th, Ag and Ba, and a good negative correlation with CaO (-0.40). In topsoil, Hf has a weak to good correlation with the REEs, a good correlation with Nb, a weak correlation with Y, Ta, Ag and Ti, and a weak negative correlation with CaO.

## Hf in stream water

Hafnium values in stream water range over hardly two orders of magnitude, from <0.002 µg $l^{-1}$ to 0.072 µg $l^{-1}$ (excluding an outlier of 0.12 µg $l^{-1}$), with a median value of 0.004 µg $l^{-1}$. About 25% of the data are less than the analytical limit of quantification (0.002 µg $l^{-1}$).

Lowest Hf values in stream water (<0.002 µg $l^{-1}$) are predominantly found in most of Spain, in northern Portugal, in most of France, northern Italy, Switzerland and Austria, in south-western Germany, in western Scotland, in south-western and northern Norway, in southern Poland and eastern Slovakia, east Croatia and in most of Greece. Highest Hf concentrations (>0.02 µg $l^{-1}$) are found in central and southern Sweden, in central and southern Finland, and in southern Italy (Sicily).

Enhanced values in stream water (between 0.01 and 0.02 µg $l^{-1}$) also occur in southern Norway, most of Sweden and Finland, in Latvia, Lithuania (partly agrogenic as a result of application of zircon-rich fertilisers imported from the Kola peninsula) and northern Poland. In Poland as well as in other Baltic Sea countries and in southern Fennoscandia, high Hf concentrations are correlated with DOC (dissolved organic substances), which shows a regional relationship with peat lands. Isolated enhanced values occur in northern Germany, in France (Brittany and Lorraine) and in central-southern Italy. The latter values occurring in Italy are certainly controlled by recent alkaline volcanism of the Roman and Neapolitan geochemical provinces; the ones in Sicily may also be related to volcanic beds that occur interlayered with sedimentary evaporitic rocks. Hafnium data correlate, in many respects, with Nb and Zr, especially in areas of relatively high concentration.

The described Hf distribution in stream water shows clearly the similarity with the REEs and associated elements patterns in acidic, low-mineralisation and high-organic-matter waters. The aqueous species are $Hf(OH)_2^{2+}$ and organic complexes. The other association, with the pattern type of Alkaline rock elements, appears to be responsible for high Hf concentrations in Italy including Sicily and Sardinia, in Albania, Poland, Lithuania and Latvia. In comparison with high Hf in solid sample media the concentrations in stream water differ very much, except in southern Sweden, Lithuania and in the Italian province with alkaline volcanism.

## Hf in stream sediment

The median Hf content in stream sediment is 8.11 mg $kg^{-1}$, with a range from 0.12 to 174 mg $kg^{-1}$. Hafnium substitutes for Zr in all its minerals, especially in zircon. This leads logically to a strong correlation; the observed correlation coefficient Zr-Hf is 0.84. Stream sediment contains on average more Hf than soil, because the heavy mineral zircon is concentrated in active stream sediment.

The Hf distribution map for stream sediment shows low values (<4.68 mg $kg^{-1}$) in eastern and southern Finland, north-eastern Spain, most of northern and central Italy, central Austria, coastal Croatia, and throughout Greece including Crete.

High Hf values in stream sediment (>14.1 mg $kg^{-1}$) are found throughout the Massif Central in France, south-central Spain (peraluminous epizonal granite in Extremadura, and Pedroches batholith near Córdoba), southern France (including the Aquitaine Basin), northern France (Eocene detrital sediments), eastern Scotland (Caledonian granite, schist, gneiss), south-western Norway, south-western and parts of northern Sweden, north-east Germany and central Poland (glaciofluvial detrital zircon), Estonia and adjacent Latvia. Point anomalies appear in the Poitou region in France, and in the south-eastern Netherlands. In the southern Massif Central, high Hf values obviously correlate with Zr, La, Ce, Y, Sn and Be anomalies inherited from late tectonic leucogranite intrusions.

Hafnium in stream sediment shows a very strong correlation with Zr (0.84), a strong correlation with Lu and Yb, a good correlation with most of the REEs, Y and Si, and a weak correlation (between 0.3 and 0.4) with Eu, Nb and Th. It has a weak negative correlation with CaO (-0.31).

## Hf in floodplain sediment

The total Hf concentrations in floodplain sediment vary from <0.05 to 22.0 mg $kg^{-1}$, with a median of 4.51 mg $kg^{-1}$).

Low total Hf values in floodplain sediment (<2.86 mg $kg^{-1}$) occur over the carbonate, clastic and mafic-ultramafic rocks of Albania and Greece; carbonate and clastic terrain of Ebro River basin, crystalline rocks of the Iberian Meseta Central, carbonate rocks of eastern Spain and crystalline rocks of Galicia in Spain; crystalline rocks of Brittany and Poitou to the alluvial sediments of the lower Garonne river, the calcareous regions of Rhône-Saône river and Paris basins in France; the carbonates and crystalline rocks of the Western Alps, southern Italy, and the Dalmatian part of Croatia, the molasse basin of western and central Austria, sandstone of the English Midlands, and the glacial drift covered region of Poland.

It is noted that high Hf patterns in floodplain sediment cross established geological boundaries, as is the case in Norway, and a good explanation cannot be offered. However, some of the high Hf values are related to specific lithologies or known mineralisation. High total Hf values (>6.51 mg $kg^{-1}$) are found in most of Norway over variable lithology and mineralisation (*e.g.,* Søve Nb-REE-Th to the south-west of Oslo), central and north Sweden, the glacial drift covered Baltic countries with fluvio-glacial zircon, but also due to fertilisers, part of Massif Central, Aquitaine Basin and northern France, west-central Spain (Palaeozoic detrital rocks of the Iberian Massif, and Tertiary basin of Old Castilla, with sediments derived from granitic intrusions); the Roman Alkaline Province in Italy; a wide belt extending from the Ardennes to the Harz Mountains, Erzgebirge, Bohemian Forest and Moravian Mountains in the Czech Republic, which may be due, as in soil, to Quaternary loess deposits rich in weathered-resistant heavy minerals; in eastern Slovakia and eastern Hungary (felsic intrusives).

The highest Hf values in floodplain sediment occur in Germany (22.0 mg $kg^{-1}$), related to the glacial drift deposits probably derived from Norway, in France (17.1 mg $kg^{-1}$) over Tertiary clastics, and two values in southern (16.7 mg $kg^{-1}$) and northern Norway (16.7 mg $kg^{-1}$).

It is interesting to note that in most of Europe the Hf and Zr in floodplain sediment show a coherent pattern, except in Scandinavia where there is an antipathetic relationship. Norway has higher Hf values, and Sweden higher Zr values. In Norway the high Hf values show a remarkable similarity with the heavy REE patterns, suggesting a high Hf content in REE minerals, such as monazite.

Hafnium in floodplain sediment shows a strong correlation (>0.6) with Zr, Tb, Dy, Ho, Er, Tm, Yb and Lu (heavy REEs), a good correlation (>0.4) with La, Ce, Pr, Nd and Sm (light REEs), Eu, Gd, Y, Ta, and a weak, but significant, correlation (>0.3) with Tl, Ti, Nb and $K_2O$. It has a weak negative correlation with CaO (-0.38).

It is concluded that the distribution map of total Hf in floodplain sediment shows the geochemical differences of the geological substratum and mineralised areas quite well, and no distinguishable influences from anthropogenic activities are recognised, except possible contamination in the Baltic states by Zr-rich fertilisers.

## Hf comparison between sample media

Patterns in Hf distribution between topsoil and subsoil are very similar, but there are significant differences between the distribution patterns in soil and sediment. Stream sediment are generally higher in Hf, because zircon (which contains most of the Hf) is concentrated in the heavy mineral fraction in active stream sediment. Stream sediment is relatively higher in Hf in an area extending from Denmark over north and eastern Germany to southern Poland compared to floodplain sediment and soil; the same pattern is observed over the Central Massif and in Estonia. However, Hf is relatively low in stream sediments in an area extending from northern France to central Germany, as well as the alkaline magmatic province of Italy, and in Croatia and Slovenia. Floodplain and stream sediment in Norway are generally higher in Hf than in soil, which is in contrast to the behaviour of Zr (no explanation).

A boxplot comparing Hf variation in subsoil, topsoil, stream sediment and floodplain sediment is presented in Figure 20.

Patterns in stream water Hf data are different from distributions in the solid sample media, especially throughout northern Europe. Distributions are controlled strongly by DOC, since Hf is highly insoluble unless complexed with organic materials. Highest concentrations are, therefore, associated with the organic rich environments of most of southern and central Fennoscandia, as well as in Lithuania and Latvia. Patterns in Hf distribution throughout most of southern Europe, especially around the Mediterranean area, are similar in stream water and solid sample media, with the exception of Sardinia, Sicily and Albania.

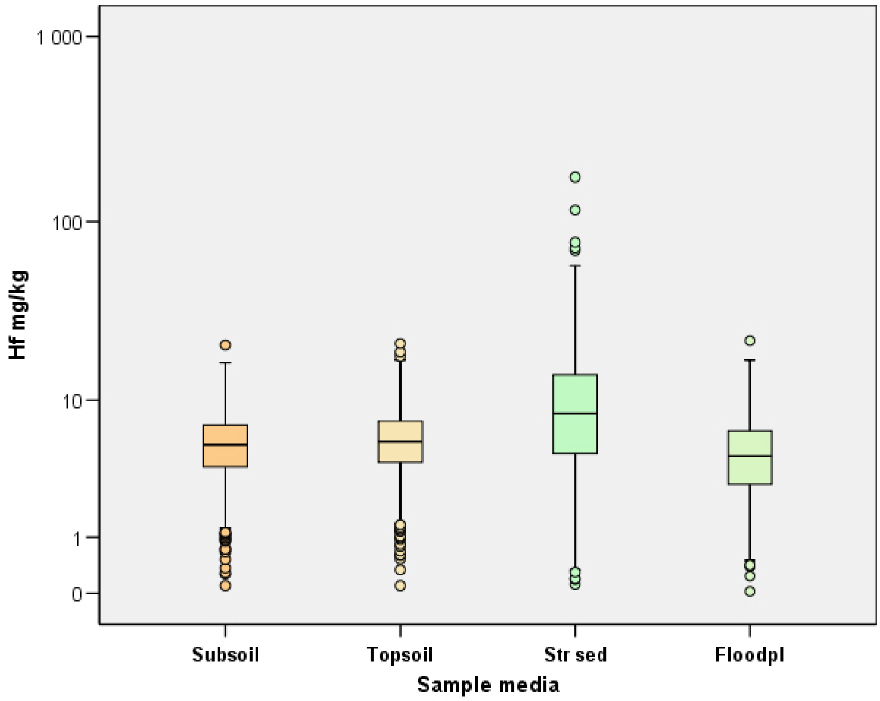


Figure 20. Boxplot comparison of Hf variation in subsoil, topsoil, stream sediment and floodplain sediment.