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## Zr- Hf fractionation during Water-Rock Interaction

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### Abstract

Zr and Hf are two elements having same ionic charge and similar ionic size at a given coordination number. Despite the Zr/Hf ratio is considered to be quite constant in meteorites and lithospheric rocks, seawaters collected from the surface down to varying depths of several Pacific Ocean stations reveal that the Zr/Hf ratio increases by one order of magnitude. Very recent studies have shown that, in both ground waters and lake waters, the Zr/Hf ratio is either higher or lower compared to the interacting minerals displaying a large variability in the distribution of these twin elements. In this communication the possible processes responsible for such a large fractionation are discussed but further work is needed to test the validity of these interpretations. This basic problem of scientific significance needs more attention from the water-rock interaction community.

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### 1. Introduction

Zirconium and Hf are chemically close relatives with similar geochemical behavior caused by the similar ionic radius and the same charge. The Zr/Hf ratio in most terrestrial mineral rocks and chondrites is assumed to be constant with a narrow range of 70–78 used to describe the Bulk Silicate Earth(BSE)<sup>1</sup>. The greatest deviation from the terrestrial rock ratio is observed in seawater where the Zr/Hf ratio has been found to be up to 500<sup>2</sup>. In the Saint Laurence estuary freshwaters<sup>3</sup>, the increase of the atomic Zr/Hf ratio up to 110 takes place at middle to high salinity reflecting the enhanced release of Zr from re-suspended particles and slower removal rates compared to Hf. Indeed, similarly to other lithophile metals, Zr and Hf are considered insoluble in water and readily adsorbed onto particle

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surfaces which results in very low dissolved concentrations in river and seawater. At the typical pH of groundwater and surface waters, Zr and Hf can be easily found as hydroxyl complexes or could potentially be complexed by inorganic or organic acids which may increase their solubility. The inorganic speciation of Zr and Hf in water at circum-neutral pH is dominated by hydroxyl groups ( $\text{Zr}(\text{OH})_5^-$ ,  $\text{Hf}(\text{OH})_5^-$ ,  $\text{Zr}(\text{OH})_4$ ,  $\text{Hf}(\text{OH})_4$ ). Recently<sup>4</sup> found that the Zr/Hf ratio is lower in the marine Fe–Mn-oxyhydroxides than in seawater indicating that Hf is more easily removed than Zr during the formation of marine Fe–Mn oxyhydroxides. This starting point indicated that in natural waters the geochemical behavior of this twin pair is not simply ruled by charge and ionic radius as in magmatic rocks and meteorites. These new observations has been possible in this last decade because of analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS) that has enabled accurate analysis of most of the trace elements across the periodic table in rock and minerals at all concentration levels and as low as parts per trillion ( $10^{-12}$ ). Systematic investigations in the variety of natural surface and deep groundwater are less developed for Zr and Hf because of the difficulties due to the matrix component. Recent measurements in seawaters show that the Zr/Hf ratios collected from surface to deep waters varies significantly<sup>5</sup>. In this work we focused on the acidic volcanic waters from the Nevado del Ruiz complex in Columbia<sup>6</sup>, the Dead Sea Fault waters of Israel<sup>7</sup> and the lake waters of the Italian Pantelleria Island<sup>8</sup>. These environments were chosen because of their huge fractionation of these two elemental twins and because they are representative of the large variation of pH ranging from hyper acidic to neutral and alkaline waters in which the anthropogenic input is assumed to be negligible.

## 2. Evolution of the Zr/Hf ratio as a function of pH

Despite the limited number of publications, the levels of Zr and Hf in natural waters range from 0.7 to 35100 pmol/kg and from 0.01 to 900 pmol/kg, respectively. In Figure 1 we report the variation of the Zr/Hf ratio as a function of water pH in different natural waters. Large variation from the strong acidic waters of Nevado del Ruiz volcanic complex (Colombia) with a minimum pH value of 1 and Zr/Hf ratio of 5 to the alkaline solutions (pH up to 9) from the Dead Sea Fault system and neutral pH and high Zr/Hf ratio close to 300 in the Pantelleria lake waters close to the thermal springs. All the water composition reported in Fig. 1 consists of samples filtered through 0.45 micrometer diameter pore and all have a positive Eh value. According to the water composition and saturation state we have distinguished 4 different water groups. In the more acid group (Group 1, pH up to 2), the Zr/Hf ratio is low with respect to the average local rock (sub-chondritic ratio) indicating a decoupling of Zr-Hf. In this acidic group, waters are under-saturated with respect to neogenic secondary phases although their presence in the filter deposits was not observed indeed. Waters from Group 2 are still acidic but in the pH range between 2.5 and 3.64; these waters are saturated or over saturated with respect to alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ) and jarosite ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) the typical minerals found in volcanic lakes and in sulfide mining waste weathering. Microscopic analysis of the material deposited during filtration confirmed the presence of aluminum and iron hydroxides as well the presence of minerals having alunite and jarosite chemical composition. Waters from Group 3 are characterized by Zr/Hf ratios changing from chondritic to super-chondritic values, with Zr enriched 2-3 times with respect to Hf. These waters come from volcanic or/and sedimentary environments and are over-saturated (or saturated) with respect to Al-Fe oxy-hydroxides, clay minerals (mainly kaolinite) and occasionally calcium carbonate minerals. The highest fractionation of the Zr/Hf ratio is found in waters from Group 4 corresponding to the lake waters of Specchio di Venere at Pantelleria where the deposition of siliceous and carbonate-rich microbial mats is invoked as responsible of the observed Zr/Hf ratio value up to 300<sup>8</sup>.

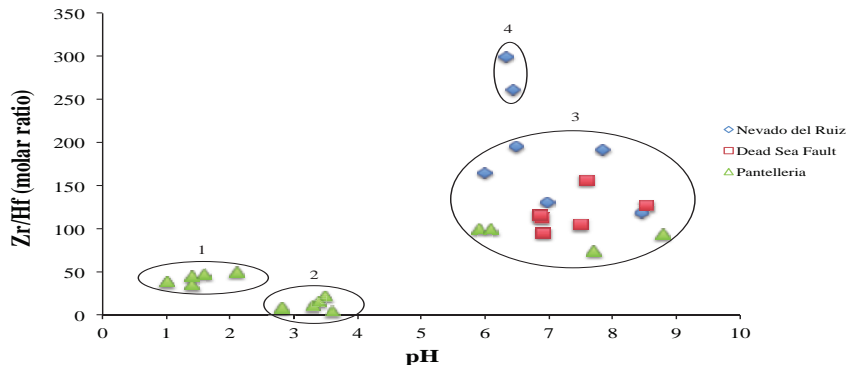


Fig.1. Evolution of the Zirconium-Hafnium molar ratio as a function of pH, in different continental water environments. (Rhombos and Triangles are from<sup>6,7</sup>). Four different water groups have been identified according to chemical composition and solution saturation state (see text for explanation). In all waters reported in this plot the redox potential (Eh) is positive.

The reason of the variable subchondritic value found in water of Groups 1 and 2 is not easy to explain quantitatively. The inorganic speciation of Zr and Hf in water is generally dominated by hydroxyl group suggesting that different charge of the metal complexes may determine different absorption behaviors of the two elements onto solid surfaces. However, the occurrence of different complexation reactions may be invoked in waters of Group 1 that are oversaturated with respect to authigenic phases. These particular waters have variable chloride-sulfate predominance. Given the lack of appropriate apparent complexation constants for this extreme environment only a qualitative approach can be used. Statistical molecular dynamic calculations<sup>9</sup> suggest that in high chloride media Hf-chloride complexes are enhanced with respect to Zr while laboratory experimental studies<sup>10</sup> indicate that Zr and Hf can be easily transported by fluoride and chloride complexes. In Groups 1 and 2, the abundance of chlorine and sulfate ions changes significantly and the Zr/Hf ratio increases as a function of the Cl/SO<sub>4</sub> ratio. This may reflect the possible different Zr and Hf complexes with Cl or SO<sub>4</sub> as major ligands enhancing the solubility of these ions that in turn control the relative abundance of Zr and Hf in these waters.

Waters from Groups 3 and 4 have Zr/Hf values spanning from the chondritic signature up to 300 (super chondritic). All waters are in equilibrium with neogenic minerals such as hydroxides and clay minerals and the potential surface absorption over the mineral particle can be responsible for the observed low fractionation as earlier suggested<sup>2,4</sup>. Our results confirm the large variability of the Zr/Hf ratio observed in the estuaries and Pacific Ocean waters showing that similar variations can be found also in continental groundwater and freshwaters. Moreover, the biological activity, probably controlled by microorganisms, may contribute to the decoupling between Zr and Hf but possible processes are still unknown. The assumption of the constancy of the ratio in rocks and minerals and the initial congruent dissolution needs probably more investigations as variations of the Zr/Hf ratios have been found in basalts from islands arcs<sup>11</sup>, in mantle xenoliths<sup>12</sup> and in Archean suite<sup>13</sup>. We are also far from the evaluation of the anthropogenic input of both Zr and Hf in continental surface waters as we assume that they are introduced into the environment with a defined Zr/Hf ratio.

### 3. Conclusions

The results of recent investigation shows that contrary to the solidification of pure silicate melts where the Zr and Hf behavior is controlled by both ionic charge and radius (CHARAC behavior) producing a constant Zr/Hf ratio in the lithosphere, the Zr/Hf ratio in natural continental waters ranges from 5 (subchondritic) to 400 (superchondritic) showing a non-CHARAC behavior. Our recent data show that the Zr/Hf ratio in continental waters can be either lower or higher when compared to the average rock ratio value being influenced by pH, the chemical composition of the waters and adsorption processes.

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