



## **The behaviour of REE and Zr-Hf fractionation in the volcanic waters of Nevado del Ruiz system (Colombia)**

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The geochemical behaviour of Rare Earth Element (REE), Zr and Hf have been investigated in the thermal waters of Nevado del Ruiz volcanic system. These fluids are characterised by a wide range of pH ranging between 1.0 and 8.8. The acidic waters are sulphate dominated with different Cl/SO<sub>4</sub> ratios. The Nevado del Ruiz waters allowed to investigate the behaviour of investigated elements in a wide spectrum of pH and chemical composition of water. The important role of the pH and the ionic complexes have been evidenced in the distribution of REE, Zr and Hf in the aqueous phase. The pH rules the precipitation of authigenic oxyhydroxides of Fe, Al producing changes in REE, Zr, Hf amount and strong anomalies of Cerium and Europium.

Y-Ho and Zr-Hf (twin pairs) have different behaviour in strong acidic waters with respect to the water with higher pH. Yttrium and Ho have the same behaviour of Zr and Hf in waters with pH near neutral-to-neutral, showing super-chondritic ratios. The twin pairs showed to be sensitive to the co-precipitation and/or adsorption onto the surface of authigenic particulate suggesting an enhanced scavenging of Ho and Hf respect to Y and Zr, leading to super-chondritic ratios. In acidic waters a different behaviour of twin pairs occurs with chondritic Y/Ho ratios (reflecting the Y/Ho ratio of average local rock) and sub-chondritic Zr/Hf ratios. For the first time, Zr and Hf have been investigated in natural acidic fluids to understand the behaviour of these elements in extreme acidic conditions and different major anions chemistry. Zr/Hf molar ratio changes from 4.75 to 49.29 in water with pH<3.6. In strong acidic waters, a different fractionation of Zr and Hf have been recognised as function of major anion contents (Cl and SO<sub>4</sub>), suggesting the formation of complexes leading to sub-chondritic Zr/Hf molar ratios.