Water-rock interaction in Pantelleria hydrothermal system (Italy): The behaviour of Zr, Hf and REE

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The thermal CO_2-rich fluids circulating in Pantelleria volcanic island are mainly Na-Cl-HCO_3 waters, with a marine component up to ≈50% and pH between 6 and 9. The total amount of REE ranges between 1.09 and 6.85 nmol/l, whereas the average shallower seawater of the Strait of Sicily has a total REE content close to 0.31 nmol/l [1]. The PAAS-normalised REE distribution in these waters is characterized by an increasing trend from La to Lu with variable Ce anomalies (from 0.3 to 1.5) Moreover, Ce anomaly is correlated to water redox potential (-107<Eh< 161 mV). Additionally, these waters display a W-type tetrad effects in the third and fourth tetrads, while in the PAAS normalised patterns of Pantelleria volcanic rocks [2] the tetrad effect is M-type in the third and fourth tetrads. This evidence can represent an effect of the large water-rock interaction occurring in the hydrothermal aquifer. We found a similarity between normalised REE pattern of the Pantelleria thermal waters, and the nearby Strait of Sicily average seawater. However the Strait of Sicily seawater pattern is 1-2 orders of magnitude lower. The high amount and distribution of REE in the Pantelleria thermal waters may be explained by the formation of REE complexes with carbonate ions, while the observed Ce anomaly may result from oxidation scavenging process onto Fe oxyhydroxides [3], as revealed by the saturation state of the Pantelleria thermal CO_2-rich waters.

The Zr/Hf molar ratio is 2-3 times higher respect to the local rocks. The super-chondritic Zr/Hf values suggest that the distribution of these elements in thermal waters is driven by the dissolved complexation probably as hydroxo-complexes [4]. In the higher temperature waters (Polla 3 and Gadir springs), the F^- concentration close to 0.5 mM could allow to the formation of $[ZrF_5]^-$ and $[HfF_5]^-$ complexes [5], leading to higher Zr/Hf molar ratios.

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