Geochemistry of REE in hyperacid and hypersaline waters in hydrothermal systems

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The REE (Rare Earth Elements; lanthanides and yttrium) are economically important resources. Here, recent progresses concerning the study of the REE geochemistry in natural systems are presented. Specifically, the REE behaviour was studied in hyperacid and hypersaline waters with variable redox conditions.

The important role of the pH (from 1 to 8.8) and the chemical composition of the water on the distribution of REE was investigated in the Nevado del Ruiz volcano-hydrothermal system. The ΣREE (from 0.8 to 6722 nmol l^{-1}) is inversely correlated to pH values. The pH rules the precipitation of Fe-, Al-bearing minerals inducing changes in REE abundances and a strong cerium anomaly. The REE patterns normalized to average local rock show significant LREE (Light REE) depletion in acidic sulphate waters from which alunite and jarosite precipitate [1].

The key role of the Eh values (from -400 to 256 mV) and water composition on the distribution of REE was evaluated in waters along the Dead Sea Fault with TDS values ranging from 0.3 to 193.5 g l^{-1}. The ΣREE ranges from 0.02 to 2.98 nmol l^{-1}. PAAS-normalized patterns show MREE (Middle REE) enrichments in waters with relative higher Ca and SO_4 contents deriving from gypsum dissolution. The redox conditions influence the amplitude of Ce and Eu anomalies. Oxidized waters show negative Ce anomalies related to the oxidative Ce scavenging [2], while positive Eu anomalies are found only in waters characterized by Eh values < -100 mV, consistently with the Eu occurrence as dissolved Eu^{2+}. This reducing conditions enhances the Eu^{2+} stability in the dissolved phase relatively to its trivalent neighbours along the REE series.

A very interesting point is that the ion speciation of REE in solution is not always sufficient to explain the distribution of these elements. The processes of precipitation and dissolution of solid phases are responsible of the changes in the REE distribution in waters.

[1] Inguaggiato et al (2015). *Chem. Geol.* **417**, 125-133.

[2] Seto and Akagi (2008). *Geoch. Journ.* **42**, 371-38.