



HOW Zr/Hf AND Gd ANOMALY SIGNATURES CAN DEPICT SOLID-LIQUID INTERACTIONS IN SEAWATER

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Natural positive La, Gd e Lu anomalies in seawater have been explained by larger stability of these elements in dissolved phase with respect to the neighbor Lanthanides, when these elements are not related to anthropogenic input (Kulaksiz and Bau, 2011 and references therein). Here we report original measurements based on the systematic investigation of Earth Rare Elements, Zr and Hf concentrations in the water column of Mediterranean Sea indicating the occurrence of positive Gd anomalies in open marine conditions. Obtained results indicate that amplitudes of positive Gd anomaly are strongly linearly related to Zr/Hf ratio values in shallowest water layers from (0-200 m depth) and at the oxic seawater-anoxic brine interface (3200-3400 m depth), whereas this relationship disappears along the oxic seawater column (200-3200 m depth).

Several papers investigated implications of occurrence of suspended Mn oxides and Fe-oxyhydroxides in particulates of seawater column on the dissolved REE distribution mainly according to laboratory experiments (Bau and Koschinsky, 2009 and references therein), whereas the aqueous behaviour of tetravalent Zr and Hf was essentially related to processes occurring onto hydrous Fe oxides surfaces (Bau and Koschinsky, 2006). Therefore the recognition of the above mentioned relationship between Gd/Gd* and Zr/Hf in seawater indicates that REE, Zr and Hf fates are driven by the same phenomenon, namely the scavenging onto Fe-oxyhydroxides. These materials certainly play an important role both in shallow waters because they are main components of Fe-rich coating of atmospheric dust that dissolves therein inducing the early formation of authigenic Fe-oxyhydroxides. Moreover Fe rich antigenic materials sinking along the water column dissolve at seawater-brine interface where redox Fe cycling occurs and poorly soluble Fe(II)-bearing phases can crystallize in brines under reductive conditions. On the contrary the Zr/Hf vs. Gd/Gd* linear relationship is not statistically significant along the oxic water column from 200 to 3200 m depth suggesting that further processes, probably related to migrations of water masses, took place under these conditions.

These results represent an interesting goal because indicate that dissolved REE, Zr and Hf behaviour under true natural conditions in marine systems is driven by scavenging processes onto Fe-oxyhydroxides.

REFERENCES

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