

Zr, Hf and REE behaviour in river waters: A consequence of dissolution of Fe-oxyhydroxides and evaporites

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REE distribution in river waters is regulated by Fe and colloid contents. The increasing salinity in estuaries allows to colloidal coagulation and REE release as aqueous species or scavenging onto particles. Zr and Hf mainly occur among dissolved, colloidal and suspended fractions. Here we studied the distribution of these elements in saline and reducing waters of a tributary of Platani river (Central Sicily) in order to prevent the occurrence of colloids and the deposition of Fe-oxyhydroxides. Shale-normalised dissolved REE patterns always show MREE enrichments. Some waters (Group-1), show progressive heavier-REE growth allowing to a less symmetrical shape of the normalised pattern whereas Eu-centred symmetrical patterns are observed in other waters (Group-2). In Group-1 the higher Fe contents are not correlated with the amplitude of positive MREE anomaly whereas this correlation occurs in Group-2 waters with lower Fe concentrations. These findings suggest that MREE enrichment in Group 1 is not related to the dissolution of Fe-oxyhydroxides where REE are usually fractionated [1] whereas this process is probably responsible of the REE behaviour in Group-2 waters. La/Sm and Gd/Yb ratios of Group-1 and 2 waters are differently clustered and Group-1 waters behave similarly to kainite crystals collected in Realmonte salt mine (Messinian evaporites) close to the investigated area. This evidence suggests that REE behaviour in Group-1 is caused by sulphate dissolution as suggested under different conditions [2]. In general, both the dissolution of Fe-oxyhydroxides and salt minerals rather than the scavenging onto authigenic solid drive the REE behaviour in studied river waters. This conclusion agrees with the Zr-Hf relationship in Group 1 and 2 waters showing a sub-chondritic slope in agreement with the Hf enrichment onto surfaces of Fe-oxyhydroxides and salt minerals.

[1] Bau (1999) *Geochim. Cosmochim. Acta* **63**, 67–77. [2] Bach et al. (2003), *Miner. Dep.* **38**, 916–935.