



Low Y/Ho ratios in coastal waters from Central Mediterranean Sea induced by alteration of volcanic ash

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This study presents the results of the oceanographic cruise ANSIC 2001 carried out in the Ionian Sea during the large explosive activity of Mount Etna in summer 2001. During that period input of lithogenic material took place in the Mediterranean region and was caused by the explosive activity of Mt. Etna that occurred since the last few years. This process was one of the most important sources of yttrium and REE (YREEs) in seawater of Central Mediterranean basin.

This study demonstrates that delivery of large amounts of pyroclastic during the last few years modified the distribution of these trace elements in the water mass of the investigated area during summer 2001. Kinetic investigations carried out under controlled conditions on the same materials and coexisting seawater suggest that the occurrence of anomalously low values of Y/Ho ratio in coastal seawaters of the Ionian Sea is induced by the combined effects of the dissolution of freshly erupted volcanic ash and the formation of an alteration film onto their surfaces.

The preferential dissolution of glassy fraction in volcanic material and subsequently of Mg-Fe bearing minerals induces higher mobility of light and heavy REE (LREE and HREE, respectively), whereas Eu is retained in ash residue due its preferential incorporation in plagioclase minerals (McKay, 1989). On the contrary anomalously low Y/Ho ratios in dissolved phase are related to preferential Y removal onto surfaces of alteration products. This process is controlled by differences in electronic configurations between Y^{3+} and Ho^{3+} that play an important role during non-ChaRaCh

processes (Bau, 1996), as solution complexation – surface complexation equilibria.

Yttrium scavenging from seawater is realised through the formation of inner-sphere complexes yttrium complexes with OH groups onto montmorillonite crystals edges (Takahashi et al., 2004), whereas Ho and other REEs were scavenged onto surface of alteration mineral particles dispersed in the water column as anionic organic complexes adsorbed as outer-sphere surface complexes because they can occur as strong organic complexes in highly anthropised coastal water.

The observed co-variation of Y/Ho and Ce/Ce* values along the same trend in dissolved phase and ash during leaching experiments and in seawater and SPM from the Ionian Sea indicate that YREEs release was the main source of these trace elements in the examined scenario. Furthermore scavenging mechanisms and preferential Y uptake were evaluated by amplitude and significance of tetrad effects in Gd-Ho interval and behaviour of chondrite normalized YREEs patterns of dissolved phase and suspended particulate matter in the water column.

Cited references

Bau M. (1996) - *Contrib. Miner. Petrol.* 123, 323-333.

McKay G.A. (1989) - In: Lipin B.R. and McKay G.A. eds., *Geochemistry and mineralogy of Rare Earth Elements. Reviews in Mineralogy* 21, 45-77.

Takahashi Y., Tada A. and Shimizu H. (2004) - *Analytical Sciences B*, 1301-1306.