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Alteration effects of volcanic ash in seawater: Anomalous Y/Ho ratios in coastal waters of the Central Mediterranean sea

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Abstract

This paper presents the results of a study based on data collected during the oceanographic cruise ANSIC 2001 carried out in the Ionian Sea during the explosive activity of Mount Etna in the summer of 2001. Anomalous low values of Y/Ho ratios in seawater suggest extensive scavenging processes on the surfaces of smectitic alteration products, with Y and Ho fractionation controlled by the differences in their electronic configurations and behaviour during solution/surface complexation equilibria. These processes can also be traced through the presence of significant tetrad effects recorded in the chondrite-normalised Rare Earth Elements and Yttrium (YREEs) patterns of suspended particulate matter. This suggests that the preferential Y scavenging from seawater is due to the formation of inner-sphere complexes with OH^- groups on montmorillonite crystal surfaces. The preliminary results of kinetic experiments of YREE released from volcanic ash to coexisting seawater, and the related effects on Y/Ho ratios and Ce anomalies, are consistent with the fractionation of Light Rare Earth Elements (LREEs) with respect to Heavy Rare Earth Elements (HREEs) observed in dissolved phase. They suggest a behaviour of Y similar to that reported for LREEs, particularly for Ce and Pr.

1. INTRODUCTION

Intense research activity during the last 25 years has focused on a more accurate understanding of the chemical and physical processes that regulate the distribution of Rare Earth Elements and Yttrium in seawater (Goldberg et al., 1963; Cantrell and Byrne, 1987; Elderfield, 1988; Goldstein and Jacobsen, 1988; Greaves et al., 1991). This research has aimed to: (i) evaluate their status of complexation (Cantrell and Byrne, 1987; Koeppenkastrop et al., 1991; Koeppenkastrop and De Carlo, 1992; Lee and Byrne, 1992; Millero, 1992); (ii) recognise YREE fractionation processes between dissolved and suspended phases (Elderfield et al., 1990; Alibo and Nozaki, 1999; Tachikawa et al., 1999; Quinn et al., 2004); (iii) examine the capability of YREEs as tracers of anthropogenic inputs both in rivers and coastal waters, especially in areas characterised by high population densities (e.g., Bau and Dulski, 1996); and (iv) evaluate the input mechanisms of these elements in seawater from atmospheric and riverine loads (Sholkovitz, 1993; Sholkovitz et al., 1999; Hannigan and Sholkovitz, 2001; Aubert et al., 2002).

Studies concerning the release of YREEs during rock-water interaction are scarce (Bau et al., 1998; Sholkovitz et al., 1999: Takahashi et al., 2002; Bau et al., 2004), and there is little data on the processes that regulate the alteration of volcanic materials at low temperature and in seawater (e.g. Pichler et al., 1999).

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In particular, the fate of YREEs during the latter processes is influenced by:

- Their behaviour in the dissolved phase, strongly driven by hydrolysis and complexation equilibria (Byrne and Li, 1995; Byrne and Liu, 1998; Klungness and Byrne, 2000; Luo and Byrne, 2004; Sonke and Salters, 2006; Pourret et al., 2007);
- Their sorption (surface complexation) on particles and colloids (Davranche et al., 2004, 2005);
- Their scavenging effects on the alteration surfaces of newly formed mineral phases.

These mineral phases are essentially represented by poorly-crystallised montmorillonite-like phases that show both permanent negative charges in surface layers, due to isomorphic substitutions, and pH-dependent charges located on the hydroxyls, at the edges (Tombácz and Szekeres, 2004). The behaviour of the dissolved YREEs in the presence of montmorillonite was investigated by Takahashi et al. (2004), and Coppin et al. (2002), although the latter authors excluded Yttrium from their investigation.

The intense volcanic activity of Mount Etna during 2001 provided a unique opportunity to simultaneously monitor YREE distribution in unaltered atmospheric particulate matter, seawater, and suspended particulate matter (SPM). The eruption took place on the upper slopes of Mount Etna between July 13 and August 9.

This study combines extensive data sampling, precise YREE compositional data, and the results of reaction kinetic experiments to fill the knowledge gap regarding Lanthanide release to seawater during volcanic activity. Furthermore, we recognise that the "anomalous" Y/Ho ratios in seawater observed in this study represent a geochemical proxy indicative of the adsorption processes occurring in the marine environment.

2. SAMPLING STRATEGIES AND ANALYTICAL METHODS

2.1. Sampling

Samples were collected during the ANSIC 2001 cruise at six sampling stations along the Ionian coast of Sicily

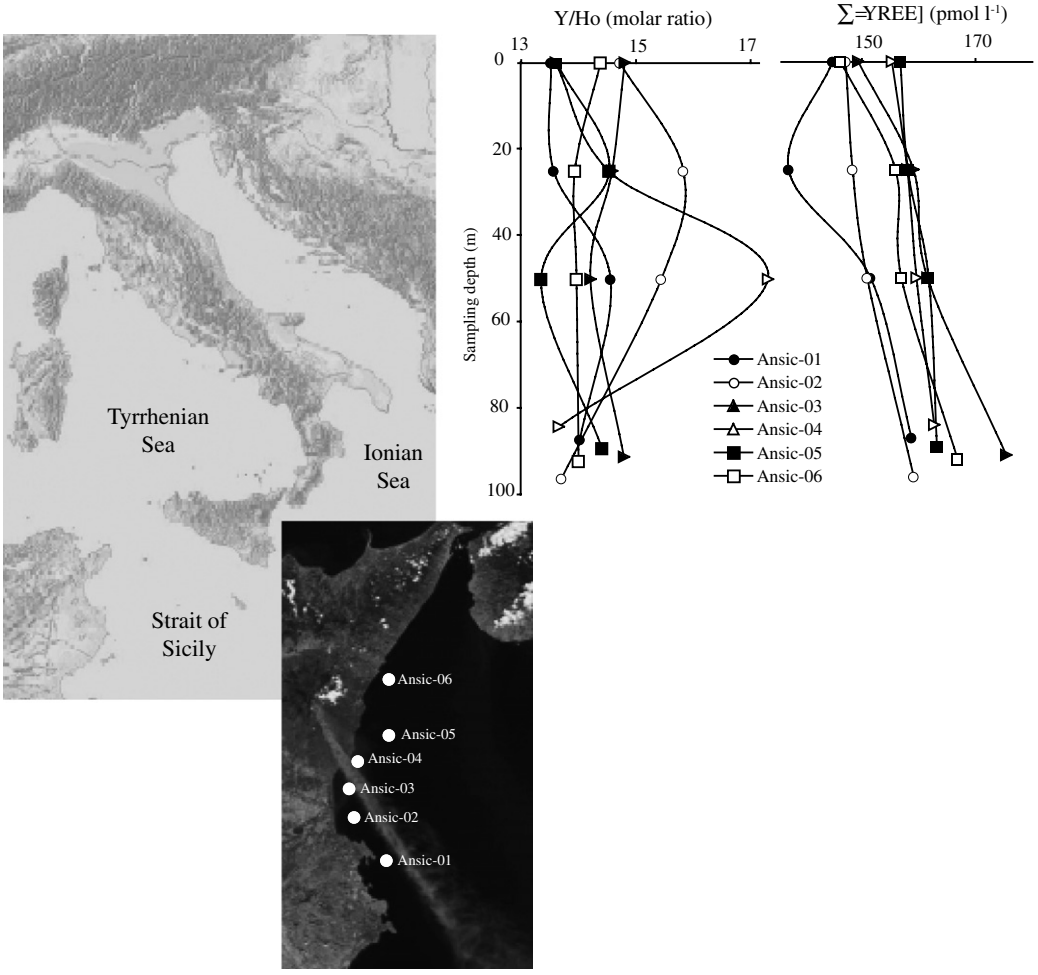

Fig. 1. Location of sampling sites. Satellite image showing the Etna plume during volcanic activity in 2001 is provided by www.visibleearth.nasa.gov/view_detail.php?id=1868. YREE concentrations and Y/Ho profiles are reported for the six studied sampling stations.