ZIRCONIUM, HAFNIUM AND RARE EARTHS BEHAVIOUR DURING THE TRANSPORT IN VOLCANIC FLUIDS. GEOCHEMICAL EFFECTS THROUGHOUT THE SUBLIMATION AND AFTER INTERACTION WITH AQUEOUS MEDIA

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INTRODUCTION

This research indicates the fate of Zr, Hf, and REE (lanthanides and yttrium) during the deposition of authigenic solids (hereafter defined sublimates) from the intermediate-temperature gas phase (100-420 °C), as well as in hot submarine springs and shallow wells in volcanic systems with different geodynamic settings. The processes associated with volcanic sublimation represent the last natural “inorganic” interface where a detailed investigation into the behaviour of REE had never been conducted. Sharp temperature and compositional changes in the volcanic gas phase cause the deposition of volcanic sublimates in fumaroles and during this process the effects on the Zr, Hf, and REE partitioning are poorly understood. The knowledge regarding the mutual behaviour of Zr, Hf, and REE at the sublimate-volcanic gas interface was the stated goal of this research.

MATERIALS AND METHODS

The research was carried out in active volcanic systems at Vulcano (Aeolian Islands, Italy), Santorini (Cyclades Islands, Greece), Phlegrean Fields (Naples, Italy), Tenerife (Canary Islands, Spain) and Isla de Fogo (Cape Verde Islands), where both fumaroles and thermal waters from submarine springs and inland wells were collected and investigated.

For the sampling and the chemical treatment of hydrothermal waters, condensates, and sublimates, containers in Teflon (PTFE) and quartz have been used. Calibration of volumetric labware was verified. Prior to use, all materials were washed with ultra clean acids. All the chemical reagents (concentrated HNO_3, HCl, NH_3 and H_2O_2) were of ultrapure grade (BAKER ULTRA II™, Milan, Italy). Ultrapure water 18.2 MΩ cm, produced with an EASY pure II (Thermo, Italy), was used for all standard solutions and sample preparations.

Volcanic condensates were sampled as in Sortino *et al.* (2006). The anionic species were determined in ionic chromatography (Dionex ICS-1100). For the REE, Zr and Hf analyses, an aliquot of NH_4OH condensing solution was filtered (Millipore™ membranes, 0.22 µm), transferred into a PTFE vessel and placed on a hot plate CB 300 Stuart (about 150 °C) to remove any NH_4OH traces and enrich solutes. The resulting solution, treated with the addition of 1% HNO_3, was analysed in Quadrupole ICP-MS (AGILENT 7500 CE) without further preparation. Sublimates were collected as described by the Le Guern & Bernard (1982). The temperature was measured, before and after the tube installation, in the fumarolic vent. A sublimate aliquot (≈ 0.5 g) was put into a silica glass vessel with 2 ml 70% HNO_3 and 4 ml 30% HCl, boiled for 10 min and then cooled. The obtained solution was transferred to a PFA flask, diluted to 50 ml with ultrapure water and for the REE, Zr, and Hf determination, treated by the co-precipitation method as in Raso *et al.* (2013). The resulting solution was analysed in Quadrupole ICP-MS.

Submarine hydrothermal springs were collected using a cylinder in polypropylene (PP) positioned directly at the vent in order to limit, as far as possible, the effects of mixing with seawater. A Teflon tube, equipped with a three-way cock, was connected to the cylinder for transferring the samples into 1L bottles in polyethylene (PE). The measures of T, pH and conductivity were carried out *in situ*. The content of the major constituents (Na^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^- and SO_4^{2-}) was determined in Ionic Chromatography. The concentrations of minor constituents were measured by ICP-OES (Horiba JobinYvon Ultima-2). REE, Zr, and Hf contents were determined as in Raso *et al.* (2013). The analyses were carried out in Quadrupole ICP-MS.

RESULTS AND DISCUSSION

Fumarolic Condensates and Sublimates

REE concentrations in the alkaline condensates range from 0.02 and 16.17 nmol L^{-1}. The largest values were found in samples collected in the Vulcano fumaroles, Tenerife and Isla de Fogo, whereas those collected from the Bocca Grande and Bocca Nuova vents (Phlegrean Fields) showed lower REE contents. On Santorini Island, where lower emission temperatures were found, condensates were not collected since the fluid flux was very low. Since fumaroles at Vulcano and Isla de Fogo were those with the highest emission temperatures, their larger REE contents in sublimates, relative to samples from Tenerife, Phlegrean Fields and Santorini suggested that temperature can play an important role in the REE concentration in volcanic fluids.

Y/Ho molar ratio in these materials spans between 40.7 and 84.6, even if a large number of condensates show Y/Ho values close to the chondritic signature (51.2±5). Chondritic Y/Ho values prevail in condensates from higher temperature vents samples whereas the few super-chondritic terms are found in samples coming from some vents with lower emission temperature. This evidence suggests that in general Y and Ho behave as a geochemical twin whereas their decoupling is sometimes observed at temperatures close to 200-250 °C.

Features of REE-normalised to Post Archean Australian Shale (PAAS, Taylor & McLennan, 1995) in alkaline condensates are reported in Fig. 1. Shale-normalised patterns of condensates showed Eu anomaly values ranging from 0.21 and 1.88, with prevailing values Eu/Eu* ≤ 1 in samples coming from Vulcano and Phlegrean Fields. Instead, positive Eu anomaly values were found in condensates collected in Canary and Capo Verde Islands. The Eu/Eu* values are not related to the temperature of emission vents and this could represent evidences on interactions of volcanic fluids with outcropping rocks.

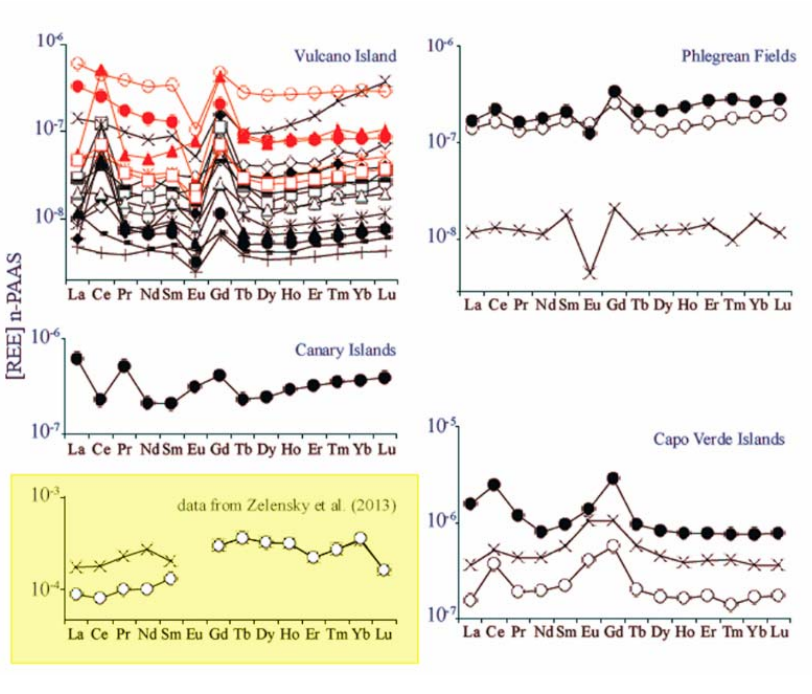

Fig. 1 - Shale normalised REE concentrations (*vs.* PAAS) measured in alkaline condensates from investigated areas. REE distributions in condensates from Erta Ale volcano (Zelensky *et al.*, 2013) are reported for comparison.

The occurrence of positive Gd anomalies is another characteristic feature of shale-normalised REE patterns found in condensates, especially from fumaroles with temperature between 400 and 260 °C (1.3 ≤ Gd/Gd* ≤ 8.9). On the contrary, Gd/Gd* values were lower in those collected in emission vents with temperature between 82 and 250 °C (1.3 ≤ Gd/Gd* ≤ 5.3). The amplitude of Gd anomaly was calculated according to the equation from Alibo & Nozaki (1999) and depends on the HCl/HF ratio of fluids in the highest temperature condensates (Fig. 2). This evidence suggests that Gd and other REE are preferentially transported as chloride complexes in high temperature fluids (Haas *et al.,* 1995; Gilbert & Williams-Jones, 2008). In condensates from lower temperature fumaroles, this covariance is not observed, thus resulting related to the emission temperature.

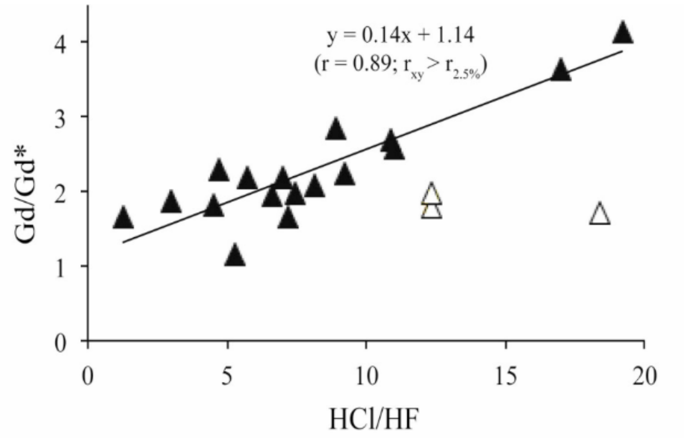

Fig. 2 - Relationship occurring be-tween Gd anomaly and HCl/HF molar ratio values in condensates from higher temperature fumaroles (full triangles) and lower temperature vents (open triangles).

Positive Gd anomalies are also coupled with significant Ce anomalies (0.4 ≤ Ce/Ce* ≤ 10) whose amplitude is calculated according to the equation from Alibo & Nozaki (1999). A positive relationship between Gd and Ce anomalies is more evident in vents with temperatures ranging between 400 and 260 °C, whereas at lower temperatures Ce/Ce* and Gd/Gd* values in condensates are clustered around 2. This observed relationship represents further confirmation that chloride-complexes are responsible for the REE transport in volcanic fluids. In fact, Ce and Gd usually have a different geochemical behaviour in the REE series. Ce is coherent with other light REE (LREE), in low oxygen fugacity condition occurring as Ce(III), having larger particle reactivity compared to heavier REE (HREE). On the contrary, HREE, mainly Gd, preferentially remain in the dissolved phase during solid-liquid processes (Byrne & Li, 1995). As a consequence, the coupled Ce and Gd behaviour is expected only during the formation of chloride-complexes at temperatures ranging between 400 and 250 °C when the stability of $[(Gd,Ce)Cl_3]^0$ and $[(Gd,Ce)Cl_4]^-$ species is larger relative to those formed with their neighbours (Haas *et al*., 1995).

Zr concentrations in the fumarolic condensates range from about 480 to 21000 pmol L^{-1} in the Vulcano samples, from about 200 to about 4000 pmol L^{-1} for the Phlegrean Fields, and from about 3500 to 6000 pmol L^{-1} at Isla de Fogo and the Canary Islands. In the same samples, Hf concentrations span between 2-210 pmol L^{-1}, 2-42 pmol L^{-1}, and 60-82 pmol L^{-1}, respectively. It follows that the Zr/Hf molar ratios are distributed on chondritic terms up to significantly super-chondritic values. These findings show a significant linear relationship (r = 0.99) for the concentrations of Zr and Hf in the condensate samples. Similarly, to what is observed for the REE, the efficiency of the Zr and Hf transport in volcanic fluids increases with temperature and this increase leads to a greater enrichment in Zr of residual fraction of the fluids after sublimation occurred.

In sublimates, REE values range from 0.18 to 213.68 μmol Kg^{-1} showing larger REE concentrations relative to the whole REE contents in alkaline condensates. Sublimates collected from the Phlegrean Fields and Santorini show the largest REE concentrations, whereas lower concentrations occurred in samples coming from the Vulcano and Isla de Fogo vents. This evidence is opposite in alkaline condensates where the largest REE contents were found in higher temperature emissions at Vulcano and Fogo islands.

Y/Ho molar ratio in sublimates spans between 34.1 and 103.1 and several sublimates show chondritic values around 50-54. According to evidence reported for alkaline condensates, super-chondritic values are prevailing in sublimates especially for temperatures ranging from 130 to 250 °C. These findings are consistent with Y/Ho behaviour in alkaline condensates showing preferential Ho scavenging relative to Y at lower temperature.

Shale normalised REE patterns show different features summarized in Fig. 3 in terms of $(La/Sm)_n$ and $(Tb/Lu)_n$ ratios. Comparing REE patterns of sublimates with those calculated from the Erta Ale volcano (Zelenski *et al.*, 2013), similar features are observed in terms of middle REE (MREE) enrichments relative to LREE and HREE, respectively. Consequently, sublimates from Erta Ale fall close to those collected at Isla de Fogo and Phlegrean Fields. Considering that the temperatures of these fumaroles are different (145, 200-266, and 1084 °C, at Phlegrean Fields, Isla de Fogo and Erta Ale, respectively), REE behaviour observed in these sublimates should not be influenced by the emission temperature. A possible explanation of the MREE enrichment shown in sublimates could be provided by recognising similar evidence in plume particles from Etna (Aiuppa *et al.*, 2003) and in anhydrite samples from several submarine hydrothermal fields (Bach *et al.*, 2003). The non-silicate fraction of volcanic plumes is mainly formed by sulphur-bearing compounds (Oppenheimer *et al.*, 2014 and references therein), which, like sublimates, consist of a wide spectrum of oxides, sulphates and halides (Aiuppa *et al.*, 2003). Very often, these solids are Na- or Ca-rich phases where REE can be scavenged through an electrostatic mechanism, complexation onto surfaces according to an inner-sphere mechanism or co-precipitation according to a crystal-chemical control. The REE occurrence as $[REECl_3]^0$ complexes in the studied volcanic fluids avoids the fractionation of these elements onto the same sublimate surface, because of the gaseous REE-complexes have the same charge. The surface complexation, according to an inner-sphere mechanism, is questionable since it is usually coupled to M-type tetrad effects in REE patterns of sublimates that were not recognised. The same suggestion was made by Bach *et al.* (2003) to explain MREE enrichment characterising the shale normalised patterns of hydrothermal anhydrite samples from Manus Basin (Pacific Ocean) as a consequence of the crystal-chemical control on the REE substitution for Ca^{2+} in anhydrite crystal lattice. This indication is corroborated by similar REE behaviour during carbonate, sulphate and phosphate crystallization and might be expected also for Na^+-REE substitution, since Na^+ and Ca^{2+} have similar ionic radii in six and eight-folder coordination. Therefore, the REE behaviour in sublimates, falling in quarter II of Fig. 3, is consistent with the deposition of solids incorporating elements close to Ca^{2+} and Na^+ dimensions. On the contrary, if crystallising solids incorporate ions larger that Ca^{2+}, as Sr^{2+}, Ba^{2+}, Pb^{2+} and NH_4^+, the preferential LREE partitioning in sublimates should be observed according to the lanthanide contraction rule and sublimates will fall in quarter III (Fig. 3).

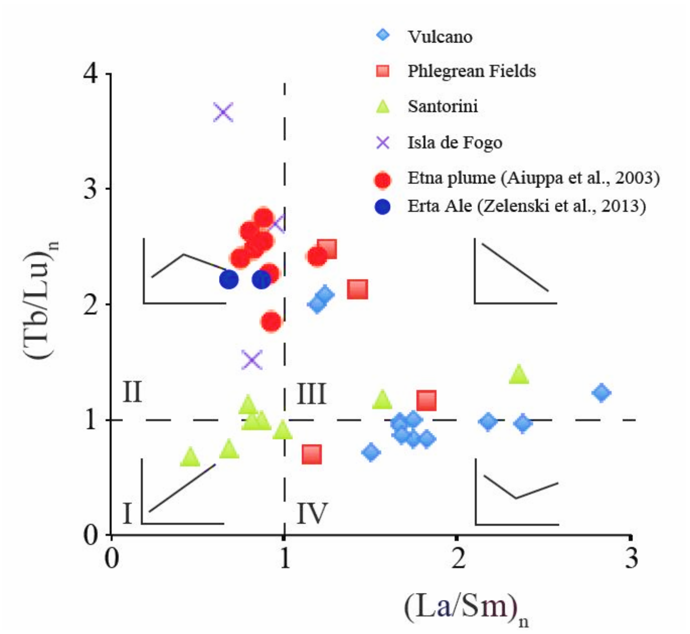

Fig. 3 - Features of shale-normalised REE patterns in sublimates from studied areas in terms of La/Sm and Tb/Lu normalised ratios. Reference samples (Aiuppa *et al*., 2003; Zelenski *et al*., 2013) are reported for comparison.

Confirmation of the crystallographic control of the REE fractionation in sublimates is provided by the geochemical behaviour of several sublimates from Vulcano fumaroles. These materials contain both several large ions bearing halides (NH_4^+, Bi^{3+}, Cd^{2+}, Pb^{2+}) and sulphosalts associated to Zn and Fe. Therefore, the preferential incorporation of LREE and HREE, relative to MREE, should be expected substituting larger and smaller ions that Ca^{2+}, respectively, as showed in sublimates falling in quarter IV. Therefore, the hypothesis that the REE behaviour observed in sublimates can be induced by a mineralogical control cannot be ruled out.

As observed, the REE, Zr and Hf are also enriched in sublimates. Therefore, these results suggest that the sublimation process is less efficient in distilling a depleted fraction in Zr and Hf than REE. Moreover, the fractionation degree is higher for Hf, which is enriched in sublimates more than Zr. As a result, the concentrations of Zr span between about 1.3 10^5 to more than 4 10^6 pmol Kg^{-1}, between 1.7 10^5 and 1.1 10^6 pmol Kg^{-1}, between 1 10^7 and 1.7 10^8 pmol Kg^{-1}, at Vulcano island, Phlegrean Fields, and in other studied areas, respectively.

Against this background, as it was to be expected from the data for the condensates, the Zr/Hf ratios are mainly sub-chondritic. This confirms the greater capacity of the volcanic fluids to transport Zr rather than Hf in the gas phase. Considering the lack of data on Zr and Hf transport in volcanic fluids, some studies were carried out to determine the stability constants for halogen and sulphate complexes of Zr and Hf according to approach of Pershina *et al.* (2014). Although far from the complexity of the natural system, this approach is still the only one that enables us to predict the speciation of Zr and Hf in natural systems. A larger tendency to form stable halogen complexes of Zr and Hf is reported by Pershina *et al.* (2002) confirming a larger stability of halogen-complexes of Zr rather than Hf.

Environmental consequences

The positive Gd anomaly measured in volcanic residue gas from different fumarolic areas can reflect an excess of Gd with respect to its neighbours along the REE series. The amplitude of this ‘Gd_{excess}’ can be calculated according to the equation from Moller *et al.* (2007). The presence of a high level of dissolved Gd organic compounds in German rivers was progressively found from the mid-1990s (Bau & Dulski, 1996) because of the discharge of these chemicals used as contrast agents in magnetic resonance imaging (MRI). The measured values are of the order of magnitude of the volcanic Gd flux assessed from the fumaroles studied, especially at Vulcano, with the significant difference that chloride-Gd volcanic complexes are highly water-soluble and aqueous Gd^{3+} is highly toxic. This indication suggests that the delivery of highly mobile Gd-chlorides from volcanic sources can have effects on the Gd distribution in the environment close to volcanic areas.

Waters

The REE concentrations were measured in the submarine hydrothermal vents and wells from Vulcano and Santorini islands. Moreover, it was decided to analyse the natural boiling pools at Vulcano Island, to study the influence of the atmospheric contribution to these systems. The submarine hydrothermal springs span a wide range of concentrations, between 807.7 and 8.6 10^3 pmol L^{-1} and between 2.3 10^4 and 4.9 10^4 pmol L^{-1}, for Vulcano and Santorini islands, respectively.

The Y/Ho molar ratios were calculated between 13.3 and 116.1 (Vulcano Island) and from 62.2 to 129.6 (Santorini Island). Most of the samples exhibit super-chondritic ratios, with the exception of some waters from Vulcano that are characterized by significantly sub-chondritic ratios ($13.3 \leq Y/Ho \leq 34.2$). The latter values suggest that the dissolution of Ho-enriched phases occurs in these waters.

In the hydrothermal wells and pools, REE concentrations span between 121.6 and 1.9 10^5 pmol L^{-1} at Vulcano and between 876.5 and 5.6 10^3 pmol L^{-1}at Santorini. The highest concentrations have been measured in the natural boiling pools, acid-sulphate waters located in the isthmus at Vulcano. These waters show the lowest pH values of those found in the investigated waters, up to 2.0 and have Y/Ho values predominantly sub-chondritic. Super-chondritic terms were found in a few wells at the Vulcano Island under acidic pH conditions. Here, Y/Ho values next to the chondritic signature ($Y/Ho \approx 52$, Taylor & McLennan, 1995) are recorded only in one case, suggesting that the REE distribution is probably the result of solid-liquid interactions, with the aquifer rocks and the mineral phases and authigenic particulate. The natural pools are characterized by Y/Ho values from weakly sub-chondritic to chondritic (up to 50.7).

Shale-normalised patterns of REE are different depending on whether the waters have negative or positive Eh values (Fig. 4). In the first case, the patterns are poorly fractionated with weak enrichments (HREE) and values of the Y/Ho ratio around the chondritic signature are found. In the waters with positive Eh values, normalised patterns show a greater enrichment in HREE than the LREE. This is coupled with different behaviour for Y and Ho, which show molar ratios both super- and sub-chondritic. The REE behaviour in the water of two springs on Vulcano Island is marked by patterns that show a flat trend, with a slight decrease in normalized concentrations from Gd to Lu. This evidence suggests that the REE are the product of the leaching of solids having a "chondritic" composition of these elements. The atmospheric particulate could represent this type of material, having an almost flat pattern of the normalised REE (Censi *et al.*, 2004). In the investigated waters, Eu anomalies values span between 0.27 and 2.49. However, only 4 for samples coming from the island of Vulcano show Eu/Eu* > 1.

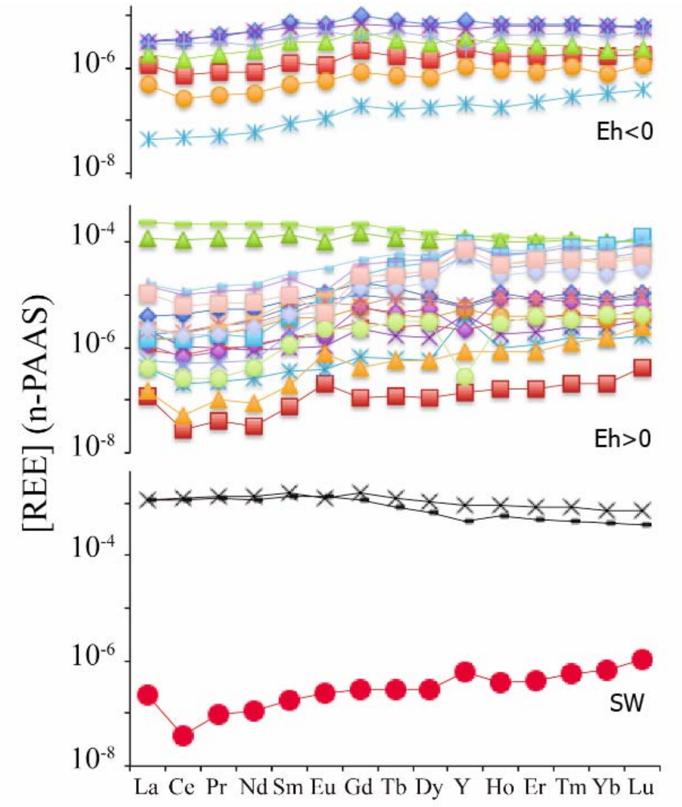

Fig. 4 - Shale-normalised patterns of REE in hydrothermal waters from Vulcano and Santorini islands.

The speciation of REE, shows that the waters with negative Eh values are those in which the dominant species sulphate- and halogen complexes. Moreover, for these waters it is possible to model an equilibrium or super-saturation with respect to carbonate minerals, mainly dolomite and Mg-calcite. The waters having these characteristics will be henceforth defined as group 1. Instead, clustered in group 2 are the waters with positive Eh values, for which the most abundant species of REE are the carbonate-complexes. In group 2, the waters are mostly saturated or super-saturated with respect to Fe-oxyhydroxides.

The concentrations of Zr and Hf measured in the investigated submarine springs, are distributed as follows: *i*) Zr = 1.2 10^4 - 23.9 pmol $L^{-1}$and Hf = 147.7 - 0.68 pmol L^{-1} for Vulcano island; *ii*) Zr = 4.1 10^3 - 63.0 pmol L^{-1} and Hf = 49.6 - 0.03 pmol L^{-1} for Santorini island. These two elements are linearly related. The waters of group 1 have concentrations of Zr and Hf that display a trend with a slope close to 100, while the samples of group 2 are aligned along a trend with a slope close to 250. The difference among the two groups of waters, being saturated or supersaturated with respect to different mineralogical phases, suggests that the mutual behaviour of Zr and Hf is influenced by the reactivity that the dissolved species of these elements can have in respect to the areas with which they may come into contact.

In order to assess this aspect, speciation calculations have been extended to Zr and Hf. They show that the dominant species occurring in the investigated waters are $[Zr(OH)_4]^0$ and $[Hf(OH)_5]^-$, respectively. Only in the water of "Vasca" at Vulcano isthmus the dominat Hf specie is $[Hf(OH)_3]^+$ with pH close to 2.

In hydrothermal systems, features of normalised REE patterns are often considered useful indications of the rocks aquifers and sources of deep fluids (Moller *et al.*, 2003, 2007, 2012). On the other hand, it cannot be excluded that the form assumed by the normalized patterns in hydrothermal water aquifers is rather influenced by solid-liquid separation processes due to the formation of authigenic solids (Censi *et al.*, 2013) and not just because of rock-water interactions. In order to evaluate which of the above-mentioned processes can be responsible for the geochemical behaviour of REE in the investigated water, the study of the pattern's shape in

Fig. 5 has been rationalised basing on the normalised La/Sm and Tb/Lu ratios. Since REE are subdivided into LREE, MREE and HREE, the normalised ratios La/Sm and Tb/Lu are representative of the splitting LREE-MREE and MREE-HREE, respectively.

Since the distribution of the REE, typical of the rocks making up the aquifers of Santorini and Vulcano, is characterised by LREE enrichment (De Astis *et al.*, 1997), the absence of the latter evidence in the waters suggests that the distribution observed of REE in the dissolved phase is only partially influenced by water-rock interactions.

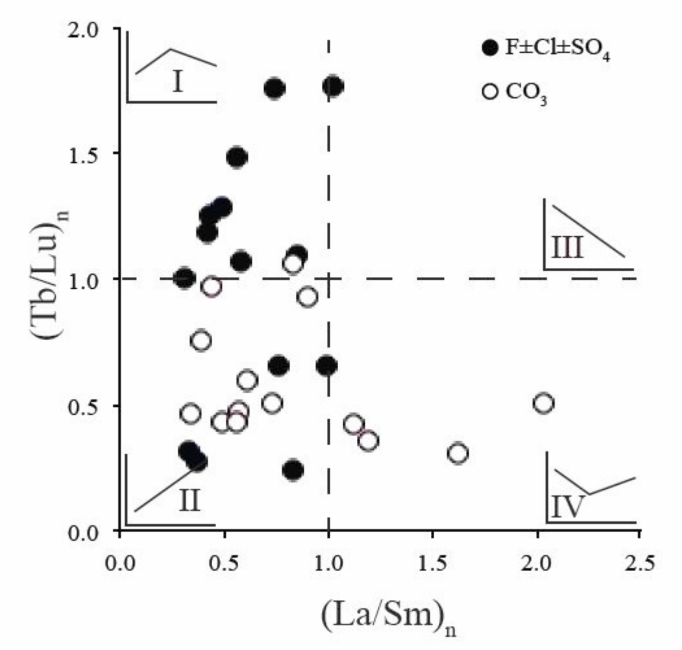

Fig. 5 - Shale- normalised REE patterns rationalised basing on the calculation of the normalised La/Sm and Tb/Lu ratios.

The samples of group 1 fall in I, II fields of Fig. 5, corresponding to MREE enrichment (range I) or characterized by monotonic increasing trends of normalised patterns (range II). Instead, the samples of group 2 fall in the fields II and IV in the graph, which differ from each other only in the degree of LREE enrichment. Furthermore, model calculations indicate that the two groups of water also differ in order to be balanced with carbonates (group 1) and Fe-oxyhydroxides (group 2), as confirmed by the finding of phases in authigenic suspended particulate in the water. The effect of the formation of authigenic carbonates and Fe-oxyhydroxides could influence the dissolved REE behaviour in studied samples in terms of Y/Ho *vs.* Eu/Eu* values that are inversely correlated.

The depletion in LREE (I, II fields of Fig. 5) as that in HREE (range I) could suggest that there is a fractionation of REE induced by the formation of authigenic carbonates, predicted by the model calculation. Hence, exists a mineralogical control on the behaviour of REE in the waters of group 1. This is in agreement with the results of Bau & Moller (1992), which show that both the LREE as the HREE are depleted during the crystallization of carbonate from hydrothermal solutions in natural hydrothermal systems of low and medium temperature.

The waters of group-2 are enriched with HREE with respect to MREE (II, IV fields Fig. 5), whereas a slight LREE enrichment is sometimes observed in some samples (IV field). In agreement with previous observations, the shapes of the REE pattern falling in field II can suggest an effect of carbonate complexation. However, the possibility that the latter features can be caused by the leaching of authigenic solids formed during the between hydrothermal fluids and seawater (Bach & Irber, 1998) cannot be ruled out. Given this hypothesis, the latter suggestion can also explain the features observed in REE patterns clustered in field II, whereas those falling in field IV agree with deeper dissolution of authigenic solids. The suggestion that authigenic solids are formed during the mixing between hydrothermal fluids and shallow aquifers in wells or with seawater is consistent with W-type tetrad effects observed that occur especially in submarine spring waters. These findings confirm that dissolved REE distribution is a consequence of the dissolution by solid interaction (Masuda *et al.*, 1987). Submarine hydrothermal waters show from chondritic to superchondritic Y/Ho values consistently with the preferential Ho removed during the deposition of Fe-oxyhydroxides. This scenario is consistent with the relationship observed between Y/Ho values and the amplitude of tetrad effects in a submarine spring from group

2 waters. Y-Ho decoupling can also occur during the authigenic carbonates deposition, as recognised in natural systems (Censi *et al.*, 2014). Therefore, the discovery of a superchondritic marker also in group 1 waters is justified.

Surfaces of Fe-oxyhydroxides are weakly positively charged as carbonate surfaces at pH < 8. Since the dominant Zr and Hf species in the studied water are $[Zr(OH)_4]^0$ and $[Hf(OH)_5]^-$, respectively, the preferential Hf scavenging relative to Zr is expected and the chondritic to superchondritic Zr/Hf signature observed in group 1 and 2 waters is consistent with processes invoked for the waters studied.

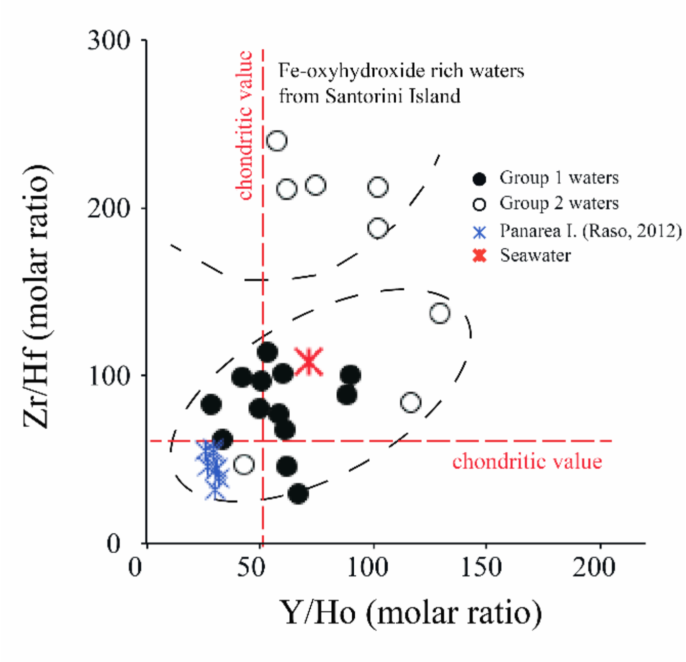

Fig. 6. - Distribution of Zr/Hf *vs.* Y/Ho values in studied waters from Vulcano and Santorini islands. Seawater composition measured far from hydrothermal vents and the composition of hydrothermal vents from Panarea island (Aeolian archipelago) are reported.

However the possibility that interactions between $[Hf(OH)_5]^-$ and Fe-oxyhydroxides can achieve the inner-sphere surface complexation for hafnium cannot be ruled out.

The Y/Ho and Zr/Hf signature of the waters studied was compared with those collected close to submarine springs at Panarea Island (Aeolian Archipelago) and with Mediterranean seawater not subjected to interactions with deep fluid. It can be observed that waters from Vulcano mainly fall in an elliptical field characterised by progressively increasing Y/Ho and Zr/Hf ratios, from chondritic values towards super-chondritic terms (Fig. 6).

This behaviour suggests that the formation of authigenic carbonates equilibrated with group 1 waters contributes only to limited Y-Ho and Zr-Hf fractionations in opposition to the formation of Fe-oxyhydroxides, which we consider primarily responsible for the behaviour of Zr and Hf in the waters of Santorini. Only submarine spring waters from Santorini island fall far from this field, showing higher Zr/Hf ratio values.

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