The carbonatites of Mt. Vulture as a (re)source of rare earth elements

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Abstract. Mt. Vulture volcano is situated at the easternmost border of the Italian Apennine compressive front. It is a composite volcano whose activity was both explosive and effusive from middle to upper Pleistocene. The final volcanic products have carbonatitic composition and represent the object of this study. In particular, two lava flows (upper and lower) and a dyke were sampled and analyzed. The mineralogical assemblage is similar in all samples: calcite, clino- and/or orthopyroxene, melilite, phlogopite, amphibole and ± plagioclase are the primary minerals, while apatite, opaque minerals, ± rutile and ± zircon are the accessory phases. The main difference between analyzed rocks are the amounts of primary calcite and plagioclase, the Ba contents and the $(La/Yb)_{ch}$ values, larger in the lower lava flow. In all samples, rare earth elements have very high concentrations and show high LREE/HREE fractionation that, through the R-mode factor analysis and PCA extraction method, has been attributed at different mineral phases.

Keywords. Rare earth elements, alvikites, Pleistocene, Italy

1 Introduction

Rare earth elements are an interesting group of metals that have recently become quite useful in high-tech applications due to their unique catalyst, magnetic, and optical properties (for example, cell phones and laptops contain rare earth elements). Today they are strategic materials in the world economy and therefore the rapid rise in world demand for the rare-earth elements (REEs) has expanded the search for new REE resources (Tucker et al. 2012). In addition, the rare earth elements are a major research tool in studying igneous rock petrogenesis and the processes underlying the genesis of chemical sediments.

Different types of deposits concentrate different amounts of the rare earth elements depending on many factors, such as geochemical behavior of REEs within a selected geological system and the physico-chemical features of mineralizing fluids.

The most common REE deposits are associated with alkaline magmatic rocks, carbonatites, pegmatites, laterites and sulphide accumulations occurring in widespread areas of the Earth (mainly China, United States, Brazil, India, Russia and Australia). Among these, carbonatites and alkaline intrusive complexes, as well as their weathering products, are the primary sources of REEs (Long et al. 2010).

Carbonatites are igneous rocks composed of more than 50 modal per cent magmatic carbonate and containing less than 20 wt.% SiO_2 (Le Maitre 2002). They are usually associated with alkaline igneous rocks and the study of carbonatites-alkaline rocks association provide important clues to reconstructing mantle and crustal processes as well as the secular evolution of the mantle (e.g. Ray et al. 2000, and references therein). However, the increasing interest in carbonatites is led mainly by their high REE contents that are the highest in any igneous rocks. In addition, ores of Cu, Nb, Mo, fluorite, phosphate, and vermiculite are also associated with carbonatites (Xu et al. 2010) and increase their importance within the industrial minerals framework.

In southern Italy carbonatites occur at the Mt. Vulture volcanic area only. Literature related to these carbonatites is focused on the petrologic and geodynamic aspects of their genesis, which is still a matter of debate (e. g. Stoppa and Principe 1997; D'Orazio et al. 2007; Rosatelli et al. 2007; Stoppa et al. 2008). These studies, however, mainly concern the mineral chemistry and isotopic records, and data on REE concentration (D'Orazio et al. 2007; Rosatelli et al. 2007) are few.

The aim of this study, therefore, is to provide new chemical data for a set of carbonatitic rocks from the Mt. Vulture volcano, and to evaluate their potential of exploitable REE (re)source.

2 Geological setting

The southern Apennines are a roughly NW–SE oriented segment of a fold-and-thrust belt that belongs to the complex geodynamic setting characterizing the central Mediterranean. Since the Tortonian, the thrust front has migrated to the southeast due to the convergence of Africa and Europa plates (Gueguen et al. 1998), the rollback of a west dipping slab and the following back-arc basin opening to west (Malinverno and Ryan 1986).

Mt. Vulture is located at the outer edge of the Italian Apennine belt (Fig. 1) and represents the most striking example of an asthenospheric upwelling along slab wrench faults (Caracausi et al. 2012, and references therein). It is a relatively small stratovolcano composed both of pyroclastic deposits and lava flows. Its volcanic activity started at 742±11 kyr and continued until 142±11 kyr, interrupted by several long inter-eruptive periods (Büttner et al. 2006, and references therein). The volcanism is strongly silica undersaturated, from alkaline potassic to ultrapotassic affinities (De Fino et al. 1982, 1986). Giannandrea et al. (2006) have grouped the volcanic units in two distinct supersynthems: 1) Mt.

Vulture and 2) Monticchio units. The Mt. Vulture units are the oldest volcanic products and are represented by lavas and pyroclastic deposits that range in composition from basanite–foidite to phonolite. The Monticchio units are products of the most recent eruptions. They produced some maar-type vents with tuff aprons and have a carbonatitic–melilititic composition (Stoppa and Principe 1997).

According to D'Orazio et al. (2007), the studied rocks belong to a volcanic sequence erupted from a small volcanic center occurring at the north-western slope of the Mt. Vulture, in the Vallone Toppo Lupo site (Fig. 1). In particular, the samples comes to: (1) two distinct massive alvikite Ca-carbonatite lava flows, hereafter named upper (ULF) and lower (LLF) lava flow, that are divided by a 5-10 meters-thick pyroclastic level; (2) a 70 centimeter-thick, carbonatitic dyke (DY) cross-cutting both the lavas.

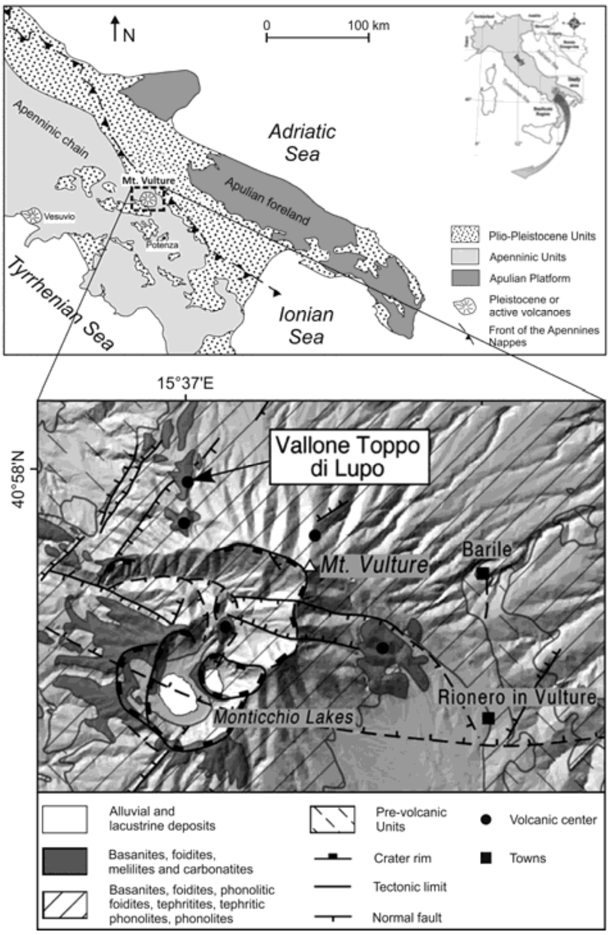

Figure 1. Geological sketch map of Southern Apennines and zoom of the Mt. Vulture volcano area (after Bentivenga et al. 2004 and D'Orazio et al. 2007, modified). The sampling site (Vallone Toppo di Lupo) is shown.

3 Analyses and results

All carbonatite samples were subjected to petrographic and chemical analyses. Thin sections were observed both with an optical polarizing microscope and an environmental scanning electron microscope (ESEM) XL30 Philips LaB6, equipped with an energy dispersion spectrometer (EDS). The abundances of major, trace, and RE elements were determined by inductively coupled plasma–mass spectrometer (ICP-MS), instrumental neutron-activation analysis (INAA), and thermal desorption mass spectrometry (TD-MS). Average errors are less than ±5%, except for elements occurring at concentrations of 10 ppm or less, for which the error is ±5–10%.

3.1 Petrography

The lavas and dyke show porphyritic texture. Large calcite and/ or pyroxene phenocrysts and wide calcite aggregates are widespread in a glass-bearing hypidiomorphic matrix. The optical microscope observations revealed the same mineralogical composition for the three volcanic rocks. The paragenesis consist of calcite, (clino- and/or ortho-) pyroxene, melilite, phlogopite, amphibole and ± plagioclase as primary minerals, and apatite, opaque minerals, ± rutile and ± zircon as accessory phases. Calcite, zeolite and rarely saussurrite (as alteration phase of plagioclase in LLF only) are secondary phases.

Crystals of primary calcite show polysynthetic twinning and have prismatic to granular habit. Fine-grained crystals of secondary calcite instead are observed in amygdales where show various optical orientations. These amygdales, permeating the rocks, are often infilled also by zeolite and plagioclase.

The composition of amphibole is variable. It is richterite in the lavas and hastingsite in the dyke. The amphibole shows prismatic habit and often forms aggregates that rim the pyroxene.

In the analyzed rocks melilite, amphibole, and the accessory phases (mainly zircon, apatite and opaque minerals) are commonly pseudomorphs after, or enclosed by, pyroxene and/or phlogopite. Occasionally, phlogopite and amphibole form aggregates with pyroxene.

Some significant compositional differences among studied volcanic rocks were observed: the abundance of primary carbonate (calcite) in LLF is higher than those of both ULF and DY; in LLF the clinopyroxene contents are lower than those of the other analyzed rocks; large, mantle-derived xenoliths of clinopyroxene xenocrysts have been also found within lower lava samples only.

3.2 Chemistry

As for the chemical composition, CaO is the dominant oxide followed by SiO_2, Al_2O_3, and Fe_2O_3(T) which, as expected for alvikites, show very low concentrations just like those of the remaining major element oxides.

The greater abundance of primary calcite of the lower lava samples, in respect to those of upper lava and dyke, determine for LLF a larger CaO content (ranging from 40.96 to 45.10 wt.%), a highest CaO/(CaO+MgO+FeO(T)+MnO ratio (fluctuating in the 0.88-0.90 range) and lower amounts of the other principal oxides (SiO_2, Al_2O_3 and Fe_2O_3(T)) due to dilution effect. Among the major element oxides, only

P_2O_5 shows contents generally higher than 1.79 wt.% in keeping with the large amount of apatite observed.

Regarding trace elements, the transition metals (Sc, Cr, Co and Cu) and alkaline elements (Rb and Cs) have low contents. The actinides (Th and U) and Pb have generally low concentrations, except for LLF sample where these are appreciably higher. The amount of Sr and Ba is large in all samples. However the highest Ba concentrations are detected in the lower lava flow samples resulting in lower values of Sr/Ba ratio for this rock (from 0.68 to 0.98 for LLF and from 1.03 to 1.83 for ULF and DY).

The total amount of REE is high in all analysed rocks and ΣREE ranges between 1956 and 2404 ppm. The REE chondrite-normalized distribution patterns (Fig. 2, chondrite data are form Evensen et al. 1978) are characterized by a remarkable LREE/HREE fractionation and negative Eu anomalies (in the 0.80-0.86 range).

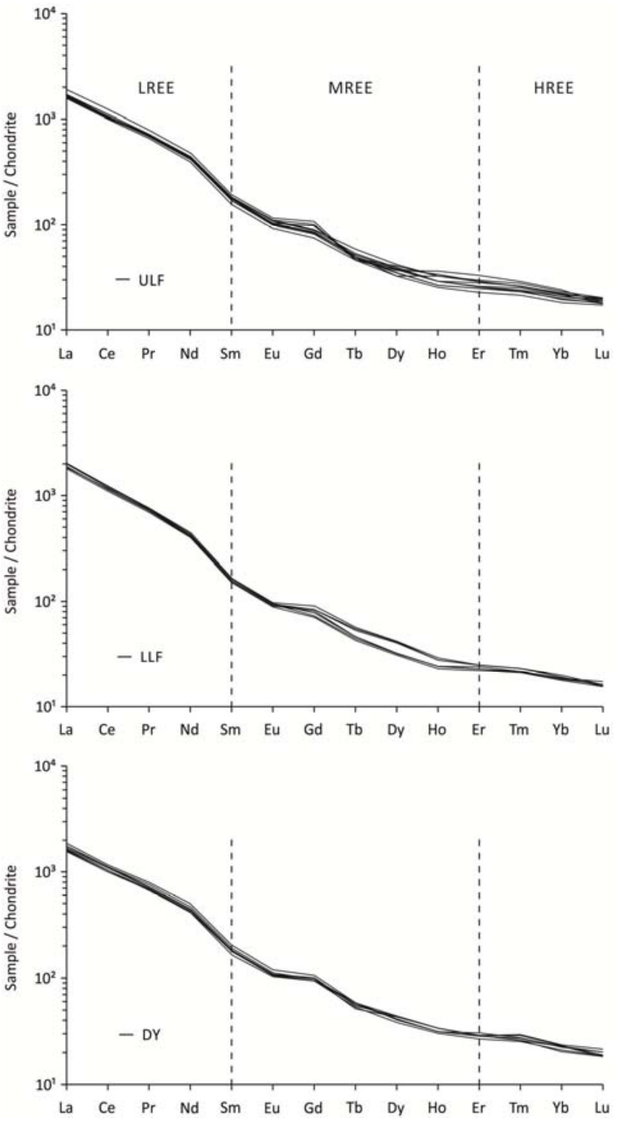

Figure 2. REE chondrite-normalized distribution patterns for upper lava (ULF), lower lava (LLF), and dyke (DY) samples.

The $(La/Yb)_{ch}$ index values, as well as the LREE/MREE fractionation (expressed as $(La/Sm)_{ch}$), is larger in LLF samples and in particular is from 100.0 to 110.2 for lower lava and between 71.7 and 88.8 for upper lava flow and dyke. On the contrary, the values of MREE/HREE fractionation, expressed as $(Gd/Yb)_{ch}$, are very similar in all samples (from 3.86 to 4.63).

4 Discussion and conclusions

Although the composition of most magmas can be represented by the basalt-andesite-rhyolite spectrum, some deviate from this trend and are compositionally unusual. These magmas give rise to volcanic rocks that are rare as well as economically significant due to their content of a wide range of ore-forming metals such as mainly Cu, P, Zr, U, Th and all rare earth elements.

To identify the mineral phases determining the REE enrichments in the Mt. Vulture carbonatites, the R-mode factor analysis were performed on ULF, LLF and DY samples using the StatGraphic® Centurion XVI.I software. To extract factors from the data sets, the Principal Components Analysis method was applied. This operation was performed on the standardized correlation matrix, thus weighting all the variables equally, and allowing us to convert the principal component vectors into factors. Subsequently, the factor loadings, which represent the correlation coefficients between the variables and the factors, were considered. The factor loadings forming the factor matrix are shown in Table 1.

	Factor 1	Factor 2	Factor 3
SiO_2	0.92		
CaO	-0.69	0.66	
P_2O_5		0.67	
Sc	0.89		
Ba	-0.83		
Sr			0.86
Zr	0.91		
Cr	0.68		
Co	0.84		
Cu	0.81		
La		0.85	
Yb	0.91		
ΣREE		0.93	
Pb		0.72	
Th	0.82		
U			0.55

Table 1. Factor matrix for the Mt. Vulture carbonatitic rocks resulting after Varimax rotation. Numbers are weights of the variables in the extracted factors. Variables having weight less than 0.55 are omitted.

Three factor were detected for carbonatites. The first factor includes most of the selected variables. Among these, CaO and Ba only show negative weights suggesting their independence from the other variables of this factor. The presence of both primary and secondary calcite in studied rocks justifies the weights of CaO in this factor. The association of Ba and CaO, instead, is due clearly to the previously stated presence of secondary Ba-bearing zeolite and calcite within amygdules widespread in the rock samples. The first factor is also characterized by significant weights of SiO_2, as major element oxide, of all transition metals, Zr, Th and Yb, suggesting a clear relationship between silicate phases and all selected elements. It is a well known fact that pyroxene, phlogopite, and amphibole are able to host transition metals (Stoppa et al. 2005; Reguir et al. 2009). It is worthy of note, that in the Factor 1 the HREE only, represented by Yb, are included. The fractionation of heavy rare earths from the other REE may be likely ascribed to the presence of zircons, that commonly concentrate heavy REE (Harley and Kelly 2007) and Th in their crystal structure likely as inclusions (e.g. Seifert et al. 2012). In fact, besides Yb, also Zr and Th are contained within the first factor.

The Factor 2 comprises CaO and P_2O_5, as major element oxides, and Pb, La and total REE amount. It is obvious that the large content of apatite in the carbonatites determines the link between CaO and P_2O_5. However, also the presence of La enclose in this factor may be related to presence of apatite crystals suggesting the inclusion of LREE in this phase. In addition, it is no surprising that ΣREE contents are comprise in this factor. As previously noted, the Mt. Vulture carbonatites are characterized by very high values of LREE/HREE fractionation index suggesting the higher concentrations of light RE elements than those of heavy RE elements in these rocks. The Pb and CaO relationships, instead, likely involves that most of the lead in the Mt. Vulture carbonatite is housed in calcite, according to the fact that Pb contents detected in calcite from carbonatite are not negligible (Chen and Simonetti 2012).

The third factor includes only Sr and U, proving that these two elements are not related to the main mineral phases of carbonatites but likely to accessory phases enclosed in their glassy matrix.

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