G Model
CHEMER-25440; No. of Pages 15
ARTICLE IN PRESS
Chemie der Erde xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Chemie der Erde

journal homepage: www.elsevier.de/chemer

Geochemistry of coastal sands of Eastern Mediterranean: The case of Nisyros volcanic materials

I.T. Tzifas[a,*], P. Misaelides[a], A. Godelitsas[b], P.N. Gamaletsos[c], P. Nomikou[b], A.G. Karydas[d], V. Kantarelou[d], A. Papadopoulos[e]

[a] Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece
[b] Department of Geology and Geoenvironment, University of Athens, Panepistimioupolis, 15784 Zografou, Greece
[c] Center for Electron Nanoscopy, Technical University of Denmark, 2800 Kongens Lyngby, Denmark
[d] Institute of Nuclear and Particle Physics, NCSR Demokritos, 15310, Athens, Greece
[e] Department of Mineralogy, Petrology and Economic Geology, School of Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

ARTICLE INFO

Article history:
Received 6 March 2017
Received in revised form 28 June 2017
Accepted 4 July 2017

Keywords:
Coastal sands
Heavy minerals
Rare earth elements
Actinides
Hellenic volcanic arc
Nisyros
Micro-XRF

ABSTRACT

Coastal sand samples collected from the northern part of Nisyros volcanic island (Dodecanese, Greece) were investigated for first time for their potential in strategic metals and compared with parental rocks of the island which are Quaternary volcanics with alternating lava flows, pyroclastic layers and lava domes and relevant materials located near granitoids of Northern Greece. The PXRD and SEM-EDS study of the sands revealed enhanced content of feldspars, Fe-Mn oxides, magnetite, tourmaline, pyroxenes, ilmenites, along with zircons, apatite and sulfide inclusions. The fresh hydrothermally deposited clayely material collected from the Nisyros caldera crater had a rather different mineralogical composition from the coastal one (alunite, anhydrite, opal-CT, quartz, kaolinite). UCC-normalized spidergrams indicated that the weathering processes contributed to accumulation of heavy minerals (mainly ilmenite), and strategic metals including V (1920 mg/kg) and Nb (245 mg/kg), in the coastal sand. The low REE concentration (ΣREE + Y = 240 mg/kg) could be attributed to the absence of REE-rich minerals. Moreover, the sands exhibit different geochemical patterns compared to the volcanic source rocks of the island, which are especially enriched in Large-Ion Lithophile Elements (LILE) and depleted in High Field Strength Elements (HFSE), such as Nb and Ta. On the other hand, the caldera material is enriched in volatile components, sulfur, chalcophile elements (Se, Bi, Hg, As, Pb) and Ba. Micro-XRF analyses of representative crystals showed that the high Nb content of the sands was associated with the Ti/Fe-rich phases (e.g. ilmenites). The geochemical composition of N Greece sands showed, because of their origin, enrichment not only in HFSE but also in REE.

The study of the coastal heavy mineral sands originating from different geological environments of Greece provides information about the association of their mineral components with REE, other elements of economic interest (e.g. Co, Nb, Ta) and natural actinides. In addition, the study of the black sands of Nisyros island could be considered as a characteristic example of those from other parts of Hellenic Volcanic Arc (HVA) and other relevant Mediterranean regions.

1. Introduction

Coastal sands of certain areas of the world are enriched in heavy minerals and show high concentrations of rare earth elements (REE) and strategic metals (e.g., Co, Nb, Ta), which are of continuously increasing importance for the clean energy, military and consumer electronics technology as well as for the preparation of alloys for specialized applications. The current annual global demand is ca. 10^5 thousand tons of rare earth oxides (Hatch, 2012; Alonso et al., 2012) whereas the USGS estimation of their total world reserves is of the order of 110 million tons. However, these reserves are unequally distributed over the earth and a large percentage of them located in deep-sea manganese nodules or in small or low-concentration deposits. On the other hand, the supply of strategic metals, such as Co, Nb and Ta, currently meets the demand and their supply-demand equality is, by the most sources, predicted to endure in the near future.

* Corresponding author.
E-mail address: tzifioan@chem.auth.gr (I.T. Tzifas).

http://dx.doi.org/10.1016/j.chemer.2017.07.002

Please cite this article in press as: Tzifas, I.T., et al., Geochemistry of coastal sands of Eastern Mediterranean: The case of Nisyros volcanic materials. Chemie Erde - Geochemistry (2017), http://dx.doi.org/10.1016/j.chemer.2017.07.002

The enhanced need for REEs and other strategic metals in western world and particularly in the European Union was the reason that the European Commission characterized their exploration and exploitation as priority research field.

The potential REE deposits in Europe are mostly concentrated in Nordic countries including Greenland. Exploration for REE deposits are also in progress in SE European countries, including Greece. In the latter, their presence in coastal black sands, in addition to minor content in bauxites and laterites, is of special interest and worth of investigation (Eliopoulos et al., 2014; Gamaletsos et al., 2016; Gamaletsos et al., 2017). Relatively high LREE (La, Ce) content has also observed in the porphyry Cu-Au system of Vathy Kilkis (Melfos and Voudouris, 2012).

Generally, the REEs occur in a range of minerals which are present in a variety of geological formations. The most significant primary types of REE enrichment are those associated with alkaline silicate igneous rocks and carbonatites. REE enrichments can also be found associated with hydrothermal veins, breccias and metasomatic zones in a variety of sedimentary and metamorphic environments.

Many studies are focused on beach sands, the so called "placer deposits", which are represented in any waterborne sand or gravel deposits containing concentrated valuable heavy mineral (e.g. gold) or magnetite grains originally eroded from bedrock and then successively transported and concentrated by flowing water (Komar, 2005). Their crystals are sufficiently resistant to weathering processes and their accumulation in coastal areas is due to the gravity segregation. These phases occur, in mixture along with common tectosilicates, phyllosilicates, Fe- and Cr-spinels, Ti-oxide and minerals (rutile, titanite), phosphate minerals and specific heavy silicate minerals of the epidote group (e.g., zircon and allanite) in heavy mineral sands. The above mentioned materials are, by nature, enriched, depending on the geological environment, in strategic metals, lower actinides (e.g. Th, U) and REEs.

Coastal sands of volcanic islands could present, depending on the extractability of heavy minerals hosted in the "accessory minerals", economic importance (Lefond, 1975; Kuzvart, 1984; Vanecek, 1994). In addition, heavy mineral bearing sands show an increasing environmental importance due to the presence of U, Th, and their decay products posing a potential radiological risk (Eisenbud and Gesell, 1997).

Several studies of heavy mineral coastal sands from N Greece have already appeared in the literature. Characteristic examples are the sands from the coastal area of the city of Kavala (Pergamalis et al., 2001; Papadopoulos et al., 2015, 2016a,b), Touzla Cape close to the city of Thessaloniki (Filippidis et al., 1997), the Sithonia peninsula in Chalikidiki (Papadopoulos et al., 2014, 2015a,b) and the Atticocycladic zone (Papadopoulos et al., 2016a,b).

The objective of the present study was the mineralogical and geochemical investigation, for the first time, of the coastal heavy mineral bearing volcanic sands of the Nisyros island (Dodecanese, Greece). The Mediterranean coastal area is rich in heavy mineral sands due to a number of volcanoes, some of them still active nowadays (Braccini et al., 2013). In this way, this work could also act as a model study for sands of the whole Hellenic Volcanic Arc (HVA) and relevant volcanic areas in Mediterranean coasts.

In addition, the Nisyros sands were compared with those located near granitoids of N Greece coastal area. The purpose of the comparison was to illustrate the geochemical differences among materials created by processes in different geological environments.

2. Geological setting of Nisyros

The Hellenic Volcanic Arc (HVA) (Fig. 1a) is a young 5 Ma-to-present volcanic arc developed in the pre-Alpine to Quaternary continental crust of the Hellenic Subduction System (HSS). Its development is related to the northward subduction of the last remnant of the oceanic crust of the African plate beneath the southern edge of the active margin of the European plate, resulting in the formation of numerous Plio-Quaternary volcanic centers, namely Crommyonia (Soussaki), Methana-Aegina-Poros, Milos-Kimolos-Polyegos, Santorini-Christianna and Nisyros-Yali-Kos (Papanikolaou, 1993; Royden and Papanikolaou, 2011).

Nisyros volcano (Fig. 1b) is composed exclusively of Quaternary volcanic rocks with alternating lava flows, pyroclastic layers and lava domes erupted during successive periods of activity (Georgalas, 1958; Di Paola, 1974; Papanikolaou et al., 1991). The evolution of this volcano is associated with the formation of a big caldera in the middle of the island presenting significant post-volcanic activity. In fact, Nisyros constitues a stratovolcano which has an average diameter of 8 km (based on sealevel) with a caldera (4 km in diameter) formed during the explosive eruption of a large pumice. The caldera floor consists of several hydrothrmal craters, with the largest (named Stefanos) having a depth of 27 m and diameter of 330 m. Hydrothermal venting from the craters continues to this day with the last significant hydrothermal eruptions occurring in 1871-1888 CE (Marini et al., 1993; Brombach et al., 2003). Present-day activity is documented by fumarolic degassing of mainly H_2S, CO_2, H_2O, H_2 and CH_4. The pre-caldera period is characterized by a succession of four lavas and four pyroclastic flows that formed the stratovolcano (Papanikolaou et al., 1991). This succession was followed by the rhyolites of Nikia, in the southern part of Nisyros, and by pumice deposits. The post-caldera magmatic activity (Zellmer and Turner, 2007) has produced a series of rhyodacitic domes (Profitis Ilias Synthem) filling the north-western section of the caldera floor, as well as, the south-western flank of the island. Geothermal drill-holes have been studied in order to give information about the basement beneath Nisyros (Marini et al., 1993). The boreholes showed intersected units of diorite, limestone, and marble. In addition, the detected skarns were formed by contact metamorphism and hydrothermal alteration of the limestones. Carbonate-rich rock-types, as xenoliths, were also found in some pyroclastic deposits on the island (Di Paola, 1974; Francalanci et al., 1995; Limburg, 1991; Seymour and Vlassopoulos, 1992). The volcanic stratigraphy of Nisyros has been described by many authors (Di Paola, 1974; Volentik et al., 2002, 2005a; Nomikou, 2004; Nomikou et al., 2014). The earliest magmatism at Nisyros was also related to submarine flows that deposited porphyritic pillow lavas of basaltic-andesite composition that crop out on the north-western shore, as a result of active uplift of this section of the island (Nomikou and Papanikolaou, 2011; Tibaldi et al., 2008). There is evidence of erosion and reworking of these volcanic rocks, indicating exposure above sea level for part of the depositional history (Volentik et al., 2005b). It should also be mentioned that the black heavy mineral sands occurring in the northern coast of the island have not been investigated by the aforementioned authors.

3. Materials and methods

The Nisyros sand samples were collected from the northern coast of the island (Fig. 1). The material appeared fine grained and black-coloured, because of its high content in Fe-spinels and other heavy minerals. Furthermore, another clayely sample was collected from the recent deposits of the interior of the main hydrothermal crater of the Nisyros volcano caldera (Fig. 2). The second sample was studied for comparison reasons, as "fresh" volcanic material, in contrast to the weathered (reprocessed) volcanic coastal sands.

The mineralogical characterization was performed by optical microscopy, powder X-ray Diffraction/PXRD (Siemens D5005 diffractometer) and Scanning Electron Microscopy/SEM–EDS (JEOL