



Reflections of the geological characteristics of Cyprus in soil rare earth element patterns



Limin Ren^{a,b}, David R. Cohen^{a,*}, Neil F. Rutherford^a, Andreas M. Zissimos^c, Eleni G. Morisseau^c

^a School of Biological, Earth and Environmental Sciences, University of New South Wales, 2052 NSW, Australia

^b Faculty of Earth Science, China University of Geosciences, Wuhan 430074, Hubei Province, China

^c Cyprus Geological Survey, Ministry of Agriculture, Natural Resources and Environment, Lefkonos 1, Lefkosia 1415, Cyprus

ARTICLE INFO

Article history:

Available online 25 February 2015

Editorial handling by D.B. Smith

ABSTRACT

Rare earth elements (REEs) are used as indicators or proxies for a range of geological and mineralogical processes due to their unique geochemical characteristics. Total and aqua regia-extractable concentrations of REEs and 57 other elements have been determined for 5350 soil samples as part of the high sampling density Geochemical Atlas of Cyprus. The bedrock geology of Cyprus is dominated by the sequence of ultramafic to mafic units formed at a spreading ridge and subsequently obducted to form the Troodos Ophiolite (TO), and the surrounding carbonate-rich Circum-Troodos Sedimentary Sequence (CTSS) deposited in environments ranging from deep marine to sub-aerial. Total and aqua regia-extractable REE patterns are similar for each element and are largely controlled by parent lithology. Soil-to-rock REE ratios are generally elevated in the TO units (>4 for LREEs and 1.5–3 for HREEs) due to loss of more mobile elements during weathering but are close to 1 in the CTSS units. HREEs are more elevated than LREEs in soils derived from TO units with upper continental crust-normalised patterns indicating the main source to be pyroxenes and zircon. Trace element trends indicate REEs in the CTSS were largely derived from detrital material shedding off the TO and deposited in progressively shallowing basins under largely anoxic conditions (absence of Ce⁴⁺ anomalies), with a minor contribution from seawater via adsorption onto secondary Fe + Mn oxides or co-precipitation with carbonates. Heavy mineral-associated elements such as Zr and Th display a relative consistent ratio in the CTSS soils. Peak HREE concentrations occur in the mafic cumulates and intrusives where the median La_{UCC}/Yb_{UCC} is ~0.12, whereas in CTSS units the LREEs are more elevated with a median La_{UCC}/Yb_{UCC} ~0.7. Due to the strong lithogeochemical controls, soil REE spatial patterns reflect even subtle mineralogical variations within the various TO units, the location of major transform faults and other structures, and areas that have been affected by hydrothermal alteration.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Rare earth elements (REEs) are used as proxies for a range of geological and mineralogical processes due to their unique geochemical characteristics and fractionation trends generated by the lanthanide contraction and the multiple valencies for Ce and Eu (Henderson, 1984; Banfield and Eggleton, 1987; Leybourne and Johannesson, 2008). Examples include modeling of magmatic and crustal evolutionary processes, analysing water-rock-regolith interactions, and characterizing the provenance of sedimentary rocks (McLennan, 1989; Elderfield et al., 1990; Sholkovitz and Szymczak, 2000; Nyakairu and Koeberl, 2001; Leybourne et al., 2006; Antonina et al., 2013).

Hydrothermal alteration in particular may significantly alter REE patterns depending on temperature, the source of fluids, host lithology, the extent of alteration and types of secondary minerals formed, including depletion of LREEs (La to Eu) relative to HREEs (Gd to Lu) in groundmass-replacement minerals and the converse in zeolites, carbonates and some secondary Fe oxide minerals (Michard, 1989; Bau, 1991; Gillis et al., 1992; Wells et al., 1998; Guy et al., 1999). In alteration involving seawater, including processes such as spilitization, LREE enrichment occurs due to the higher stability constants and solubilities of most trivalent HREE phosphate, carbonate, and hydroxyl species (Piepgras and Jacobsens, 1988; Lee and Byrne, 1992; Åström and Corin, 2003). Under strongly reducing conditions and elevated temperature, hydrothermal fluids emanating from mid-ocean ridges and back-arc spreading centers are characterized by elevated Eu values (Michard et al., 1983; Sverjensky, 1984; Klinkhammer et al., 1994; Bierlein, 1995; Bau and Dulski, 1999) due to higher solubility

* Corresponding author. Tel.: +61 2 93858084.

E-mail address: d.cohen@unsw.edu.au (D.R. Cohen).

of Eu^{2+} compared with trivalent REEs and Ce^{4+} (Kamber, 2010). Associated massive sulfide deposits and related sediments commonly preserve the strongly positive Eu anomaly of the precursor hydrothermal fluids (Peter et al., 2003; Leybourne et al., 2006).

In sedimentary and weathering environments there are various factors that can influence REE mobility and distribution patterns, including direct precipitation of carbonates, phosphates or oxides, adsorption or co-precipitation with clays and secondary Fe + Mn oxyhydroxides, and the influx of detrital material and REE-bearing heavy minerals. Accumulation of REEs in clay exchange sites is the basis of some economic deposits (Hoatson et al., 2011; Kynicky et al., 2012; Sadeghi et al., 2013b).

Except where conditions are highly acidic, the aqueous solubilities of REEs are typically very low (Wood, 1990). In marine environments, REEs, Th and most transition metals are more strongly incorporated into Fe + Mn oxides rather than carbonates under oxic to sub-oxic conditions across much of the Eh spectrum (Elderfield et al., 1981; Bayon et al., 2002; Koschinsky et al., 2003; Négrel et al., 2006). LREEs tend to be more strongly adsorbed by authigenic Fe + Mn oxyhydroxides than HREEs in marine sediments and soils (Caetano et al., 2009) although Mn oxides have limited ability to incorporate trivalent REEs ions into their structure (Haley et al., 2004). A change from anoxic to oxic conditions and conversion of Ce^{3+} to Ce^{4+} results in Ce depletion in water and positive anomalies in the associated sediments (Shaw and Wasserburg, 1985; Pourret et al., 2008). Changes in redox conditions may occur in various settings such as anoxic ground waters discharging to surface (Leybourne et al., 2000) or deep oceanic waters welling up (Liu et al., 1988).

Lithological REE patterns (and those of other immobile elements such as Zr, Ti, Th and Hf) are generally preserved during weathering and other regolith-forming processes especially where REEs are hosted in resistate phases such as zircon and monazite. Total concentrations typically increase due to mass loss during regolith formation, though there is a tendency for greater loss of HREEs (Gregorauskiene and Kadūnas, 2006; Beyala et al., 2009). A number of studies have investigated the behaviour of REEs under chemical weathering and subsequent transportation of the dissolved and suspended REE fractions by separating various element-mineral associations using a combination of total and partial geochemical extractions (Sholkovitz and Szymczak, 2000; Leybourne and Johannesson, 2008; Galbarczyk-Gąsiorowska, 2010; Fu et al., 2011). Aqua regia extractions in particular display similar chondrite-normalised trends to total REE patterns in weathered materials but with a pronounced positive Gd anomaly (Marmolejo-Rodríguez et al., 2007).

Along with other elements that display significant primary lithological variation and low chemical mobility in surface environments, soil REE concentrations have been used to map underlying parent lithologies (Halfpenny and Mazzucchelli, 1999; Mann, 2006) and other regolith-landform patterns in a number of regional soil and sediment geochemical mapping projects (Xie and Cheng, 2001; De Vos and Tarvainen, 2006; Klassen, 2009; Woodruff et al., 2009; Caritat and Cooper, 2012).

This study draws on the extensive dataset derived from the high density soil Geochemical Atlas of Cyprus (Cohen et al., 2011, 2012a, 2012b), to examine factors controlling the distribution of REEs, including parent lithology, palaeo- and modern environmental conditions, land use and regolith-landform settings.

2. Geological setting of Cyprus

2.1. Lithology

The geological development of Cyprus commenced in the Cretaceous with formation of a co-magmatic vertical sequence of

ultramafic and mafic cumulate units, basaltic to doleritic sheeted dykes, overlying tholeiitic basaltic volcanic units (mainly pillow basalts) and associated chemical sediments (Robertson and Hudson, 1973; Desmet, 1976; Morris et al., 1998). This package of rocks, formed as part of the oceanic lithosphere during sea floor spreading, was obducted in the late Miocene to form the Troodos Ophiolite (TO) (Mukasa and Ludden, 1987; Robinson and Malpas, 1990; Fig. 1). Abutting the south-western side of the TO is the Mamonía Terrane which contains tholeiitic to normal mid-ocean ridge basaltic volcanics (Malpas et al., 1992, 1993) and pelagic sedimentary units containing limestones, mudstones, quartzose sandstones and small amounts of metamorphic rocks (schists and marbles). The Kyreneia Terrane in the north is dominated by carbonate-rich sedimentary units but contains some allochthonous clastic sedimentary units.

Zones of intense hydrothermal alteration occurred throughout the sheeted dyke complex (Kelley and Robinson, 1990) and probably indicate proximity to the feed vents that generated the Cyprus-type Cu–Fe ± Zn sulfide deposits and associated ferruginous sediments (Constantinou and Govett, 1972; Friedrich et al., 1984). Along with spilitization, hydrothermal alteration has resulted in a range of secondary minerals including chlorite, carbonates and zeolites. REE and Sr isotope patterns of secondary minerals in these deposits demonstrate a predominantly seawater source involving incorporation of the REEs with strong positive Ce anomalies into poorly crystalline Fe–Mn oxyhydroxides and associated umbers including some amorphous high-Mn material (Robertson, 1975; Robertson and Fleet, 1976; Chapman and Spooner, 1977; E. Morisseau, unpublished data). Groundmass-replacing minerals such as chlorite typically have a similar REE composition to the original host mafic rocks (Gillis et al., 1992). Glasses in the host rocks have relatively low REE abundances, LREE depletion and a flat HREE profile typical of calcalkaline and tholeiitic basalts (Thy et al., 1985; Rautenschlein et al., 1985). The composition of umbers and other ferruginous sediments that overly the pillow basalts have elevated REEs and low Mn, relative to the underlying basalts, with normalised patterns suggesting deposition in an oxygen-poor marine environment (Robertson, 1978). Various geochemical and petrological indications of penetrative hydrothermal alteration have been identified throughout much of the TO, especially in the upper parts of the complex (Spooner, 1977).

Subsequent obduction of the TO coincided with deposition of marine carbonates and subordinate siliciclastics in progressively shallowing sedimentary basins on the TO flanks, forming the Circum-Troodos Sedimentary Sequence (CTSS). The principal CTSS units are the deep marine (2000–3000 m) Lefkara Formation that is mainly composed of pelagic marls and chalks, and the unconformably overlying shallow marine Pakhna Formation containing reefal limestones, hemi-pelagic marls and chalks (Eaton and Robertson, 1993; Kähler and Stow, 1998). The Pakhna Formation was deposited during a period of more rapid tectonic uplift of the TO, resulting in a higher detrital component from the TO than in the Lefkara Formation. Sea levels in the Mediterranean dropped rapidly in the late Miocene leading to the Messinian “salinity crisis” (Rouchy et al., 2001), exposing both sediments and the TO sub-aerially, allowing formation of palaeosols. The subsequent Pliocene marine transgression resulted in deposition of sediments in more oxygenated marine waters than the Pakhna Formation (di Stefano et al., 1999). A component of clastic sediments containing TO-derived materials, was deposited in these marine basins on the northern and southern flanks of the TO and may represent different seismogenic events in the uplift and erosional history of the TO (Lord et al., 2009). The CTSS sedimentary facies stratigraphy is summarised in Fig. 2 (Malpas et al., 1992). Large volumes of erosional products were transported

Download English Version:

<https://daneshyari.com/en/article/4435705>

Download Persian Version:

<https://daneshyari.com/article/4435705>

[Daneshyari.com](https://daneshyari.com)