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Ce, La and Y concentrations in agricultural and grazing-land soils of Europe

Martiya Sadeghi [a,*], Paola Petrosino [b], Anna Ladenberger [a], Stefano Albanese [b], Madelen Andersson [a], George Morris [a], Annamaria Lima [b], Benedetto De Vivo [b] and The GEMAS Project Team [1]

[a] Geological Survey of Sweden, Uppsala, Sweden
[b] Dipartimento di Scienze della Terra Università di Napoli Federico II, Naples, Italy

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ABSTRACT

Ce, La and Y from agricultural (Ap) and grazing land (Gr) soils of Europe have been investigated using new geochemical data produced by the GEMAS (Geochemical mapping of agricultural and grazing land soils) project. Interpolated maps showing Ce, La, and Y distributions in Ap and Gr were generated using ArcView and classified with the concentration — area (CA) fractal method. The median values of the investigated elements show similar concentrations in Ap and Gr soils, while the median values obtained by XRF-total analyses are generally higher than those obtained by aqua regia extraction, ICP-MS (aqua regia). In general, high pH alkaline soils have higher REE concentrations while specific anomalies can often be correlated with known phosphate and REE mineralizations. The GEMAS and the topsoils media from the FOREGS (Forum of European Geological Surveys) Project databases are compared. FOREGS geochemical data shows larger extended anomalies, such as the European wide north–south division, which are difficult to attribute to local processes, while the GEMAS anomalies are spatially more restricted, and can be related to a number of more local factors (e.g., climate, geology, pH, clay content and presence of till).

1. Introduction

GEMAS is a collaboration project between the Geochemistry Expert Group of EuroGeoSurveys (EGS) and Eurometaux (European Association of Metals) (Reimann et al., 2012a,b). The main goal of the GEMAS project is to produce an internally consistent set of soil geochemistry data at the European scale based on REACH (EC, 2006) requirements. More information concerning the methodology, the collection and the preparation of samples can be found in Reimann et al. (2009, 2012a) and EGS (2008). REE data from the FOREGS (Geochemical baseline mapping data base) database has previously been investigated at a national and European scale (Salminen et al., 2005a,b; Salpeteur et al., 2005; Sandström et al., 2005; Tarvainen et al., 2005). Fedele et al. (2008) investigated anthrophogenic sources of REEs in Europe while Petrosino et al., 2013-this issue compared the REE concentrations in Sweden and Italy, and Sadeghi et al., 2013-this issue investigated the REE distribution compared with mineralization in Sweden.

REEs show similar chemical and physical properties and represent a geochemically coherent group (Hu et al., 2006). REEs show an affinity for oxygen and are found in concentrated form in phosphorites and in argillaceous sediments. REEs in soils generally originate from locally derived geological parent materials (Liu, 1988), however the use of fertilizers is also an important entry path for REEs into soils. The solubility of REEs in water varies based on the host mineral. The exchangeable REE content in soils also varies between trace and concentrations of up to 24 mg/kg (Hu et al., 2006). Ca-minerals, particularly igneous rock-forming minerals such as hornblende, augite, apatite, and fluorite, can bind most REEs during magmatic and hydrolisation processes (Liu, 1988). Considerable amounts of REEs in soils exist in the form of carbonates. Some researchers (e.g., Zhu and Xing, 1992) therefore suggest that carbonate-bound REEs should be classified as an independent REE form within soils. Many factors play a role in the REE concentrations in soil, e.g. adsorption and desorption processes, physical and chemical characteristics of the soils (Ran and Liu, 1993), pH (Dong et al., 2001), presence of organic material (Beckwith and Bulter, 1993), and timing for establishment of an equilibrium of desorption (Li et al., 2000).

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* Corresponding author at: Geological Survey of Sweden, Villavägen 18, PO Box 670, SE 751 28, Uppsala, Sweden. Tel.: +46 18 179232; fax: +46 18 179210.
E-mail address: martiya.sadeghi@sgu.se (M. Sadeghi).

[1] A. Arnoldussen, R. Baritz,M.J. Batista, A. Bel-lan,M. Birke, D. Cicchella, A. Demetriades, E. Dinelli, W. De Vos, M. Duris, A. Dusza-Dobek, O.A.Eggen, M. Eklund, V. Ernstsen, P. Filzmoser, T.E. Finne, D. Flight, S. Forrester, M. Fuchs, U.Fugedi, A. Gilucis, M. Gosar, V. Gregorauskiene, A. Gulan, J. Halamić, E. Haslinger, P. Hayoz, G. Hobiger, R. Hoffmann, J. Hoogewerff, H. Hrvatovic, S. Husnjak, L. Janik, C.C. Johnson, G.Jordan, J. Kirby, J. Kivisilla, V. Klos, F. Krone, P. Kwecko, L. Kuti, J. Locutura, P. Lucivjansky, D.Mackovych, B.I. Malyuk, R.Maquil,M. McLaughlin, R.G.Meuli,N. Miosic, G. Mol, P. Négrel, P. O'Connor, K. Oorts, R.T. Ottesen, A. Pasieczna, V. Petersell,S. Pfleiderer,M. Poňavič, C. Prazeres, U. Rauch, C. Reimann, I. Salpeteur, A. Schedl, A. Scheib,I. Schoeters, P. Sefcik, E. Sellersjö, F. Skopljak, I. Slaninka, A. Šorša, R. Srvkota, T. Stafilov, T. Tarvainen, V. Trendavilov, P. Valera, V. Verougstraete, D. Vidojević, A.M. Zissimos, Z. Zomeni.

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There are several potential anthropogenic sources of REEs in the environment including acid mine drainage (Haxel et al., 2002; Protano and Riccobono, 2002), contamination from nuclear reactors and their waste streams (Brookins, 1984; Rard, 1988), and REE-doped zeolites which have been used as fluid-cracking catalysts in the petroleum industry since the 1960s (Pines, 1981) and have subsequently been detected in offshore sediments (Olmez et al., 1991). The increasing use of REEs in industrial processes suggests that REE release into the environment is likely to increase in the future with potential impacts on human health (Haley, 1991; Hirano and Suzuki, 1996). In the GEMAS project only the REEs Ce and La were analyzed, therefore, in this paper, we focus on these two elements and on Y which, while not a REE itself, follows the heavy REEs chemically and can therefore be used as an analog for those elements (McLennan, 1989).

Cerium (Ce), atomic number 58, is the lightest and the most abundant of the REEs, and forms several minerals including monazite, xenotime, bastnäsite and cerite. Cerium, generally found in the trivalent state, differs from other REEs because, under highly oxidizing conditions, it can also occur as Ce^{4+}, leading to a 15% size reduction and to a smaller solid-state ionic radius. The relationship between Ce^{+3}/Ce^{+4} is useful for understanding marine and surficial redox geochemistry. Accessory minerals such as allanite, apatite, zircon and sphene are important in the enrichment of Ce in igneous rocks. The crustal average for Ce is 60 mg/kg, with a lesser content in mafic rocks (average 30 mg/kg) then in granite, where it can reach 8230 mg/kg (Mason and Moore, 1982). The abundance of Ce in soils varies from 15.8 to 97.4 mg/kg, with a mean of 48.7 mg/kg. Kabata-Pendias (2001) mentioned that soils developed on calcareous parent rocks show a comparative enrichment in REEs.

Lanthanum (La), atomic number of 57, usually occurs with an oxidation state of +3. It is the largest of the trivalent REEs. Lanthanum is a lithophile element under most conditions and forms several minerals, including monazite, which is relatively common, and cerite; it is also widely dispersed in trace quantities in most rocks and minerals (e.g., biotite, apatite, pyroxene and feldspar). Lanthanum levels in igneous rocks vary depending on the rock type (e.g. basalt up to 15 mg/kg, granite 45–55 mg/kg, giving an average crustal abundant of 37 mg/kg). The behavior of La during metamorphism is not well understood, however partial melting is known to contribute to La enrichment in the lighter minerals/leucosome during migmatization. High La values are generally found in felsic rocks, especially intrusives, and in the soils derived from them. In soils derived from sedimentary rocks, La concentration closely corresponds to that of the parental rock, with the exception of limestones, where the soil is enriched with respect to the parent rocks (Wedepohl, 1995).

Yttrium (Y) belongs to the group 3 of the periodic table, which also includes Sc, Lanthanides and Actinides. The element has an atomic number of 39 and occurs with an oxidation state of +3. Under most conditions Y is lithophile. Chemically, it resembles the heavier REEs. The major importance of Y in geochemistry is that it has a geochemical behavior intermediate between that of the smaller REE lanthanide elements dysprosium (Dy) and holmium (Ho) (McLennan, 1989) and therefore provides a good proxy for the heavy REEs. It is strongly partitioned into garnet, hornblende, clinopyroxene and biotite, but also shows a slight enrichment in granitic rocks (ca. 40 mg/kg) relative to intermediate (ca. 35 mg/kg) and basaltic (ca. 32 mg/kg) igneous rocks. Yttrium concentration in basalt is sensitive to the degree of partial melting involved in the formation of the magma (Wedepohl, 1978, 1995). Low Y concentrations may occur in calc-alkaline magmas as a result of the stabilization of phases rich in heavy REEs in the source region, and/or of their removal from the magmas during fractional crystallization. Elevated Y values are generally found in felsic rocks, especially intrusive, and in the soils and stream sediments derived from them. There is little information about the behavior of Y in the soils (Kabata-Pendias, 2001) but the average value of Y concentration is 23 mg/kg and 15 mg/kg in uncultivated and cultivated soils, respectively.

The main aim of this paper is to illustrate the distribution of La, Ce and Y in European agricultural (Ap) and grazing (Gr) soils, using the GEMAS database, to identify patterns that can be related to bedrock geology and mineralisation, and to compare our results with those obtained on topsoils medias by the FOREGS European Project.

2. REE mineralizations in Europe

A number of maps and papers covering different themes within the study area of the GEMAS project (e.g., geology, structure and fracture zones, distribution of different rock types, topography, and distribution of main sedimentary basin and soil of Europe) can be found in Reimann and Birke (2010), Asch (2003) and Jones et al. (2005).

Since 2003, the Geological Surveys of Finland, Norway, Russia and Sweden have carried out a joint project on the metallogeny of Fennoscandia (FODD project) (Eilu, 2011) compiling significant information gathered from mining and exploration company reports. In 2009 the ProMine project started. This project has been the European commission's principal project in the field of exploration and efficient use of mineral resources within Europe. The project has been carried out by 30 partners from 11 EU countries. The mineral resources map for the whole of Europe is downloadable from the ProMine portal (Promine.gtk.fi). All mineralizations from the ProMine and FODD databases where REEs and phosphates are the main commodities were extracted. Fig. 1 shows the distribution of volcanic and plutonic rocks of Europe extracted from IUGS digital map (Pawlewicz et al., 2002) and the location of known REE and phosphate ore deposits within GEMAS project study.

Visually there is a very good spatial association between anomalies based on GEMAS interpolated maps and distribution of granitoids/felsic alkalic volcanic rocks. In general the interpolated maps from GEMAS data (e.g. in Scandinavia, Italy, Spain, UK etc.) show good spatial association between REEs distribution and phosphate mineralization.

3. Results and discussion

3.1. Distribution of Ce, La and Y in Europe

Elemental concentrations in Ap and Gr media were obtained by partial leaching of sample in aqua regia followed byanalysis of the leachate by ICP-MS (hereafter denoted aqua regia), and by whole sample analysis by XRF (denoted *XRF-total*). Basic statistical parameters for La, Ce and Y are presented in Table 1. Figs. 2–4 show interpolated geochemical maps produced with Arcview GIS software using the inverse distance weighted (IDW) algorithm to generate a regular grid with a 6×6 km cell size and a circular window with fixed radius of 150 km. Color intervals were assigned using the fractal CA model (fractal concentration-area model) available in GeoDAS (Cheng et al., 2001) in order to avoid excessive data smoothing and preserve the original data distribution (Lima et al., 2003, 2008). Since the distribution patterns of La, Ce and Y for Ap and Gr European soils are quite similar, only maps for Ap soils analyzed by aqua regia (Table 1) are given (Figs. 2–4). Of particular note, the spatial distribution of Ce, La and Y between northern and southern Europe are significantly different, reflecting both geological and climate variations. In the northern part of Europe, north from the last glacial maximum, Ce, La, and Y concentrations are generally low except for on the Scandinavia peninsula. In the latter area the distribution of high Ce, La and Y concentrations reflects either exposed crystalline rocks (e.g., in northern Sweden) or marine, clay rich sediments (e.g., in central Sweden and southern Finland). As shown in Fig. 5, in Norway, Sweden and Finland, Ap soils tend to display higher median values of Ce, La, and Y than Gr soils. This is thought to be related to differences in pH between none plowed grassland (lower pH) and arable soils (more alkaline pH). All REEs are more concentrated in alkaline than in acid soils, hence soils developed on calcareous rocks have a comparative enrichment of REEs,