Journal of Geochemical Exploration 154 (2015) 81–93

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

GEMAS: Cobalt, Cr, Cu and Ni distribution in agricultural and grazing land soil of Europe

Stefano Albanese [a,*], Martiya Sadeghi [b], Annamaria Lima [a], Domenico Cicchella [c], Enrico Dinelli [d], Paolo Valera [e], Marco Falconi [f], Alecos Demetriades [g], Benedetto De Vivo [a], The GEMAS Project Team [1]

[a] Dipartimento di Scienze della Terra, dell'Ambiente e delle Risorse, Università di Napoli Federico II, Naples, Italy
[b] Geological Survey of Sweden, Uppsala, Sweden
[c] Department of Science and Technology, University of Sannio, Benevento, Italy
[d] Department of Biological, Geological and Environmental Sciences, University of Bologna, Bologna, Italy
[e] Dipartimento di Geoingegneria e Tecnologie Ambientali, University of Cagliari. Piazza d'Armi, 09123, Cagliari, Italy
[f] Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA), Roma, Italy
[g] Institute of Geology and Mineral Exploration, Acharnae, Athens, Hellas

ARTICLE INFO

Article history:
Received 18 June 2014
Revised 10 January 2015
Accepted 19 January 2015
Available online 26 January 2015

Keywords:
European soil
Mafic–ultramafic rocks
Metals
Geochemical mapping
Soil guidelines

ABSTRACT

In the framework of the GEMAS project, 2211 samples of agricultural soil (Ap, 0–20 cm, regularly ploughed fields), and 2118 samples from land under permanent grass cover (Gr, 0–10 cm, grazing land soil) were collected across almost the whole European continent, at a density of 1 sample site/2500 km^2, in accordance with a common sampling protocol.

Among many other elements, the concentrations of Co, Cr, Cu and Ni in European soil were determined by ICP-MS after a hot aqua extraction, and WD-XRFS analytical methods, and their spatial distribution patterns generated by means of a GIS software.

The presence of mafic and ultramafic rocks, ophiolite complexes and mineralisation, is widespread across the European continent, and seems to explain most of the variability of the elements studied in this paper. A large belt, north of the last glaciation maximum limit, is generally dominated by lower concentrations compared with central European and Mediterranean areas and to some areas in Northern Europe where higher Co, Cr, Cu and Ni values also occur.

The application of the guideline value set for Cu and Ni by the EU Directive 86/278/EEC to the Ap soil samples of the GEMAS data set highlighted that at the continental scale the use of a unique reference interval is a tool of limited effectiveness; the lithological variation, occurring across a whole continent, generates changes in the geochemistry of soil, which cannot be accommodated by using a single reference interval even if it is very wide. The GEMAS data set should form the sound basis to set at the European scale the geochemical background reference intervals, at least, for regions sharing common lithological settings and a common geological history.

1. Introduction

1.1. Framework

The first attempt to generate a harmonised geochemical database at the European scale was successfully completed in 2006 with the publication of the two-volume FOREGS Geochemical Atlas of Europe (De Vos, Tarvainen et al., 2006; Salminen et al., 2005). Samples of stream water, stream sediment, topsoil, subsoil, floodplain sediment and humus from approximately 800 drainage basins, identified on the Global Reference Network within Europe (Darnley et al., 1995), were collected, using standardised field sampling methods (Salminen et al.,

---

[*] Corresponding author.
E-mail address: stefano.albanese@unina.it (S. Albanese).

[1] The GEMAS Project Team, M. Andersson, R. Baritz, M.J. Batista, A. Bel-lan, M. Birke, W. De Vos, M. Ďuriš, A. Dusza-Dobek, O.A. Eggen, M. Eklund, V. Ernstsen, P. Filzmoser, D.M.A. Flight, S. Forrester, M. Fuchs, U. Fügedi, A. Gilucis, M. Gosar, V. Gregorauskiene, W. De Groot, A. Gulan, J. Halamić, E. Haslinger, P. Hayoz, R. Hoffmann, J. Hoogewerff, H. Hrvatovic, S. Husnjak, L. Janik, G. Jordan, M. Kaminari, J. Kirby, V. Klos, F. Krone, P. Kwecko, L. Kuti, A. Ladenberger, J. Locutura, P. Lucivjansky, A. Mann, D. Mackovych, M. McLaughlin, B.I. Malyuk, R. Maquil, R.G. Meuli, G. Mol, P. Négrel, P. O'Connor, K. Oorts, R.T. Ottesen, A. Pasieczna, V. Petersell, S. Pfleiderer, M. Poňavič, C. Prazeres, U. Rauch, S. Radusinović, C. Reimann, I. Salpeteur, R. Scanlon, A. Schedl, A. Scheib, I. Schoeters, E. Sellersjö, I. Slaninka, J.M. Soriano-Disla, A. Šorša, R. Svrkota, T. Stafilov, T. Tarvainen, V. Trendavilov, V. Verougstraete, D. Vidojević, Z. Zomeni.

http://dx.doi.org/10.1016/j.gexplo.2015.01.004

1998), and the distribution of more than 50 elements was mapped across the whole Europe by means of 360 geochemical maps (De Vos, Tarvainen et al., 2006; Salminen et al., 2005).

As a follow-up activity, especially focused on productive soil, the Geochemical Mapping of Agricultural and Grazing Land Soil (GEMAS) project was established in 2008 as a joint project of the Geochemistry Expert Group of EuroGeoSurveys and Eurometaux (European Association of Metals). The project aimed at providing harmonised geochemical background data according to the specifications of the new European Chemicals Regulation, known as REACH (Registration, Evaluation and Authorisation of Chemicals; EC, 2006), making the industry responsible for assessing and managing the risks posed by chemicals, and for providing appropriate safety information to their users. In the framework of the GEMAS project, 2211 samples of agricultural soil (Ap, 0–20 cm, regularly ploughed fields), and 2118 samples from land under permanent grass cover (Gr, 0–10 cm, grazing land soil) were collected across almost the whole European continent, at a density of 1 sample site/2500 km^2, in accordance with a common agreed sampling protocol (EuroGeoSurveys Geochemistry Working Group, 2009).

The main aim of this paper is to describe and discuss the statistical and spatial distribution patterns of Co, Cr, Cu and Ni in European agricultural (Ap) and grazing land (Gr) soil from the GEMAS project (Reimann et al., 2014a,b).

1.2. Nature and sources of Co, Cr, Cu, Ni in the environment

Cobalt, Cr, Cu and Ni are transition metals, and belong to Periodic Table groups 9, 6, 11 and 10, respectively.

Cobalt is commonly found in association with Ni, and they are both characteristic components of iron meteorites. The oxidation states that Co may take +2, +3, and (rarely) +1. Natural Co is composed of one stable isotope, ^{59}Co. This element is found in minerals, such as erythrite [$Co_3(AsO_4)_2 \cdot (8H_2O)$], glaucodot [$(Co_{0.50}Fe_{0.50})AsS$] and skutterudite ($CoAs_{3-x}$), as well as substituting into pyrite (FeS_2). It is mainly produced as a by-product of Cu or Ni smelting (Shedd, 2013). Its association with Cr and Ni could be considered a marker of the presence of mafic rocks, where it is generally enriched (Albrecht, 1999; Fairbridge, 1972; Levinson, 1980; Rose et al., 1979; Wedepohl, 1978). Mielke (1979) reports an average Co abundance of 150 and 48 mg/kg in ultramafic rocks and basalt, respectively. A more recent estimate for continental basalt by Farmer (2014), Co varies from 29.9 to 197 mg/kg.

After weathering, Co is most mobile in the surface environment under acidic and reducing conditions; it co-precipitates under oxidising, near-neutral or alkaline conditions as Fe and Mn secondary oxides (Taylor, 1968). Humic and fulvic acids and inorganic colloids could reduce Co mobility in soil while some bacteria are known to mobilise Co from metal chelates (De Vos, Tarvainen et al., 2006 and references therein).

In Europe, according to the ProMine database (available at www.promine.gtk.fi; Cassard et al., 2012; Demetriades and Reimann, 2014) (Fig. 1), Co occurs as the main commodity of the surveyed mineralisation in deposits that are found mainly in Fennoscandia (mostly in Finland), in western and southern Spain and in Germany.

The main industrial application of Co is in alloys with Fe, Ni and other metals to produce both corrosion-resistant products (designed for high temperature applications) and high abrasion-resistant steels. Because of its unique blue colour, Co oxide is used worldwide as an additive in paint, glass and ceramics. Other anthropic sources of Co in the environment include coal combustion, fertilisers, Pb, Fe and Ag mining and processing (Reimann and de Caritat, 1998).

Chromium is characterised by two main oxidation states (+3 and +6) and its most abundant natural isotope is ^{52}Cr, representing 84% of its total mass. It is mainly found in nature in the form of chromite ($FeCr_2O_4$), and also occurs in the rare mineral crocoite ($PbCrO_4$), as well as an accessory element in several other minerals, such as spinel, amphibole, mica, pyroxene and garnet. Mielke (1979) reports an average abundance of 1600 and 170 mg/kg for ultramafic rocks and basalt, respectively; Farmer (2014) gives for continental basalt an average Cr concentration between 39 and 1082 mg/kg. At high concentrations Cr, as well as in association with Co and Ni in mafic and ultramafic rocks (as stated above), could be found in laterite and in clays and oxides produced by the weathering and erosion of igneous sedimentary rocks bringing minerals of the spinel group as a detrital phase; while at low concentrations and in association with a high content of U, Th, K and REEs, it could be considered a marker for felsic rock (De Vos, Tarvainen et al., 2006).

Chromium mobility is very low under moderately oxidising or reducing and neutral acidic conditions and it is influenced by organic matter. Acidity influences the adsorption of Cr species to clay since, at increasing pH, the adsorption of Cr^{6+} decreases and of Cr^{3+} increases. At increasing pH, the presence of organic matter can play a reducing action on Cr^{6+} that converts it into the more stable Cr^{3+}. Trivalent chromium co-precipitates with Fe^{3+} as insoluble $Cr(OH)_3$ at high pH values (De Vos, Tarvainen et al., 2006 and references therein).

Approximately half of the chromite mined in the world comes from South Africa. In Europe (Fig. 1), economic mineral deposits of Cr occur mainly in Hellas (Greece), the Balkans, Finland and Austria. Albania and Finland are the main European Cr producers (Reichl et al., 2013, 2014).

Chromium is a major component of steel alloys (10–26%), and is used in metallurgy for coating to impart corrosion resistance and gloss finish to steel, and to anodise aluminium used by the aircraft and other industries. Other applications include its use in the production of refractory bricks, the glass industry to impart an emerald green colour; Pb chromate as a pigment and its salts are widely used in leather tanning and as mordants for dyeing fabrics. In the past, hexavalent Cr was used in wood-treatment.

Copper has two main oxidation states (+1 and +2) and two naturally occurring isotopes (^{63}Cu and ^{65}Cu), with abundances of 69.17% and 0.83% of its total mass, respectively. Unlike Co and Cr, Cu can be found in nature both in minerals, such as chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4), covellite (CuS), digenite (Cu_9S_5), tetrahedrite [$Cu_6(Cu_4(Fe,Zn)_2)Sb_4S_{13}$], and in its metallic (native) form as nuggets. It is also incorporated into common minerals, such as olivine, magnetite, pyroxene, amphibole and biotite. Copper shows a good affinity for mafic rocks and their metamorphic equivalents, and it is widely dispersed in silicate minerals, such as olivine, pyroxene, amphibole, biotite and plagioclase (Ure and Berrow, 1982). Most of the Cu sulphide mineralisation types (e.g., hydrothermal or skarn deposits) are typically featured by a high chalcopyrite content with metallic Cu mostly enriched in the supergene zones above the oxidising deposits. Mafic (40–60 mg/kg) and ultramafic (40 mg/kg) rocks contain more Cu than intermediate (ca. 20 mg/kg) and granitic (ca. 12 mg/kg) rocks (Wedepohl, 1978), and Farmer (2014) estimated the average abundance for continental basalt to vary between 32.9 and 266 mg/kg. In non-mineralised sediments, Cu concentrations are principally determined by mafic detritus, secondary Fe and Mn oxides (Forbes et al., 1976), clay minerals (Heydemann, 1959) and organic matter (Stevenson and Ardakani, 1972). Fine-grained clastic rocks, particularly black shale, are typically enriched in Cu (ca. 50 mg/kg) relative to quartzo-feldspathic and carbonate sediments (5–15 mg/kg).

In the surface environment, after weathering, Cu is mobile under oxidising and slightly acidic conditions, mostly at pH values between 5 and 6. Copper shows a good affinity for natural organic matter. In the presence of Fe hydrous oxides, Cu can also co-precipitate together with Zn (De Vos, Tarvainen et al., 2006 and references therein).

Copper mineralisation and deposits are widespread across the whole Europe (Fig. 1), and one of the world's highest capacity mining centres is located in Kupferschiefer of Lower Silesia of south-eastern Poland (e.g., Rudna, Lubina and Polkowice–Sieroszowice mines) (Reichl et al., 2013, 2014).

Copper is used in building construction (roofing, plumbing), electric and electronic products, power generation and transmission, industrial