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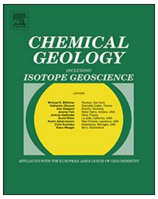

Distribution of Rb, Ga and Cs in agricultural land soils at European continental scale (GEMAS): Implications for weathering conditions and provenance

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ABSTRACT

Agricultural soil (Ap-horizon, 0–20 cm) samples were collected from a large part of Europe (33 countries, 5.6 million km^2) as part of the GEMAS (GEochemical Mapping of Agricultural and grazing land Soil) soil mapping project. The soil data have been used to provide a general view of element mobility and source rocks at the continental scale, either by reference to average crustal abundances or to normalised patterns of element mobility during weathering processes. The survey area includes a diverse group of soil parent materials with varying geological history, a wide range of climate zones, and landscapes.

Total concentrations of Rb, Ga, and Cs in European soil were determined by XRF (X-ray fluorescence spectrometry). In addition, hot aqua regia available element concentrations were analysed by inductively coupled plasma-mass spectrometry ICP-MS. Their spatial distribution patterns are shown in geochemical maps. The spatial distribution of Rb, Ga and Cs in Ap soil is quite comparable for the aqua regia and XRF results. The Cs spatial pattern reflects best the large difference between trace element concentrations in northern Europe with predominantly low concentrations and southern Europe with approximately two times higher values. The maximum extent of the last glaciation is visible as a clear concentration break on the map. Lithology of the underlying bedrock is inferred as the major source of geochemical anomalies. In search for characterising the soil parent material and degree of weathering, the soil data were examined for Ga and Cs using two methods. First, the estimated degree of extractability DE*i* of an element in a sample was calculated by dividing aqua regia available concentrations by the total concentrations obtained by XRF analysis for Al, Na, Ca, K, Rb, Ga and Cs. The different DE*i* were investigated for 10 geological parent material subgroups (alkaline rocks, granite, calcareous rocks, basalt-mafic rocks, unclassified lithologies, Precambrian granitic gneiss bedrocks, loess, organic soils, schist and soil developed on coarse-grained sandy deposits). The role of clay as main carrier of Ga and Cs phases was inferred for soils developed on several types of bedrock such as granite, gneiss and alkaline rocks. Additionally, an affinity of Cs for loess and carbonate rocks has been observed.

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1. Introduction

Gallium-aluminium and potassium-rubidium are two geochemically-related pairs of elements which follow each other either during crustal evolution or weathering (Horstman, 1957; De Argollo and Schilling, 1978). The coherence of the behavior between these pairs of elements is due to the similarity in ionic radius, valence and ionisation potential (Goldschmidt, 1954). Aluminium plays an important role in weathering/reverse weathering processes and potassium is one of the tracers of silicate weathering of felsic and mafic lithologies (granite and basalt, Horstman, 1957; Takeda et al., 2004) and therefore Rb and Ga can be used as possible analogues of the two major ions K and Al. Furthermore, Rb and Ga are elements interacting with clays similarly as caesium. Caesium has similar chemical properties to potassium, both playing an important role in weathering processes and clay formation (Tanaka and Watanabe, 2015). Therefore, all three trace elements can be used in investigations of clay distribution at the continental scale (Takeda et al., 2004; Zaunbrecher et al., 2015).

More specifically, Rb is an alkali metal and it is the 20th most abundant element in the Earth's upper continental crust (UCC) with an estimated abundance of 94 mg/kg (Rudnick and Gao, 2003; Hu and Gao, 2008). The Rb geochemistry is very closely related to that of potassium. Rubidium does not form its own minerals but, due to similarity of the ionic radii, can substitute for K in mica and K-feldspar, as well as in rarer minerals, like lepidolite or carnallite. Ultramafic (2 mg/kg) and mafic (8–30 mg/kg) rocks have low concentrations of Rb, as does limestone (4 mg/kg), while felsic igneous rocks e.g. granite and pegmatite has usually high Rb concentrations (e.g. 120 mg/kg in granite). Among sedimentary rocks, shale and its metamorphic equivalent - schist may also be enriched in Rb (140 mg/kg) (Goldschmidt, 1954). Pervasive redistribution of Rb has been reported during hydrothermal alteration of plutonic rocks (e.g., O'Brien et al., 1985). Rubidium is associated with greisen type Sn-deposits, and is found enriched in most ore zones of porphyry copper type deposits. Due to its strong sorption to clay minerals Rb's mobility in the secondary environment is generally very low. It is generally assumed that rubidium, after being dissolved during weathering, is adsorbed more strongly by the clay fraction of soils than potassium (Goldschmidt, 1954; Wampler et al., 2012). Rubidium has very few applications and is mostly used in research, photocells and some pharmaceuticals (e.g., as an antidepressant like Li). Glass dust could be one possible source of Rb transfer to the environment. Rubidium is considered to be non-essential and non-toxic; it is easily taken up together with K being its associated trace element.

The second considered element gallium is a trace element occurring in the upper continental crust with an estimated abundance of 19 mg/kg (Hu and Gao, 2008). Gallium forms several rare minerals including sulphides (e.g. gallite, $CuGaS_2$) and hydroxides. However, the most typical occurrence of Ga is as trace element in common rock-forming minerals, such as feldspar, amphibole, mica and magnetite, where it usually substitutes for Al. Gallium is preferentially concentrated in muscovite and in biotite rather than K-feldspar and plagioclase is two to three times richer in Ga than K-feldspar, (Shaw, 1957; Wedepohl, 1978). Rocks contain between 0.5 and 20 mg/kg of Ga, with shale and schist usually showing the highest Ga concentrations, and limestone and ultramafic rocks the lowest (Goldschmidt, 1954; Shaw, 1957; Hu and Gao, 2008). During hydrothermal processes, Ga is mainly concentrated in sulphides (e.g. in sphalerite), while under low temperature Ga becomes more lithophile and can be, for example, bound in phyllosilicates such as chlorite and other clay minerals forming in the argilitic zone of alteration (Wedepohl, 1978; Butcher and Brown, 2014). The mobility of Ga is rather low and is closely linked to the behavior of Al (Goldschmidt, 1954; Shiller and Frilot, 1996). The presence of gallium in soil is positively correlated with the amount of clay minerals and organic matter and controlled by Fe and Mn oxides precipitation (Połedniok, 2008). Considering its rather high abundance in the crust (almost two times higher than lead), the geochemical behaviour of gallium is still poorly known. Gallium is produced as a by-product of Al (bauxite) and Zn (sphalerite) ore processing and smelters are thus possible sources of Ga emissions. Fly ash from coal combustion and waste incineration is another source of anthropogenic gallium (Font et al., 2007). In the future, the main source of anthropogenic gallium might originate from an increasing use of liquid crystal display LCDs and light-emitting diode LEDs (Butcher and Brown, 2014). Gallium is classified as a critical metal and as such its geochemical behaviour and spatial distribution in Europe is of high importance in assessments of the mineral/resource potential and for environmental purposes.

Caesium, the third trace element discussed here is a relatively heavy (nearly twice as heavy as Ga) alkali metal with comparable chemical properties to Rb and Tl and an estimated abundance in the upper continental crust of 5 mg/kg (Hu and Gao, 2008). Caesium forms some very rare minerals (e.g., pollucite) and often substitutes for K in mica (especially in muscovite and lepidolite) and in K-feldspar and is enriched in felsic rocks during magmatic fractionation, with pegmatites showing the highest Cs levels (Heier and Billings, 1970; Wedepohl, 1978). An average Cs content in granite is 4 mg/kg, mafic and ultramafic rocks have much lower Cs concentrations (ca 0.8 and 0.05 mg/kg, respectively). Due to its high volatility, Cs has a tendency to concentrate in late stages of magmatic differentiation and in sublimates of K-rich volcanic rocks in active volcanic regions. Among sedimentary rocks, caesium concentrations range from low in limestone (0.5 mg/kg) and sandstone (1 mg/kg) to high Cs levels in shale and schist (5 mg/kg). Concerning weathering in a silicate environment, most Cs initially present in the parent rock is transferred to the weathering residuum, similarly as Rb, and subsequently enriched in the clay fraction (Nesbitt et al., 1980). Thus the mobility of Cs in soil is low, because it strongly adsorbs to clay (Zaunbrecher et al., 2015) and this strong affinity of Cs for the weathering products (i.e., clay minerals) causes a large fractionation of this element during the chemical weathering of rocks (Tanaka and Watanabe, 2015).

The main aim of this paper is to illustrate the distribution of the alkali trace elements Rb, Ga and Cs in European agricultural Ap soil, using the GEMAS database with focus on the results from aqua regia extraction and total concentrations by XRF. This agricultural soil dataset of Europe (Reimann et al., 2012a; Reimann et al., 2014a) provides an excellent base for studying large scale variations related to factors like lithology, climate, topography, soil texture and anthropogenic impact on soils (e.g. Albanese et al., 2015; Ladenberger et al., 2015; Négrel et al., 2015; Ottesen et al., 2013; Reimann et al., 2012a, Reimann et al., 2012c; Sadeghi et al., 2013; Saaltink et al., 2013; Scheib et al., 2012; Tarvainen et al., 2013) with low density sampling, well suited to provide the continental-scale overview of the spatial distribution of chemical elements (Smith and Reimann, 2008).

Here, we provide an overview, of the Rb, Ga and Cs mobility in agricultural soil and their potential source(s) at the continental scale, with special emphasis on the relation to bedrock geology and weathering effects.

2. General setting

The GEMAS project (Reimann et al., 2014a, 2014b) was carried out by the Geochemistry Expert Group of EuroGeoSurveys in cooperation with Eurometaux (European Association of Metals) and managed by the Geological Survey of Norway NGU (Reimann et al., 2012a). It was the second large geochemical mapping survey at the European scale following the FOREGS project (Salminen et al., 1998). Soil samples were collected in 33 European countries, covering an area of 5.6 million km^2 (Reimann et al., 2012a; Reimann et al., 2014a; b). The survey area is shown in Fig. 1. The main objective of the project was to detect and to map the natural element variation at the European scale, the European background. The soil samples were never taken at known contaminated sites, in the immediate vicinity of industry or power plants, cities, a railway line or a major road, directly below high power electric lines or