GEMAS: Geochemical Mapping of Mg in Agricultural Soil of Europe and its Criticality Assessment

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Introduction

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) project (Reimann *et al.*, 2014a, b). The survey area includes a diverse group of soil parent materials with varying geological history, a wide range of climate zones, and landscapes. The chemical composition of soil represents largely the primary mineralogy of the source bedrock, with superimposed effects of the last glaciation, pre- and post-depositional chemical weathering, formation of secondary products such as clays, and element mobility (Négrel *et al.*, 2015), or continental-scale distribution of elements (Reimann *et al.*, 2014a; Ladenberger *et al.*, 2015).

Magnesium is the eighth most abundant element in the Earth's upper continental crust (UCC), with an estimated elemental abundance of 14,955 mg/kg (Rudnick and Gao, 2003). Magnesium is essential for all organisms, not toxic under normal circumstances and is a key plant nutrient and essential for photosynthesis in plants. It is used in industry, for example, in transport (automotive, aircraft, train), consumer electronics (laptop, mobile phone, tablet), steel industry, titanium and zirconium production, pharmaceutical and agricultural chemical production and medical implants. Magnesium may also be a preference material in all light-weight vehicle concepts, hydrogen storage and advanced battery technology. Currently, Mg, as alloying element, is essential for the aluminium industry. The worldwide primary Mg production in 2016 was around 878 Kt, and 85% of global demand was supplied by China. Magnesium's criticality is not based on geographical lack of raw material in Europe, rather on trade issues, since China's low-cost production and export policy made primary production in Europe redundant. The last smelter in Europe was closed in 2001, since European based smelters were unable to compete with low-cost Chinese production, and as a result European primary demand depends mainly on import from China. Worldwide demand is expected to increase in the next decade. In particular, the development of R&D technologies could significantly affect the long-term demand for Mg. The overall results of the 2017 criticality assessment, classified critical raw materials with respect to economic importance versus supply risk, identified 26 raw materials as critical (European Commission, 2017), comprising Mg and elements like Sb, Nb and Ge.

The demand for 'critical' element resources activated all efforts to find new deposits and possibilities to extract them from mines throughout the world. The GEMAS data set offers European scale results for several so-called high-tech elements, and almost all listed on the Critical Raw Materials list by the European Commission (2017). Here, one of the major elements of the UCC, Mg, is used as a test critical element. The geochemical distribution of Mg in agricultural soil of Europe turns out to be a useful starting tool for identifying potential areas for the occurrence of new resources of high-tech elements.

Materials and methods

Agricultural soil samples were collected in 33 European countries at an average density of 1 site per 2500 km^2, covering an area of about 5.6 million km^2 (Reimann *et al.*, 2014a, b). The methods for GEMAS sampling, sample preparation and analysis for major and trace elements were described in detail in Reimann et al. (2014a). Agricultural soil (Ap; 2108 samples) was collected from the ploughing layer of an agricultural arable field at a depth of 0–20 cm. Each sample (ca 3.5 kg) corresponds to a composite of five sub-samples taken from the corners and centre of a 10 × 10 m square. All composite samples were sieved to <2 mm, and milled to less than 63 µm for analysis by wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). A series of project standards and replicates of project samples were used to monitor trueness, repeatability and accuracy, detection limits and QC (Reimann *et al.*, 2011). Samples were also investigated using *aqua regia* and MMI® extraction followed by ICP-MS multi element analysis not showed here.

Results and Discussion

Less than 5% of the 2108 samples of agricultural soil, analysed for Mg by XFR, are lower than the 50 mg/km detection limit. The median for Mg in the Ap samples in Europe is around 5488 mg/kg and the maximum close to 126,638 mg/kg. Compared to the UCC total Mg average, the median Mg concentration, measured by XRF, is substantially lower in the European agricultural soil samples (ratio median Ap/UCC = 0.367); this may suggest a possible overestimation of the UCC value; it may be also an indication of an overall depletion of the important plant nutrient Mg in agricultural soil. The combination plot histogram - density trace one-dimensional scattergram-boxplot (Fig. 2a) shows the Mg univariate data distribution. The one-dimensional scattergram and boxplot highlight the existence of a substantial number of outliers in the Mg distribution. The density trace and histogram are overall symmetrical in the log-scale. Liming and use of Mg fertilisers are the strongest anthropogenic interferences on natural Mg-cycles. Given the major human interference with Mg in agricultural soil, the map of Mg still clearly depicts geological process (Fig 2b). The southern limit of the last glaciation is thus still visible as a concentration break on the map, but the median Mg concentrations between northern and southern Europe are not as contrasted, as for many other elements (Reimann *et al.*, 2014a, b). Basically, areas underlain by limestone (e.g., eastern and southern Spain), dolomite (Alps) and mafic/ultramafic rocks (Hellas, Norway, Finland) appear as large Mg anomalies on the map. The Central Scandinavian Clay Belt is also visible as a Mg anomaly on the map, as well as the occurrence of Mg-silicates in northern Europe.

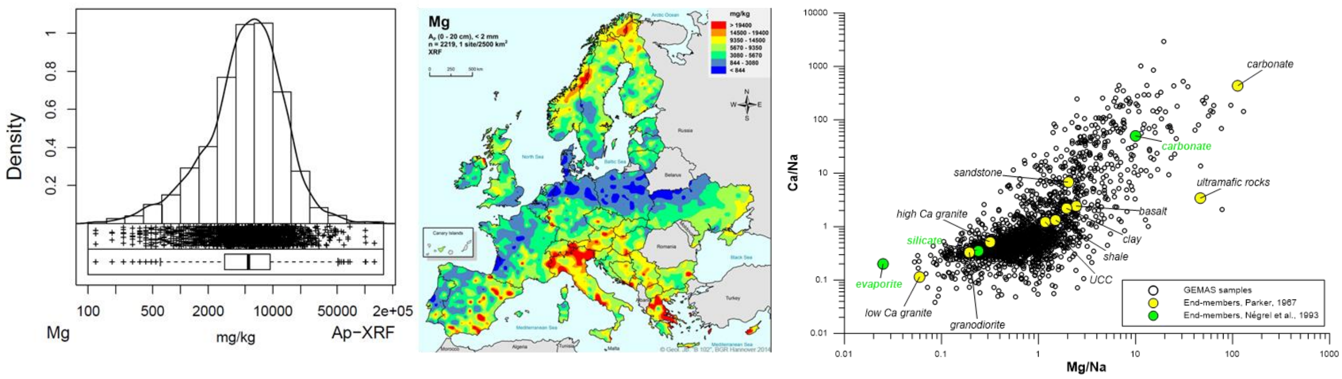

Figure 2. (a) Combination plot of histogram, density trace, one-dimensional scattergram and boxplot of the Mg distribution in European Ap samples following XRF analysis; (b) map of XRF total Mg concentrations; (c) Ca/Na versus Mg/Na ratios in Ap samples, with average values for the main lithological end-members (Parker (1967) for basalt, high and low Ca granite, clay, shale, sandstone, carbonate, ultramafic rocks and granodiorite; Négrel et al. (1993) for silicate, carbonate, evaporite).

Soil chemical composition represents to a large extent the primary mineralogy of the source bedrock, with superimposed effects of glaciation, pre- and post-depositional chemical weathering, formation of secondary products such as clays, and element mobility. Therefore, in soil, Mg, like Al and K, is often retained in weathering profiles, while Na and Ca are rapidly leached as dissolved ions. Comparison of Ca and Mg geochemical pattern, in relation to general Na distribution in soil, allows discrimination between carbonate and silicate parent materials and among various siliciclastic components (low Ca granite, sandstone and ultramafic rocks).

With the knowledge that the most important Mg mineral resources are hosted by ultramafic lithologies and their weathering/alteration products (magnesite), carbonate rocks (dolomite) and chemical deposits (carnallite), GEMAS Mg anomalies can be used to look for potential regions for more detailed Mg exploration.

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