Ge-Ga-Cs in agricultural and grazing land soils at European continental scale
Philippe Négrel, Anna Ladenberger, Clemens Reimann, Manfred Birke, Martiya Sadeghi

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Germanium-silicon and gallium-aluminum are two geochemically-related pairs of elements which follow each other during weathering. The coherence of the behavior between these pairs of elements is due to the similarity in ionic radius, valence and ionization potential. Aluminum plays an important role in weathering/reverse weathering processes and silicon is one of the tracers of silicate weathering of felsic (granite) and mafic lithologies (basalt). Thus, Ge and Ga can be used as possible analogues of the two major ions Si and Al. Furthermore, Ge and Ga are elements interacting with clays similarly as Cs. Caesium has similar chemical properties to potassium, both playing important role in weathering processes and clay formation. Therefore, all three trace elements can be used in investigations of clay distribution at the continental scale.

Agricultural soil (Ap-horizon, 0–20 cm) and grazing land soil (Gr-horizon, 0–10 cm) samples were collected from a large part of Europe (33 countries, 5.6 million km²) as part of the recent GEMAS (GEochemical Mapping of Agricultural and grazing land Soil) soil mapping project. These 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 normalized 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. The concentrations of Ge, Ga, and Cs in European soil were determined by ICP-MS after a hot aqua regia extraction, and their spatial distribution patterns generated by means of a GIS software.

The median values of the investigated elements show similar concentrations in Ap and Gr soils. The spatial distribution in Ap and Gr in land soils is very similar for Ge and Ga whereas Cs shows a strong contrast between 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.

When comparing the maps of many elements investigated in GEMAS, the majority of anomalies in soil is related to underlying lithologies. GEMAS soil data have been examined for Ge, Ga and Cs using the estimate degree of extractability $DE_i$ of an element in a sample by dividing aqua regia content by real total contents, provided by the XRF analysis for Al, Na, Ca, Ga and Cs. The different $DE_i$ have been investigated for the 10 geological parent material subgroups (e.g. alkaline, granite, calcareous, basalt-mafic, unclassified, Precambrian granitic gneiss bedrocks, loess, organic soils, schist and soil developed on coarse-grained sandy deposits). The role of clays minerals as bearing phase for Ga and Cs is evidenced for soils developed on various type of bedrock, and additional Cs affinity for loess and carbonate rocks can also be observed.

Al and Ga have also been used to discriminate provenance sources, taking into account the main lithologies of the upper continental crust UCC. Most soil samples plot between mafic (e.g. basalt) and felsic end members (low concentrations) and felsic end members represented by granites, schist, and clay and the UCC (towards higher concentrations). However, some of the Al and Ga concentrations in soil are lower than any available rock component, which may reflect the weathering effects with Al-Ga host phases resulting from advanced weathering of clay minerals.