



Laser ablation ICP-MS and traditional micromorphological techniques applied to the study of different genetic horizons in thin sections: soil genesis and trace element distribution

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This work focuses on an innovative methodological approach to investigate in situ chemical composition of trace and rare earth (REE) elements in discrete soil features from different soil horizons: laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was applied to clay coatings, pedogenic matrix and skeletal parent rock fragments in thin sections, coupled with traditional pedological investigations, specially clay mineralogy and micromorphology. Analyses were performed on 80 μm -thick sections obtained from undisturbed soil samples, which represent three reddish argillic (Bt) horizons from an Alfisol developed on late Pleistocene slope deposits and three brown organic-mineral (A) horizons from an Entisol formed on Holocene aggrading fluvial sediments in the Muravera area (southeast Sardinia, Italy). Validation of the LA-ICP-MS technique provides in situ accurate and reproducible (RSD 13-18%) analysis of low concentration trace elements in the studied soil samples (0.001-0.1 ppm). Our results showed a high reliability of this method on soil thin sections and revealed that concentrations of trace and rare earth elements in the different portions of a soil profile can be used to investigate their distribution, as a response to soil-forming processes.

A general trend of increase of most trace elements from rock fragments to (both clayey and organic-rich) soil matrix, to clay coatings in argillic horizons is clearly highlighted. On this basis a prominent role of pedogenetic processes in element fractionation and distribution during weathering can be supposed. In particular, element adsorption onto reactive sites of organic matter and clay particles (and possibly Fe-oxyhydroxides) and clay illuviation appear the main pedogenetic processes able to promote element enrichment after their release from the weathering of primary minerals. As clay coatings exhibit the highest concentration of trace elements, and specifically of REEs, and represent the most mobile solid phase in the soil profile, this tool can be used as a reliable indicator of soil weathering after a preliminary assessment of illuvial clay pedofeatures. This feature is consistent with a progressively increasing time of soil development, testified by the older age of the Alfisol than the Entisol profile. Such a result is also supported by a comparison of trace element concentrations between the clay and the fine earth fractions of the bulk soil horizons performed with ICP-MS in solution, showing REE enrichment in the clays from the former soil.

Moreover, trace element patterns show some discontinuous trends among soil features of different horizons, coherently with erosive and/or depositional discontinuities described in the field.