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Chromium and nickel distribution in ultrabasic soils of the Voltri Massif (Ligurian Alps)

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With this work we investigated the mineralogy, the mineral chemistry, and the bulk chemistry of undisturbed soil profiles chosen in an area with tectonic contacts between high pressure metamorphic serpentinites and peridotites of the Voltri Unit "(Bric del Dente Serpentinite" and "Monte Tobbio Peridotite" Formations, Ligurian Alps).

Trace element concentrations were assessed *in situ* and in laboratory by means of field-portable X-ray fluorescence spectrometer and ICP-OES. The mineralogy and the mineral chemistry were determined by optical microscopy, scanning electron microscopy (SEM-EDS), and electron microprobe analyses (WDS). Eh, pH, soil colour, and granulometry were also assessed.

All the studied soil profiles are restricted in depth (10-50 cm from the surface to the coherent parent rocks) and show a low degree of maturity, varying from lithosols, with weakly developed horizons, to rankers. The bedrock shows a decimetric oxidation halo mostly developed around open fractures and joints.

Measured concentrations of chromium and nickel (874-3020 ppm and 1900-3900 ppm, respectively) do not evidenced significant and systematic variation between the unaltered and the weathered bedrock, thus suggesting that the recognized Cr- and Ni-bearing minerals are resistant to weathering in the early steps of supergenic alteration.

The mineral distribution along soil profiles evidenced a significant increase of weathering from the parent rock toward the superficial horizons in all sites. The most weatherable minerals resulted, in order of decreasing alteration degree, olivine, pyroxene, magnetite and serpentine minerals. Conversely, chlorite, plagioclase, and chromites were weakly altered or unaltered. Authigenic secondary minerals were mainly represented by microcrystalline Fe-oxyhydroxides occurring either as replacement of primary minerals or within the clay fraction. Clay minerals are subordinate components and occur mainly toward the upper horizons and in the more evoluted profiles.

The bulk chemistry of the soil profiles evidenced a conservative behaviour of Cr which is strongly correlated with the Cr concentration of the parent rocks. Chromium concentration ranged from 1200 to 2500 ppm without significant variations along the soil profiles. Conversely, the Ni elemental distribution evidenced a high variability and a general increase in the upper horizon (up to 4500 ppm) due to the weathering of the primary Ni-bearing minerals (mainly olivine and serpentine minerals) and to the uptake by the authigenic secondary minerals (mainly Fe-oxyhydroxides and clay minerals).

These results evidenced that all the studied soil profiles have a baseline values of Cr and Ni well above the concentration limits of the Italian laws. Nevertheless, most of these ecotoxic metals are presumably not available for plant uptake because they are present in weathering resistant phases, such as Cr-spinels, or sequestered in stable authigenic minerals (Fe-oxyhydroxides and clay minerals).