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Primary and authigenic minerals in serpentine soils under temperate climate conditions: source or trap for potentially toxic elements (PTEs)

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In this study, we have analysed the mineralogy and the crystal chemistry of serpentine soils from ultramafic rocks of the metaophiolitic Voltri Massif (Liguria, Italy), in order to determine the primary and authigenic mineral species controlling the distribution and the mobility of PTEs during pedogenic processes. These serpentine soils were characterised by PTEs contents commonly exceeding the concentration limits laid down by environmental agencies, particularly for Cr (1200-2500 mg/kg) and Ni (1000-4200 mg/kg). With these hazardous PTEs concentrations, the knowledge of the distribution of PTEs-bearing minerals is of paramount importance for understanding their origin and their fate during the development of serpentine soil profiles and can allow to evaluate their effective bioavailability.

All the studied soil profiles were restricted in depth (10-50 cm) and showed a low degree of maturity with weakly developed A-C horizons. Soil samples were subdivided into three aliquots in order to separate the soil skeleton (2 mm-63 ↔m) from the silt (63-2 ↔m) and clay fraction (<2 ↔m). Quantitative mineralogical analyses were performed in all aliquots by using XRPD data collected with synchrotron sources at the MCX beamline (ELETTRA - Synchrotron, Trieste, Italy) and refined with EXP-GUI GSAS software. Trace metals were determined with energy and wavelength electron microscopy.

The mineralogy of the coarse and silty fractions was closely related to bedrock mineralogy. The following minerals were detected in decreasing order of abundance: antigorite, chlorite, tremolite, magnetite, Cr-rich spinel, chrysotile, ilmenite, clinopyroxenes, olivine. Allochthonous quartz and albite were always present as minor to trace constituents.

The clay fraction was mainly composed by Fe-oxides and -oxyhydroxides (mainly hematite and goethite) with subordinate amounts of mixed-layer clay minerals (chlorite-smectite, chlorite-vermiculite). These authigenic secondary minerals were characterised by poor crystallinity, intimate intergrowths, and fine-scale heterogeneities.

PTEs were hosted mainly in the residual primary minerals deriving from the underlying parent material and subordinately in secondary authigenic phases. Cr was mainly contained within spinels (magnetite, Cr-magnetite, ferrichromite, picotite, and hercynite), antigorite, diopside and augite. Non-negligible amounts of Cr was also present in authigenic hematite (up to 0.1 wt%) and goethite (up to 0.15 wt%). The main Ni-bearing minerals were olivine and antigorite but significant Ni concentration was also detected in authigenic hematite (up to 2.8 wt%) and goethite (up to 4.2 wt%) which thus represented effective traps for Ni leached through mineral weathering to the soils solution.

These results are the preliminary step for the evaluation of the role of mineral species in controlling the PTEs mobility during the evolution of serpentine soil profiles. Quantitative mineralogical data will be further used to perform mass balance calculations as well as to interpret and model the results of batch leaching experiments that will be conducted on the different soil fractions.