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Natural occurrence of hexavalent chromium in serpentinite hosted spring waters from Western Tuscany (Italy)

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Although many heavy metals acts as micro-nutrients playing essential roles for all living organisms, most of them, when bioavailable in high concentrations, have to be considered potentially toxic. Some of them, such as Cr, and Ni are generally highly concentrated in all ultramafic rocks as well as in serpentines and their weathering products (soils and sediments), that largely outcrop in ophiolite belts, such as those of Central Italy.
High Cr (VI) concentrations have been found in some spring waters associated with serpentinite outcrops and in Cecina Valley (Western Tuscany) soils, sediments and ground waters.
Thus, we set up a multidisciplinary research program (RESPIRA) financed by Tuscany Region and by European Union, aimed to enhance the understanding of the weathering processes of serpentinite rocks in order to assess the mobility and hence the bioavailability of heavy and toxic metals such Ni and Cr in soils and namely to study the release and mobility of Cr with in the “critical zone” where rocks, soils, meteoric waters and atmospheric gasses interact.
Sr-Pb isotopes of serpentinites suggest an interaction with recent, low-T, waters. Three isotopic end-members are identified in soils and sediments: serpentinites, marine limestones and tertiary siliciclastic rocks. Sr isotopic values of ground waters match with the higher values ($^{87}Sr/^{86}Sr \approx 0.7089$ - 0.7092) of soils and sediments compositional range.
Cr (VI) free and Cr (VI) bearing spring waters, spilling out from the serpentinite outcrops (Santa Luce, Querceto, Montecastelli), display Mg-HCO_3 chemical composition $^{87}Sr/^{86}Sr$ from 0.7074 to 0.7084 (in the serpentinite range).
Petrographic and minero-chemical analyses of both rocks and soil samples from the same sites, highlight the occurrence of secondary minerals containing significant Cr contents, such as chlorites ($Cr2O_3$ from 2 to 8 wt%) that can easily release Cr(III). Nerveless the absence of Mn-oxides, considered the more common electron acceptors, able to rapid oxidise Cr(III) into Cr (VI), implies that local presence of Cr (VI) in waters have to be ascribed to other processes. Some serpentinites contain significant amount of Fe-rich brucite and show evidences of its dissolution during surface weathering. This process could lead to the formation of both of hydrous magnesium carbonates and of Mg-rich members of "layered double hydroxide" group, which can contain high contents of Cr(III) that can be easily oxidized and mobilized during weathering reactions (Langone et al., in press).
Cr isotopes analyses, able to record any occurrence of Cr redox reactions, are analysed in order to better understand which are the mineralogical, chemical and thermodynamic parameters responsible for Cr(III)-Cr(VI) oxidation during water-rock interactions.

Langone A., Baneschi I., Boschi C., Dini A., Guidi M, and Cavallo A., (in press), Serpentinite-water interaction and chromium (VI) release in spring waters: examples from Tuscan ophiolites, Ofioliti.