Cr and Mn speciation and interactions in Greek ophiolites

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Natural processes related to weathering of ultramafic rocks have been linked to the occurrence of elevated concentrations of hexavalent chromium (Cr(VI)) in soils and groundwater. Ultramafic rocks and their derived serpentine soils are encountered in populated areas around the world and present high concentrations in Cr, Ni and Co [1]. Greece is geologically located on the Sub-Pelagonian and Pelagonian zones and has massive deposits of serpentinized ophiolites and Ni-Fe laterites [2], which result in elevated Cr(VI) concentrations in groundwater [3]. While it is known that Cr(VI) release in ultramafic formations is a result of oxidation by high valence Mn-oxides, the rate of Cr(VI) production and expected groundwater concentrations is not well known, especially under the alkaline conditions encountered in the limestone-rich geologic environment in Greece.

This paper reports on microstructural and trace metal speciation studies conducted on sediments obtained from two ophiolite-rich areas in Greece: Vergina, an agricultural area with pure serpentinites, and Asopos, an industrial area with a mixed serpentinite-limestone geologic background. Samples from various depths (up to 58 m) were subjected to analysis by micro-X-ray Fluorescence (μXRF), micro-X-ray Absorption Near Edge Structure (μXANES) and μX-ray Diffraction (μXRD). The particle size, spatial associations, valence state and speciation of Cr and Mn were examined.

Overall, the analyses indicated that the Greek geologic background in rich in Mn(IV) minerals including birnessite, with some contribution of Mn(III) and very little Mn(II), even in rock samples. The majority of the total Cr mass is bound chromite and the remaining is evenly distributed within the matrix, which consist of mostly serpentine minerals. Close spatial association between Mn(IV)-bearing phases and chromite was observed in several samples and it is hypothesized that such association is conducive to Cr(VI) production, favoring sorption of Cr(III), oxidation and release of Cr(VI) into solution.

[1] Oze *et al*. (2004) *Intern. Geol. Rev*. **46**, 97-126 [2] Eliopoulos *et al*. (2012) *Ore Geol. Rev*. **48**, 413-427 [3] Dermatas *et al*. (2015) *J. Haz. Mater*. **281,** 35-46