

**BORSA SIMP 2011 PER UN SOGGIORNO DI STUDIO ALL'ESTERO:
RELAZIONE SULL'ATTIVITA' SVOLTA**

**SPINEL CHARACTERISATION FROM SERPENTINITIC SOILS AND ROCKS
(TUSCANY – ITALY)**

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INTRODUCTION

Soils derived from peridotite and serpentinites pose ecological or environmental risk due to high levels of potentially toxic metals such as Co, Cr, Mn and Ni (*e.g.*, Oze *et al.*, 2004a, b). Although serpentine rocks and soils cover only a small area of the Earth's terrestrial surface, they are abundant in ophiolite belts and have been typically found within regions of the Circum-Pacific margin and Mediterranean Sea (*e.g.* Oze *et al.*, 2007 and references therein). In these areas, the release of Cr and Ni into the ecosystems during serpentinite weathering suggests that serpentinite landscapes are a possible source of non-anthropogenic metal contamination (*e.g.* Fantoni *et al.*, 2002; Oze *et al.* 2004a, b; Garnier *et al.*, 2006).

Chromium is predominantly contained in Cr-bearing spinels (*i.e.* chromite, Mg-Al-chromite, Al-chromite), which are highly resistant to weathering, and it generally occurs as in the trivalent state resulting not bioavailable (Oze *et al.*, 2004a). The role of chromite as source of Cr in the environmental processes is still under debate. Its resistance to the weathering may favour the accumulation of chromite within the soil profile by increasing its abundance (Garnier *et al.*, 2008). Oze *et al.* (2004) argued that Cr-spinels are not a significant source of Cr in serpentinite soils, particularly compared to Cr-bearing silicates. Garnier *et al.* (2008) demonstrated that chromite underwent a chemical modification (*i.e.* Cr enrichment) during weathering suggesting that chromites are slowly dissolved during pedogenesis. According to these authors, due to the high concentration of chromites in soils and its slow weathering with time chromites could represent a diffusive minor source of Cr within soils where Cr-bearing silicates remain still a major source.

Independently of the role of chromite as source of Cr, the release of Cr to the ecosystems requires oxidation of Cr(III) to Cr(VI). The possible electrons acceptors includes Mn-oxides, Fe(III), oxyhydroxides, H₂O₂, dissolved O₂, and gaseous O₂ (*e.g.* Fantoni *et al.* 2002 and references therein). Mn-oxides are potentially able to rapidly oxidize Cr(III) into Cr(VI) in the environment. Cr(III) oxidation by Mn-oxides have already been demonstrated in laboratory studies but very few have reported evidence for such a reaction in natural systems (Fandeur *et al.*, 2009 and references therein). Recently, Fandeur *et al.* (2009) demonstrated by X-ray Absorption Near Edge Structure (XANES) spectroscopy on both bulk natural samples and directly in thin section, the occurrence of Cr(VI) (up to 20% and 33% of total Cr on bulk analyses and on in situ analyses, respectively) in the unit of a regolith which is also enriched in MnO (up to 21.7 wt.%). According to these authors, the distribution of Cr(VI) indicates that it is associated to both Mn- and Fe-oxides, with a significant preference for the latter species. Moreover, Fandeur *et al.*, (2009) observed that the largest amounts of Cr(VI) are present in the Fe-oxides located at Mn-oxides boundary suggesting that Cr(VI) could be released from the surface of the Mn-oxides (where it has been oxidized), and subsequently reabsorbed onto the surface of the surrounding Fe-oxides.

The detection of Cr(VI) (up to 49 ppb) within spring waters from serpentinitic outcrops in Tuscany (Baneschi *et al.*, 2011) is one of the starting point of a research project (RESPIRA) of the IGG-CNR of Pisa (Italy), financed by EU and Regione Toscana (FSE-POR). The mobility of Cr from serpentinites to soils and, consequently, to the waters is the major aim of a research grant related to the RESPIRA project. The one month analytical stage at the "Institute de Physique du Globe" of Paris gave me the possibility to characterise the

chemical composition of minerals from serpentinitic soils and rocks with particular interest to their Cr and Mn contents. Chemical analyses have been performed on both soil and rocks samples from two selected localities, namely S. Luce quarry and Querceto, characterized by Cr(VI)-free and Cr(VI)-bearing spring waters, respectively. These analyses are preliminary and essential for future investigation at the synchrotron, following the approach of Fandeur *et al.* (2009).

MATERIALS AND METHODS

At Santa Luce site, serpentinites have been sampled from the quarry front, at different levels. Most of them are harzburgites, with visible retrograde pseudomorphic textures (bastite). Serpentinites are affected by later veining of white fibrous serpentine, of probably chrysotile composition. Serpentinite samples have been collected also directly from the base of the soil profiles (soil bedrock).

At Querceto, a serpentinitic samples has been collected within a cave, close to the spring water outflow. The walls of the cave are locally covered by white globular precipitations of probably hidromagnesitic composition, which have been sampled as separates and together with the serpentinitic substrate.

A pit was opened at the top of the S. Luce quarry until stones predominated and four horizons (O, A, B, C) have been recognised and sampled. The soil horizons (O, A, B, C) from the Querceto site were sampled from an exposed soil profile at the top of the spring water. The soil samples were air-dried, cleaned for the organic matter and sieved to less than 2 mm prior to the chemical analysis. For petrographic analyses the different horizons of the two profiles have been further subdivided in five fractions: > 2 mm; 2 mm $> f > 0.50$ mm; 0.50 mm $> f > 0.25$ mm; 0.25 mm $> f > 0.10$ mm; 0.10 mm $> f > 0.04$ mm. Prior to chemical analyses, thin sections and mounts of rocks and soil materials, respectively, have been studied at the FE-SEM (INGV-Rome). Petrographic observations for the S. Luce quarry samples revealed the occurrence of minerals of the peridotitic paragenesis, *i.e.* Mg-Al-chromites, pyroxenes and olivine, together with minerals from the serpentinite paragenesis, *i.e.* serpentine, andradite, magnetite and chlorite. The Querceto samples contain only Mg-Al-chromites, as relicts of the peridotitic paragenesis, and magnetite, serpentine, garnet and chlorite of the serpentinite paragenesis. Noticeably, no Mn-oxides have been detected at the SEM within the samples form both localities.

Mg-Al-chromites may be unaltered or they can be entirely replaced by chromites and/or by very fine-grained aggregates of oxides and silicates, in both cases, magnetite occurs as rims and/or veins. Commonly, the Mg-Al-chromite grains observed within the Querceto samples show a particular alteration feature consisting of a near complete replacement by chromite, the occurrence of rims and veins of magnetite and the presence of small relicts of the former Mg-Al-chromites at the boundary between chromite and magnetite (Fig. 1).

Chemical analyses have been performed at the CAMPARIS Service (ParisVI University) by using Cameca SXFive and SX100 microprobes. Silicates and spinels have been analysed on both soil separates and on thin sections of rocks. In order to understand the relationship among different spinel types, oxygen has been directly measured on spinels from the Querceto site together with Mn, Cr, Fe, Mg, Al, Ti, Ni and Si.

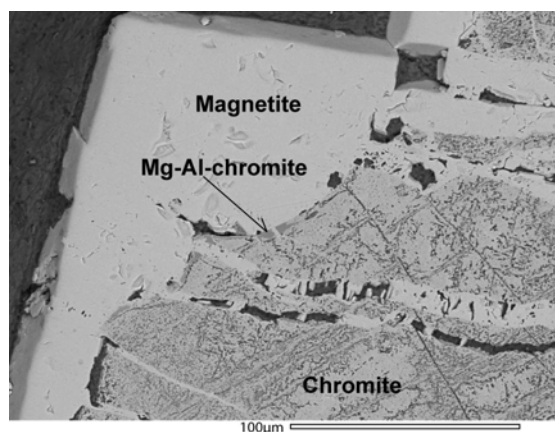


Fig. 1 – BSE images of altered Mg-Al-chromite showing the replacement by chromite, the occurrence of magnetite rims and veins and the presence of Mg-Al-chromite relicts at the boundary between magnetite and chromite.

SUMMARY OF DISCUSSION AND CONCLUSIONS

EMPA analyses revealed that the Cr₂O₃ content is very high for the (Mg-Al)chromites (24-45 wt.%) and below 8 wt.% for magnetite and silicates. No systematic differences between minerals from soils and rocks have been detected, whereas, magnetite, serpentine and chlorite from the Querceto samples are richer in Cr with respect to the equivalent mineral phases of the S. Luce quarry (Fig. 2). Generally, the MnO content of (Mg-Al)chromites from the S. Luce samples is very low except for a single value at about 7 wt.% (Fig. 3). The MnO content of magnetite varies from 0.0 to 0.3 wt.%, with one single value at 0.7 wt.%, and is comparable to the MnO content of silicates. Noticeably, the MnO content of (Mg-Al)chromites from Querceto samples is highly variable from 0.0 (Mg-Al-chromite) to about 7.0 wt.% (chromites). Analogously, the MnO content of magnetite is higher than the MnO content of magnetite from S. Luce quarry. Serpentine and garnet are near Mn-free, whereas chlorite contains up to 0.4 wt.% of MnO (Fig. 3).

The Principal Component Analysis (PCA) of spinels from the Querceto site revealed some interesting features. Chemical correlations are mainly described by two components (99.17%), the component 1 (F1) and 2 (F2). The F1 represents the inverse correlation between Fe and the other elements, in other words, it describes the subdivision between magnetite and “chromite” (Fig. 4). The F2 component describes the inverse correlation between Cr and Mn, with positive F2 coordinates, and Mg, O and Al, with negative F2 coordinates. The

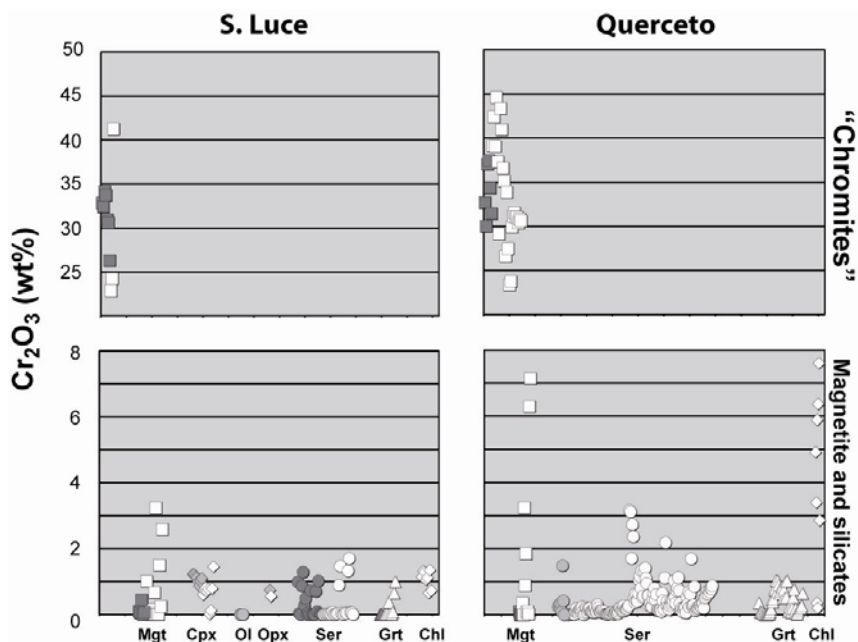


Fig. 2 - Cr₂O₃ content of minerals from serpentinites (grey filled symbols) and soils (white filled symbols).

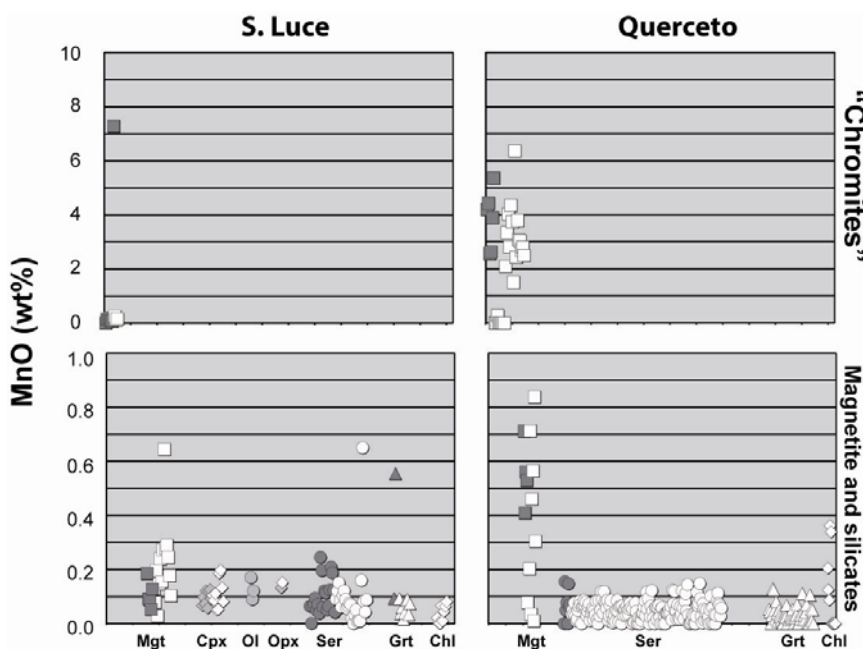


Fig. 3 - MnO content of minerals from serpentinites (grey filled symbols) and soils (white filled symbols).

chemical information associated to this component allow to confirm the existence of two types of “chromite”: the Mg-Al-chromite (Mn-free), and the chromites (Fe-rich and Mn-bearing; Fig. 4).

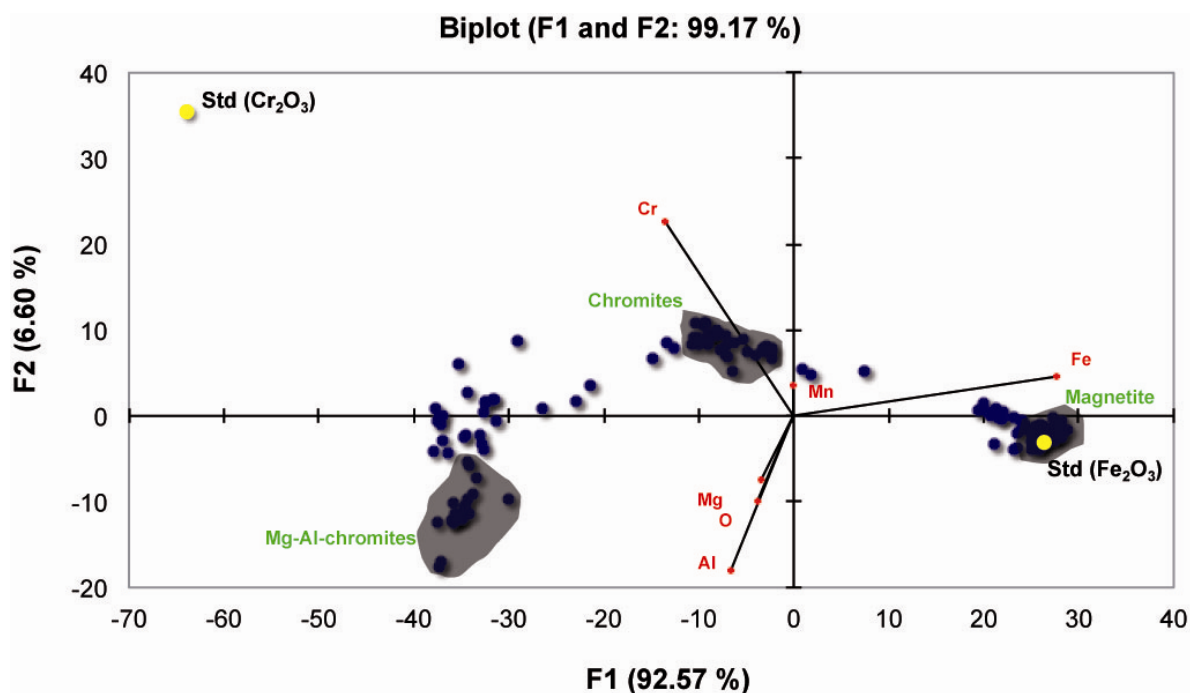


Fig. 4 - Biplot of the component 1 and 2 after a Principal Component Analysis (PCA) of elemental weight % of spinels from Querceto.

Soil and rock samples from both areas are free from Mn-oxides. However, spring waters collected at Querceto contain high concentrations of Cr(VI). Here, chromites are richer in MnO with respect to the chromites from S. Luce quarry samples. According to the petrographic and chemical analyses, for the present case study the Cr oxidation is probably not due to oxidation between Cr-bearing spinels and Mn-oxide, as reported by Fandeur *et al.* (2009) for a lateritic regolith developed on serpentinized ultramafic rocks of New Caledonia. For the Querceto samples, two possible processes may be responsible for the Cr oxidation: *i*) an *in situ* process with Cr oxidation and Mn reduction inside the Mn-bearing spinel (chromite), *ii*) a Cr oxidations by other electrons acceptors. Further investigations (*e.g. in situ* XANES spectroscopy) are needed in order to shed light on these two processes.

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